THE QUEST FOR A SAFER ACCELERATOR FOR POLYCHLOROPRENE RUBBER

by

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Doctor of Philosophy

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This thesis describes the investigation into finding a safer alternative to the polychloroprene cross-linking agent ethylene thiourea (ETU). The novel approach of utilising spectroscopic analysis in combination with a study of mechanical and physical properties of polychloroprene was employed. Currently the most effective cross-linking system for polychloroprene is ETU in combination with zinc oxide (ZnO). However, due to the health risks associated with it, ETU may in the future be banned or heavily regulated, thus a replacement is sought.

An investigation of the cross-linking mechanisms of ETU alone, and ETU in conjunction with ZnO was completed. This was necessary as polychloroprene cross-links differently to many other polymers. The study was carried out using model compounds, such as amines and thiols, in addition to work on more widely used accelerators, including thiurams and dithiocarbamates; this revealed that at least three disparate mechanisms are in operation. These mechanisms, comprise one of a cationic nature employed by ZnO, a bis-alkylation mechanism of ETU and a new proposed mechanism seen when ETU and ZnO work together synergistically. This new mechanism shows ZnO activating the polymer chain, followed by the sulfur of ETU creating a cross-link.

Using this new mechanism, several new accelerators were proposed. These accelerators contain a dithiocarbamate group and are complexed with diamines. The diamine present acts as an activator and the dithiocarbamate group a cross-linker. These new accelerators were tested in pure polychloroprene rubber on their own, and in combination with tetrabenzyl thiuramdisulfide (TBzTD) or ZnO. All the proposed accelerators were able to cross-link. The replacement which most closely matched ETU, in terms of physical and mechanical properties of the vulcanisate was a complex of piperazine-1-carbodithioic acid and 1,3-diaminopropane (named PNA5). This accelerator was taken forward and tested in a filled commercial master batch. As a successful conclusion to the project a complete PNA5-based system was shown to closely match the performance of an ETU system in a master batch. Concomitantly the use of a multi-functional additive (a complex formed between stearic acid and 1,4-diaminobutane) allowed a reduction in ZnO needed, due to environmental concerns.

Keywords

Cross-linking; Vulcanisation; Neoprene; Ethylene thiourea; Zinc oxide.

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The biggest acknowledgement of all has been saved until last and must go to Ruth, my wife, without whom I would be nothing. Thank you for everything.

Abbreviations

ABA	Amine bridged amides
AS100	di-isopropyl xanthogen polysulfide
ATR	Attenuated total reflectance
BR	Butadiene rubber
CBS	N-cyclohexyl-benzothiazole-sulfenamide
CIIR	Chlorinated poly(iso-*co*-butylene)
CR	Chloroprene rubber
CTA	Chain transfer agent
CTMAM	Cetyltrimethylammonium maleate
DAB	1,4-diaminobutane
DAD	1,12-diaminododecane
DAHp	1,7-diaminoheptane
DAHx	1,6-diaminohexane
DAP	1,3-diaminopropane
DBA	Dibutylamine
DBTU	Dibutyl thiourea
DCM	Dichloromethane
DPG	Diphenyl guanidine
DSC	Differential scanning calorimeter
EPDM	Ethylene propylene diene monomer
ETU	Ethylene thiourea
EU	Ethylene urea
FID	Flame ionization detector
FTIR	Fourier transform infra-red
GC-MS	Gas chromatography – mass spectroscopy

GPC	Gel permeation chromatography
HCl	Hydrochloric acid
HDT	1,6-hexanedithiol
IRHD	International rubber hardness degrees
IMS	Industrial methylated spirit
MBT	2-mercaptobenzothiazole
MBTS	2-mercaptobenzyl thiazole disulfide
MDR	Moving die rheometer
MeOH	Methanol
1,3-MFA	Multi-functional additive containing 1,3-diaminopropane
1,4-MFA	Multi-functional additive containing 1,4-diaminobutane
MFA	Multi-functional additive
MgO	Magnesium oxide
MH	Maximum torque
MMBI	Methyl-2-mercaptobenzimidazole
MTT	3-Methyl-thiazolidine-thione-2
NBR	Nitrile-butadiene rubber
NMR	Nuclear magnetic resonance
NR	Natural rubber
ODR	Oscillating disc rheometer
ODT	1,8-octanedithiol
PCA	Piperazine-1-carbodithioic acid
PCNSL	Phosphorylated cashew nut shell liquid
phr	Parts per hundred of rubber
PNA	Proposed new accelerator
PNA1	Complex of dibenzyldithiocarbamate and 1,3-diaminopropane
PNA2	Complex of dibenzyldithiocarbamate and piperazine
PNA3	Complex of dibenzyldithiocarbamate and 6-amino-hexan-1-ol

PNA4	Complex of cyclohexyl-dithiocarbamic acid and 1,3-diaminopropane
PNA5	Complex of piperazine-1-carbodithioic acid and 1,3-diaminopropane
PNA6	Complex between bis-(3,5,5-trimethyl-hexyl)-dithiocarbamic acid and 1,3-diaminopropane
PNA7	Complex of piperazine-1-carbodithioic acid and 1,6-diaminohexane
RAFT	Reversible addition-fragmentation chain transfer polymerisation
REACH	Registration, evaluation, authorisation and restriction of chemicals
SA	Stearic acid
SBR	Styrene-butadiene rubber
SEC	Size exclusion chromatography
SVHC	Substance of very high concern
T90	Time take for rubber to reach 90 % of the maximum torque when tested on a rheometer
TBzTD	Tetrabenzyl thiuramdisulfide
TGA	Thermogravimetric analysis
THF	Tetrahydrofuran
TLC	Thin layer chromatography
TMTD	Tetramethyl thiuramdisulfide
TMTM	Tetramethyl thiuram monosulfide
TS1	Scorch time
UV-vis	Ultra-violet-visible spectroscopy
UTS	Ultimate tensile strength
ZBEC	Zinc dibenzyldithiocarbamate
ZDBC	Zinc dibutyldithiocarbamate
ZDMC	Zinc dimethyldithiocarbamate
$ZnCl_2$	Zinc chloride
ZnO	Zinc oxide

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CHAPTER 1

INTRODUCTION

1. Introduction

1.1. Background to the Project

In general, polymers are large molecules made up of repeating units; there can be hundreds of thousands of repeat units in a single chain.[1] The repeat unit varies from polymer to polymer. Polymers can be either linear or non-linear (such as branched, star, comb, etc.) and can be made from the same unit repeated to give a *so-called* homopolymer. Alternatively, polymers can be made from several different units repeated alternately, randomly, statistically or in blocks. Consequently, there is a wide range of polymers available. Polymers can be divided up into different groups, depending upon their intrinsic properties. More pertinently for this project, commercially available polymers in general can be divided into one of two categories; elastomers (often called rubbers) and plastics.[2]

The term elastomer comes from the phrase 'elastic polymer', once deformed the polymer will return, to some extent, to its original shape.[3] Polychloroprene, the focus of this thesis, is often known by the trade name Neoprene and was one of the first manmade elastomers available.[4] Like many elastomers, to provide structural integrity, polychloroprene is cross-linked before use,[5] and it is this process that is investigated herein. In cross-linking the long chains of the polymer are bound together, creating covalent bridges between them. This networked structure provides better resistance to chemicals, as well as an improvement to many other physical properties.[6] The current commercial method for cross-linking polychloroprene is through the use of ethylene thiourea (ETU) at high temperature.[7, 8]

However, health risks have been found with ETU, where these risks may lead to its use being banned from the European Union by REACH (Registration, Evaluation, Authorisation and Restriction of Chemicals) legislation, with it currently registered as a substance of very high concern (SVHC).[9] Therefore, a replacement for ETU is sought across the industry and is the aim of this research. A scientific approach to achieve this involves understanding the mechanism by which ETU cross-links polychloroprene. Any cross-linked polychloroprene rubber (CR) produced using a replacement for ETU would need to fully meet all industrial standards, before ETU could be replaced. This project therefore seeks to elucidate the mechanism by which ETU cross-links polychloroprene, towards finding a replacement material suitable for use in industry.

1.2. Polymers and Rubber Background

There are several different classes of materials; one of the major classes is that of polymers. As aforementioned, a sub-set of that class is rubbers.[1] This section gives an insight specifically to rubber. The remainder of this section goes into greater detail with regards to polychloroprene, including its structure, properties, synthesis and vulcanisation chemistry the main subject of this thesis.

The word ‘polymer’ is Greek in origin and means 'many parts’; this derives from their general structure, that of a unit repeated many times over to form a long chain or larger molecule. The structurally simplest polymer is that of polyethylene (PE); its repeat unit consists of two methylene units connected through a saturated carbon-carbon bond.[10] Due to the nature of the repeat unit it creates a carbon backbone, as shown in Figure 1.1A.

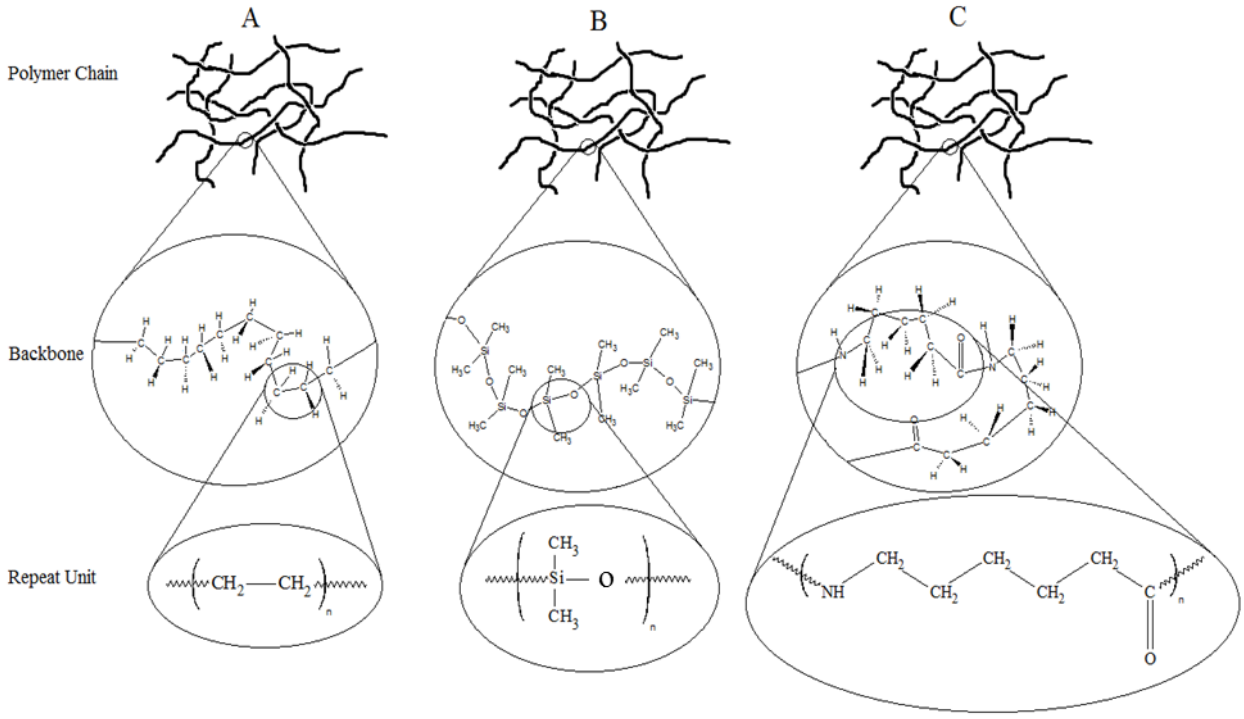


Figure 1.1. Polymer chain, backbone and repeat unit of A) polyethylene, B) polysiloxane and C) polyamide 6. Bond angels, length and tacticity are for illustrative purposes only, it is also important to note crystallinity is not shown in this figure.

Typically, commercial polymers comprise a carbon backbone with pendent substituents however, there are many examples where this is not the case. Some polymers contain heteroatoms in their backbone, predominantly those synthesised *via* step-growth polymerisation, such as polyamides (nitrogen-containing backbone – Figure 1.1C).[10] A

further example is the polysiloxane family, an important class of materials owing to their low glass transition temperature, which is built upon a silicon-oxygen backbone (Figure 1.1B). Some polymers have a partially unsaturated backbone, i.e. they have a backbone containing carbon-carbon double bonds.

As alluded to in Section 1.1, polymers are often classified within industry into one of two categories, those of plastics and elastomers. Plastics are unable to return to their original form once a stress has been placed upon them. This is known as plasticity, and can be experienced by materials other than plastics (e.g. aluminium).[11] Elastic materials (elastomers), on the other hand, exhibit a return (to some extent) to their original form after a stress has been placed upon them and subsequently removed.

A sub-category of polymers are thermoplastics, they are solid at room temperature, and then become malleable/flexible after heating to a set temperature. It is possible to mould thermoplastics at, or above the set temperature; but they then become solid once cooled back down to room temperature. This process is completely reversible and such thermal cycling can be repeated many times.

Thermosetting polymers (or thermosets) on the other hand, will set when heated, i.e. the thermal moulding process is irreversible. Generally, they will be moulded at high temperature and will then cure. This reaction often involves the inclusion of additives, which react with the polymer chain. It is an irreversible reaction, so that if heated again it would not be possible to remould the polymer. Many elastomers are thermosets as they themselves are able to undergo vulcanisation or cross-linking which are forms of thermosetting. This is discussed in more detail in Section 1.3.

A final sub category is that of thermoplastic elastomers (TPE); these are block co-polymers of a plastic and rubber, and as such have some of the advantages of both constituent parts. They will have many of the physical properties of an elastomer, with the processability of a thermoplastic.[12] A TPE will contain a two phase micro-structure, formed because of the incompatibility of the two polymer segments. A schematic for this is shown in Figure 1.2.

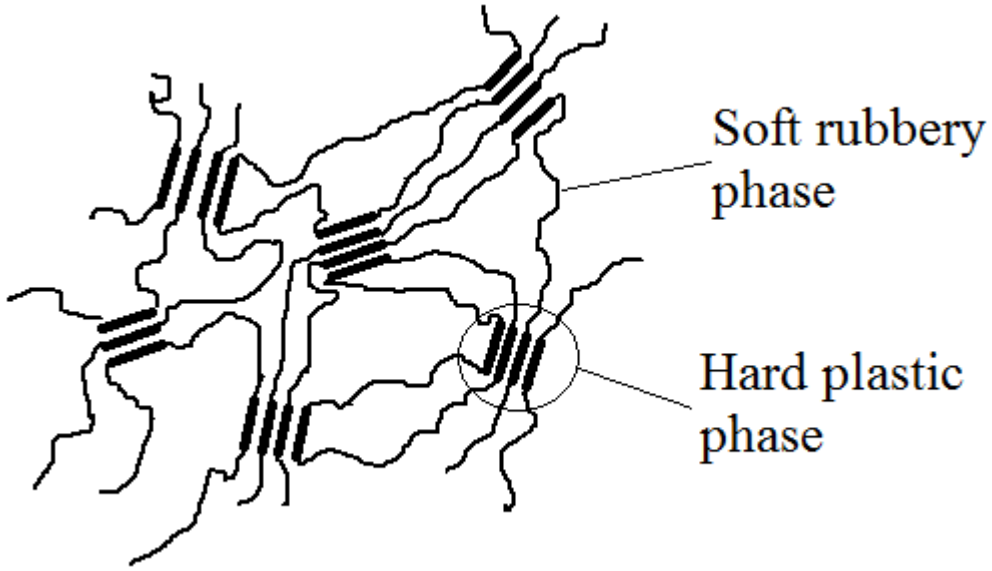


Figure 1.2. Thermoplastic elastomer microstructure, showing the hard plastic phase and the soft rubbery phase, the combination of which give thermoplastic elastomers their unique properties.

One of the first known elastomers was that of natural rubber (NR).[13] NR is the naturally occurring form of *cis*-1,4-polyisoprene. It has been used for hundreds of years and has many uses. One of the earliest manmade polymers was that of Bakelite patented in 1907 by Leo Hendrik Baekeland. Bakelite is a synthetic cross-linked phenol formaldehyde resin, it initially found widespread use as a cheap electrical insulator.[14] After this many other manmade or synthetic polymers followed, such as butadiene rubber (BR), styrene-butadiene rubber (SBR), nitrile-butadiene rubber (NBR) and polychloroprene which will be discussed in detail in Section 1.4.

1.3. Cross-linking

This section discusses general cross-linking, including what a cross-link is and what properties are altered by cross-linking. Subsequently, sulfur cross-linking, the additives used and their mechanisms in rubber cross-linking are examined. Finally other types of cross-linking are reviewed.

1.3.1. Background to Cross-linking

Cross-linking is the process that occurs when polymer molecules are linked together to form a

network structure.[15] It is also known as vulcanisation or curing. A chemical cross-link is a covalent bridge between polymer molecules, it can happen multiple times between many different chains.[15] A comparison between uncross-linked polymer chains and the network structure is given in Figure 1.3.

The mechanisms by which cross-linking occurs can be either, ionic, radical or polar.[16] Many processes may be used to induce cross-linking including heating, ultraviolet or chemical reactions.[16]

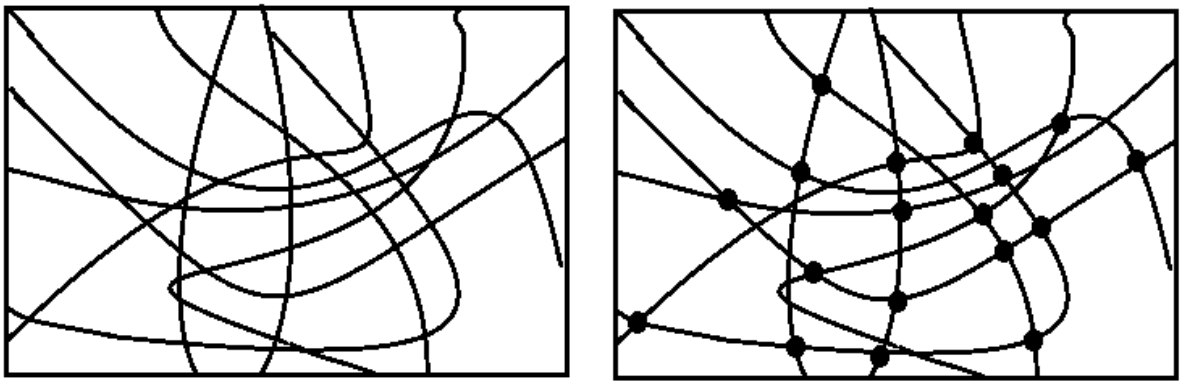


Figure 1.3. Uncross-linked polymer chains able to move *via* reptation[17] and cross-linked polymer chains, with links between the chains limiting their motion.

1.3.1.1. Sulfur Cross-linking

One of the earliest known forms of cross-linking is that of natural rubber (NR) with sulfur. This process was discovered by Charles Goodyear in 1939, he called the process vulcanisation.[16] This type of cross-linking is only made possible by the presence of unsaturation in the NR backbone. The level of cross-linking greatly affects the properties of the polymer, these changes were summarised in a paper by Morrison and Porter, and shown in Table 1.1.[18]

There are three types of sulfur cross-linking systems, sulfur only, sulfur plus accelerator and so-called “sulfur-less” cross-linking. Cross-linking rubber with only sulfur is a slow process – it can take several hours and is therefore no longer used in a commercial environment. Instead, sulfur is used in combination with an accelerator which vastly speeds up curing times to only a few minutes. In sulfur-less cross-linking an accelerator may act as a sulfur donor to create the sulfur cross-link, but no elemental sulfur is needed.

Table 1.1. Effect of degree of cross-linking on polymer properties as summarised by Morrison and Porter.[18]

Property	Change with increase in degree of cross-linking
Properties dependent only on degree of cross-linking	
Stiffness (modulus)	Increase
Hardness	Increase
Properties partly dependent on degree of cross-linking	
Breaking elongation	Decrease
Resilience	Increase
Heat build up	Decrease
Solvent swelling	Decrease
Creep, stress relaxation	Decrease
Set	Decrease
Abrasion resistance	Increase
Fatigue cracking	Increase
Low-temperature crystallisation	Decrease in rate
Tensile strength, tear strength	Increase, then decrease

The effect of accelerators, in the vulcanisation process is dealt with in more detail in Section 1.3.2. With sulfur cross-linking of rubbers, several different types of cross-link are achievable, these can be seen in Figure 1.4. The causes of these differences are due to several factors including accelerator used, accelerator to sulfur ratio and cure temperature and time.

Figure 1.4. Structures of different types of achievable sulfur cross-links and other modifications.[19]

These different types of cross-links can also affect the properties of the cured rubber, again discussed by Morrison and Porter and listed in Table 1.2.[18] Although sulfur is the most common (and best known) form of cross-linking, other cross-linking processes are possible, as discussed in Sections 1.3.3.1 to 1.3.3.4.

Table 1.2. Effect of cross-link type on polymer properties summarised by Morrison and Porter.[18]

Property	Change with increase in proportion of di and polysulfidic cross-links
Creep, stress relaxation	Increase
Set	Increase
Incremental swelling	Increase
Tensile strength, tear strength	Increase
Resilience	Increase
Fatigue failure	Decrease
Heat resistance	Decrease
Thermal ageing resistance	Decrease

1.3.2. Rubber Additives for Sulfur Cross-linking

Many different types of additives are used in commercial rubber formulations to fabricate viable products. Additives such as fillers and antioxidants are not discussed in detail; this section focuses more on cross-linking additives. That said both anti-oxidants and fillers are important ingredients within rubber compounds, and play a vital role.[20] A typical NR formulation contains the additives shown in Table 1.3 at the quoted approximate levels, where all quantities are in parts per hundred of rubber (phr).

Table 1.3. Typical natural rubber formulation.[21]

Ingredient	Quantity (phr)
Rubber	100
Filler	50
Primary accelerator	0.6
Anti-oxidant	2
Processing aid	2
Mineral oil	3
Zinc Oxide	4
Sulfur	2.4

1.3.2.1. Standard Rubber Accelerators

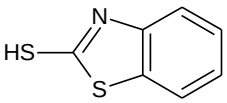
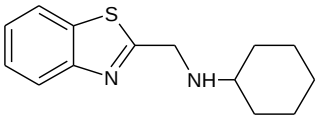
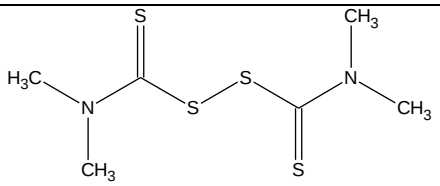
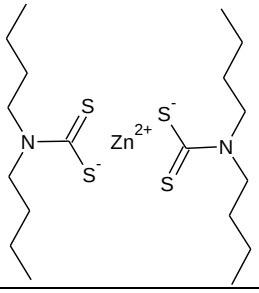
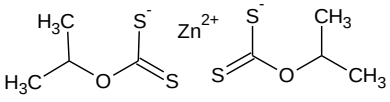
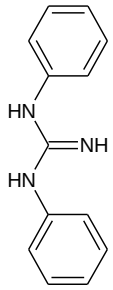
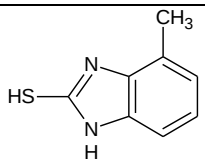
Accelerated sulfur cross-linking using organic compounds was discovered in 1906,[16] enabling cross-linking to occur much quicker and use much less sulfur. Many different types of accelerators are used in rubber cross-linking, for different reasons. Most accelerators used for cross-linking rubber containing an unsaturation are based around creating sulfur cross-links either directly themselves, or by helping elemental sulfur to cross-link.[22] A summary of the accelerator classes is shown in Table 1.4.

The various accelerator classes are used on their own or in combination with each other, to enable the desired cure characteristics to be achieved. Cure characteristics and rheological properties are explained in more detail in Section 1.5.1. From Table 1.4, it can be seen that there are some similarities between the structures of the various accelerators that may enable them to react in a similar fashion. Certain accelerators in Table 1.4, such as tetramethyl thiuramdisulfide (TMTD), act as sulfur donors negating the need for additional elemental sulfur to be added to the cross-linking system.[23] Such "sulfur-less" systems, however, like all sulfur cross-linking systems, require an activator, such as zinc oxide (ZnO) (see Section 1.3.2.2). Scheme 1.1 shows the generalised process for sulfur cross-linking of rubbers using an accelerator.

Although Scheme 1.1 shows the widely accepted mechanism by which sulfur cross-linking occurs, several authors have proposed alternative mechanisms. Ignatz-Hoover[21] described sulfur cross-linking taking place in four steps: (i) initiation, (ii) induction, (iii) activation and (iv) sulfurisation and cross-linking.

Similarly, Ghosh *et al.*[24] divided the cross-linking reactions into three sub-sections, those of accelerator chemistry, cross-linking chemistry and post cross-linking chemistry. Accelerator chemistry deals with the initial reactions, and the formation of the active sulfurating agent. Cross-linking chemistry involves the creation of actual links between the polymer chains. Post cross-linking chemistry covers those reactions occurring after cross-linking has taken place, such as cross-link shortening and degradation.

Table 1.4. Standard rubber accelerator classes used in sulfur cross-linking.[21, 22, 25, 26]

Class	Example compound	Structure	Property
Thiazole	mercaptobenzylthiazole (MBT)		Semi ultra-accelerator, scorchy[a].
Sulfenamide	N-cyclohexyl-benzothiazole-sulfenamide (CBS)		Semi ultra-accelerator, delayed action
Thiurams	tetramethyl-thiuramdisulfide (TMTD)		Ultra accelerator
Dithiocarbamates	zinc dibutyldithiocarbamate (ZDBC)		Ultra accelerator
Xanthates	zinc isopropylxanthate (ZIX)		Ultra accelerator, low temperature curing
Guanidine	diphenyl guanidine (DPG)		Medium accelerator, usually used in conjunction with other accelerators.
Imidazole	methyl-2-mercaptobenzimidazole (MMBI)		Semi ultra-accelerator.

[a]Scorchy indicates a very quick onset of cross-linking, as discussed in Section 1.4.1.

Scheme 1.1. Generalised ‘sulfur with accelerator’ cross-linking scheme for natural rubber (NR) as summarised by Morrison and Porter.[18]

The elucidation of a more detailed sulfur cross-linking mechanism is made more difficult by the ability of the sulfur ring (once cleaved) to form radicals or ions.[27] This means that the mechanism could proceed in one of several directions, there is evidence to support both ionic and radical mechanisms as well as combined mechanisms. In ‘sulfur-free’ cross-linking, where elemental sulfur is omitted from the system, a slightly different mechanism operates to create the sulfur cross-links.[28] The difference involves the initial reactions, and entail the sulfur group splitting from the donor,[29] resulting in the length of the sulfur cross-link being shorter than when elemental sulfur is used. Properties, such as crack resistance, are altered due to such shorter cross-link.

1.3.2.2. Zinc Oxide in General Rubber

The role of zinc oxide (ZnO) in the production of rubber compounds is a complicated one. Initially ZnO was used in rubber formulations as a filler, where it was found to improve many of the properties of the rubber.[30] It was seen that the cure properties were also improved and the role of such activators were discovered not long after.[31] Heideman *et al.*[31] listed the following roles that ZnO can undertake during cross-linking:

- activator for sulfur cross-linking,
- filler,
- scavenger of detrimental reaction by-products,
- vulcanising agent for halogen containing rubbers and
- processing aid for uncured rubber.

It has also been shown that many physical properties (such as heat build-up, abrasion resistance, dynamic properties and ageing properties in peroxide cures) of the cured compound were improved when ZnO was used.[31] ZnO is rarely used as filler in modern rubber compounds; instead they are loaded with cheaper fillers such as carbon black or calcium carbonate.[31]

Some studies have shown that it is not ZnO itself but instead a Zn^{2+} ion that plays an active role in the formation of the sulfurating agent[30] (see Scheme 1.1). Results also show that it is the active accelerating complex (which contains ZnO) that participates in cross-linking and not ZnO itself.[30] Consequently ZnO must react before taking part in the cross-linking reaction. In 'sulfur-free' cross-linking, it is ZnO which liberates the sulfur from the accelerator and enables cross-linking to occur.[32]

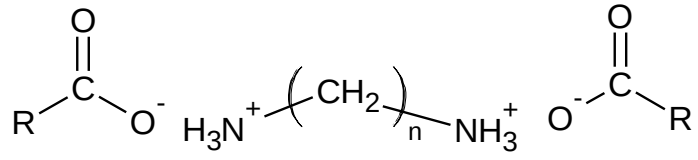
One of the major uses of ZnO is as an activator in cross-linking. This occurs through the formation of accelerator-zinc ion complexes.[32] Differential scanning calorimetry (DSC) analysis of the interaction between sulfur, ZnO, stearic acid and several accelerators has been investigated by Kruger and McGill in a series of papers.[33-36] They have shown that zinc stearate is initially formed and reacts with sulfur, to open the sulfur ring. They also showed that both ZnO and zinc stearate were able to react with thiuram-based accelerators to form the accelerator-zinc ion complex.

One disadvantage of using large quantities of ZnO in the vulcanisation process is its environmental impact.[37] ZnO is currently classified as an environmental hazard. This has led to the search for a way to reduce the amount of ZnO present in commercial rubber formulations. One potential replacement for ZnO is from a group of materials known as multi-functional additives (MFAs).

1.3.2.3. Multi-functional Additives

An MFA is a compounding ingredient which can satisfy several functions simultaneously.[31] In early papers MFAs were initially called amine bridged amides (ABA), due to their structure.[38] The first purpose of the MFA is that of a processing aid, a function which is often taken up by stearic acid in conventional rubber cross-linking. Secondly, the MFA should act as an accelerator or activator.[38] The ability of the MFA to perform this second function would negate the use of ZnO within the rubber compound, or at least allow a reduction compared to standard curing systems.

An MFA is essentially a complex of a diamine and fatty acid (Figure 1.5). Upon heating, the complex breaks down, to yield the organic fatty acid which can act as a mould release agent and processing aid, while the diamine becomes a vulcanising agent or activator (Figure 1.6).[38]



Fatty Acid Linear Diamine Fatty Acid

Figure 1.5. Multi-functional additive complex structure, comprised of two fatty acids and a linear diamine.

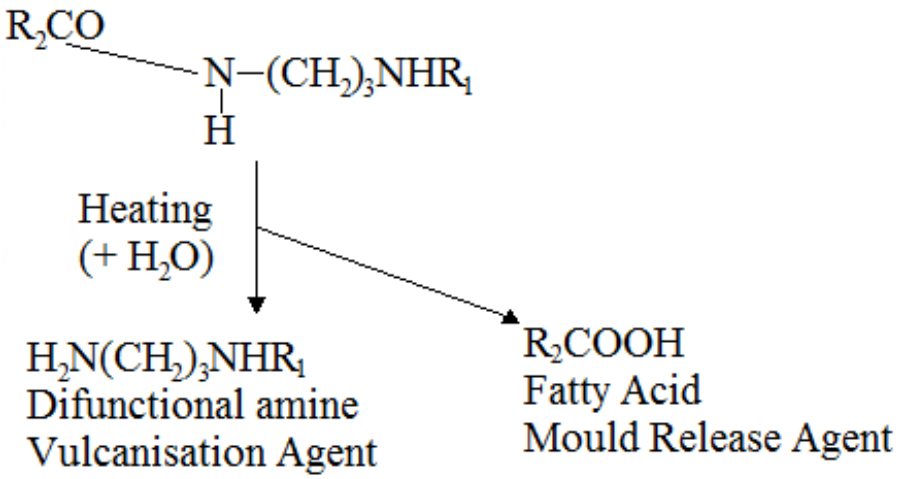


Figure 1.6. Proposed mechanism accounting for the many functions of an MFA as proposed by Hepburn and Mahdi.[38]

In addition to reducing the level of ZnO required in the vulcanisation process, the addition of MFA also benefits the final product. Physical properties of the cured material were found to be inferior with MFA formulations containing ZnO levels above 1phr.[31] The addition of the MFA to a standard formulation reduces the scorch time, which is reversed through the addition of ZnO.[39] Other advantages of an MFA include eliminating the use of a mould release agent, improved flow, better wetting and dispersion of fillers, better lubrication (for extrusion, calendaring etc.) and faster incorporation time for fillers.[37]

1.3.3. Other Types of Rubber Cross-linking

Although cross-linking of rubber is most usually achieved through the use of sulfur or sulfur-donors there are several other routes that can be followed to achieve cross-linking. Several of these methods are briefly discussed below.

1.3.3.1. Peroxide Cross-linking

Peroxide cross-linking produces carbon-carbon cross-links, and enables many polymers that are unable to cross-link *via* other methods to be cross-linked. The reason for this is the ability to cross-link saturated polymers such as polyethylene (PE) and ethylene-propylene-diene-monomer rubber (EPDM). There are several other advantages and disadvantages associated with peroxide cross-linking, as discussed by Aprem *et al.* and these are summarised in Table 1.5.[26]

Table 1.5. Advantages and disadvantages of peroxide cure, reported by Aprem *et al*.[26]

Advantages	Disadvantages
Simple compounding	Expensive cross-linking agents
Good heat ageing resistance	Low mechanical strength
Low tension set and strain	Higher curing time
No contamination	Difficult hot-air cure
Low compression set	Poor resistance to flex fatigue
Transparent rubbers possible	Needs secondary cure of high temperature

The main reactions involved in peroxide cross-linking are those of free radicals. Cross-linking using peroxides can be simplified to three steps:[40]

1. Thermal decomposition of peroxide to form a radical.

2. Hydrogen abstraction from the polymer, transferring the radical to the polymer chain.

3. Cross-link formation or coupling *via* the radical on the polymer chain. This occurs when two polymer chains containing radicals come into contact. A covalent bond is formed through the coupling of unpaired electrons.

The major limitation of peroxide cross-linking involves the choice of anti-oxidant used. Anti-oxidants are generally added to polymer compounds to prevent degradation of the polymer; by ultra-violet, heat etc. The role of the anti-oxidant is to react with radicals to prevent them from attacking the polymer. Some anti-oxidants will react with the radicals generated for cross-linking, so that the anti-oxidant and radical will be destroyed and the cross-link efficiency shall be much reduced.

1.3.3.2. Resin Cross-linking

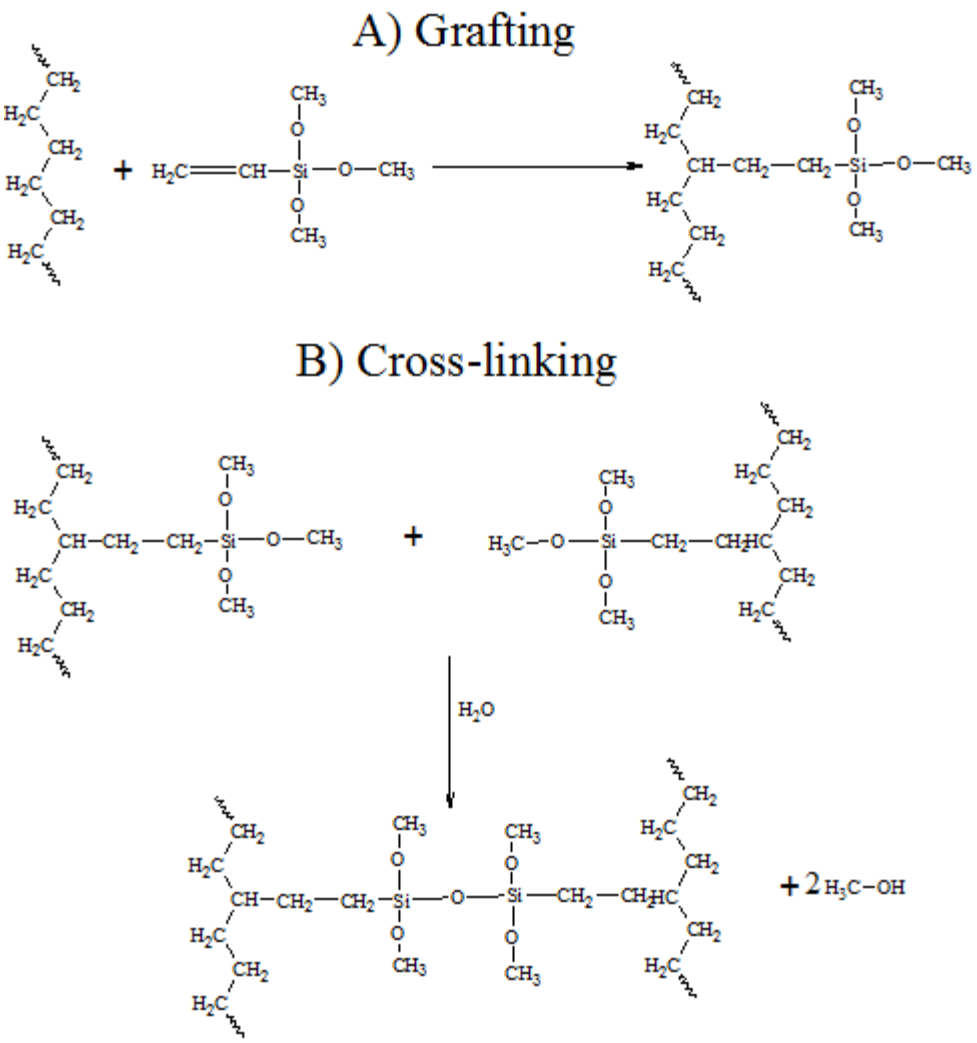
In the 1940s it was discovered that phenolic resins were able to cross-link unsaturated polymers.[26, 41] When compared to sulfur cross-linking, the reactions are slower and have to be performed at higher temperatures. In a similar fashion to sulfur cross-linking an activator is needed such as ZnO. Technically it is not the resinous properties of the agents which are important, as it is possible to use chemically similar crystalline compounds to cross-link.[16] Scheme 1.2 shows the process of resin cross-linking, typically di- or poly(methylol phenols)

are used as the cross-linking agent. The most common application for resin cross-linking is with of butyl rubber, with the final product being used for high temperature applications.[26] Although natural rubber, styrene-butadiene rubber, ethylene-propylene-diene-monomer rubber and other rubbers can also be cross-linked using this mechanism,[25] their rates of cross-linking are generally lower than those of butyl rubber.[26]

Scheme 1.2. Resin cross-linking mechanism reported by Kempermann.[29]

1.3.3.3. Silane Cross-linking

Alkoxysilane compounds are used as cross-linking agents with water. Consequently, silane cross-linking is also sometimes referred to as moisture cross-linking.[26] Silanes contain functional groups which graft onto the polymer chain. A cross-link can then be formed when two silanol groups react together. The cure for this system can be achieved at lower temperatures than that of other systems which is clearly advantageous in terms of cost and energy consumption.[26] An example of this form of cross-linking reaction is that of low density polyethylene (LDPE) with vinyltrimethoxysilane,[42, 43] as shown in Scheme 1.3.[43] The mechanism in Scheme 1.3 shows the two steps, with part (A) illustrating silane grafting to the polymer chain, and part (B) showing the actual cross-linking occurring between two polymer chains.



Scheme 1.3. Silane cross-linking mechanism, showing (A) silane grafting and (B) actual cross-linking of polyethylene.[26, 43]

1.3.3.4. Radiation Cross-linking

Radiation cross-linking in common with peroxide cross-linking produces carbon-carbon cross-links. High energy radiation, such as x-rays, produces free radicals within the polymer chain which are then able to react with each other to form cross-links.[26] For this to occur the energy of the radical producing hydrocarbon bond must be lower than that of the radiation.[16] Sources of radiation include Van de Graaff generators and resonance transformers.[44] A Van de Graaff generator works by producing electrons in a chamber. The electrons are accelerated by the application of a potential difference in a vacuum which increases their energy and allows them to break a hydrocarbon bond and produce radicals when in contact with the polymer.[16] A simple process for cross-linking is shown in Scheme 1.4.

Scheme 1.4. Radiation Cross-Linking as summarised by Aprem *et al*[26] whereby R represents an NR polymer chain and the termination step between two R radicals shows cross-linking between polymer chains.

1.4. Polychloroprene

Polychloroprene, commonly known by the trade name Neoprene,[4] was one of the first synthetic elastomers to be developed and is still considered important today.[45] The global capacity for polychloroprene in 1985 was over half a million tonnes,[2] with uses as wide ranging as the automotive industry,[46] construction industry,[46] adhesives[46] and even liner pads on missile launchers.[47]

1.4.1. Background of Polychloroprene

Developed in 1930 at Du Pont, polychloroprene, or poly(2-chloro-1,3-butadiene), was initially discovered through follow-up research to that being conducted in acetylene chemistry at the University of Notre Dame.[8] The acetylene chemistry research was originally presented at the American Chemical Society - Organic Chemistry Symposium in 1925 by Father Nieuwland.[8, 48] The work caught the attention of the Du Pont Company, and a joint research effort was established between the Du Pont Company and the University of Notre Dame from which polychloroprene was developed. Large scale production began in the mid-1930s and in 1939 a product under the Neoprene name was sold for the first time.

1.4.2. Synthesis and Polymerisation of Polychloroprene

Carothers and co-workers first studied the emulsion polymerisation of chloroprene in the early 1930s.[49-52] To date emulsion polymerisation remains the most common method for the industrial production of polychloroprene.[52-55] A simplified diagrammatical explanation of emulsion polymerisation is shown in Figure 1.7,[50, 56] and explained below.

1. Monomer is dispersed in a solution of water with surfactant.

2. The monomer forms droplets surrounded by the surfactant.

3. Excessive surfactant causes the droplets to decrease in size and form micelles.

4. An initiator is added which decomposes to produce radicals which then migrate into the micelles and react with the monomer.

5. Polymerisation within the micelles occurs – the resulting polymer particles are dispersed throughout the water, sterically stabilised by the surfactant.

6. The polymer latex is then extracted from the water.

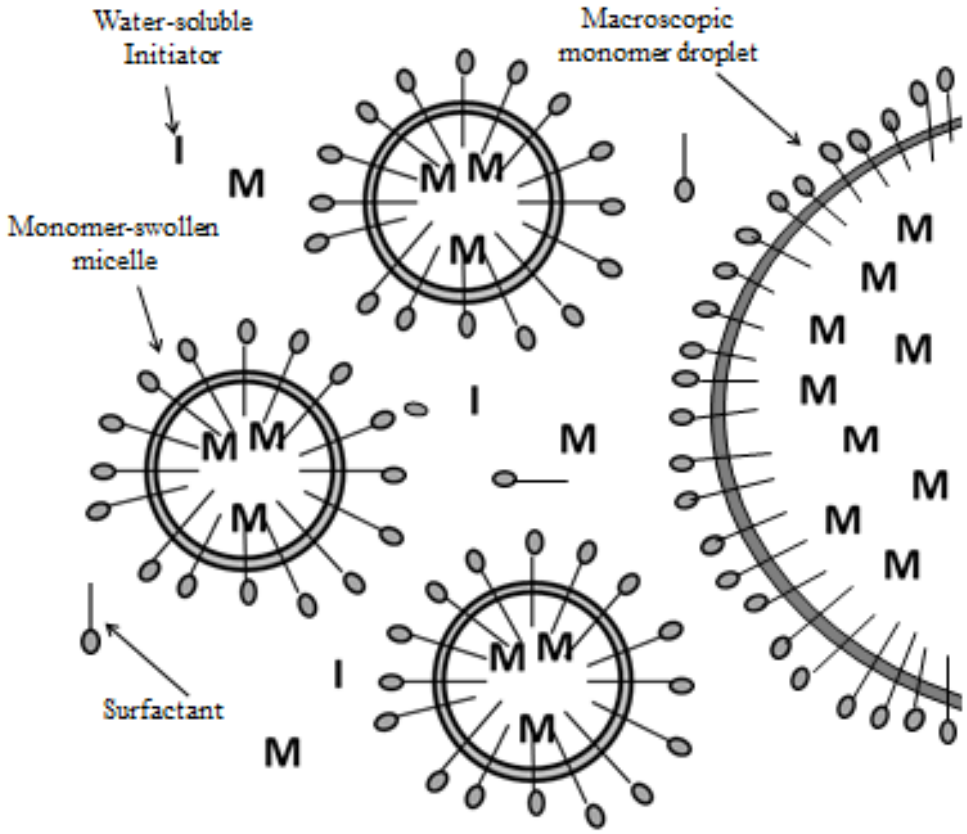


Figure 1.7. A simplified schematic diagram of emulsion polymerisation, adapted from Cowie.[17]

The most common surfactant used is anionic in character.[45] Many different initiators, such as sulfinic acid, can be used to provide a radical source, however problems can occur with impurities in certain initiators.[2, 57] These impurities can cause the formation of hydrogen peroxide which greatly reduce the polymerisation rate.[57] Inhibitors can be added to reduce the formation of hydrogen peroxide, but these in turn will themselves reduce the rate of monomer conversion.[2] More recent studies have shown that it is possible to polymerise chloroprene *via* reversible addition-fragmentation chain transfer (RAFT) polymerisation.[58] RAFT polymerisation allows for control over chain length, molar mass distribution and polymer architecture.[59] In RAFT there are several stages,[60] listed and shown in Figure 1.8.

1. Initiation – Decomposition of the radical initiator, and the reaction with the monomer molecule to form a propagating polymer radical.

2. Pre-equilibrium or reversible chain transfer – The reaction of the polymer radical with the RAFT agent to form a RAFT adduct radical. This RAFT adduct radical can then fragment to form either the starting species or an R group radical.

3. Re-initiation – If the R group radical is formed it can react with another monomer to start another active chain.

4. Main or chain equilibrium – Through the RAFT agent the polymer chains 'share' the radical, giving all chains an equal chance of growth through monomer addition. This should result in even growth and a low PDI.

5. Chain termination – The addition of two radical polymer chains will result in dead polymer and termination of growth.

Figure 1.8. RAFT Mechanism reported by Moad *et al*.[61]

1.4.3. Isomerism in Polychloroprene

Having discussed synthesis of polychloroprene, examining the structure of it reveals four different isomers.[62-65] The concentration of each isomer obtained is dictated by polymerisation temperature and quantity of surfactant and initiator used during the emulsion polymerisation process.[66, 67] Standard commercial grade polychloroprene consists of 80-90 % *trans*-1,4-isomer, 5-15 % *cis*-1,4-isomer, 1-2 % 1,2-isomer and 2-4% of the 3,4-isomer.[65, 66, 68-72] Any remaining contribution comes from chain ends and impurities.[63, 73, 74] The structures are shown in Figure 1.9[62-65, 70].

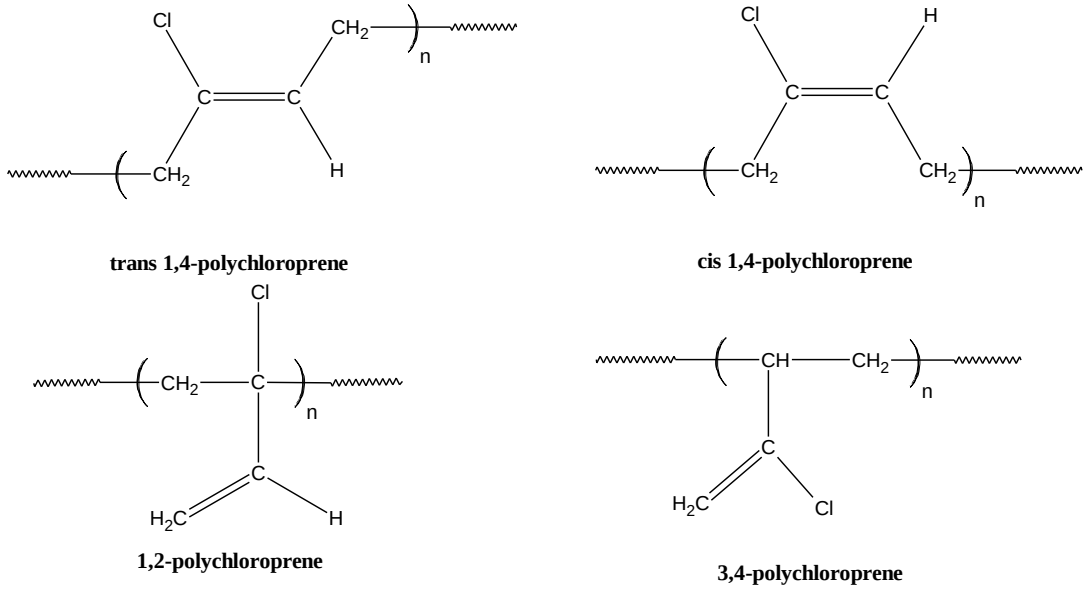


Figure 1.9. The four isomeric structures of polychloroprene.

The 1,2-isomer has been identified as the "key" isomer in the cross-linking process[16, 38, 75-79] this is due to its tertiary chlorine which has the ability to undergo allylic rearrangement.[73] It is at this rearranged site on the polymer chain that cross-linking is thought to occur (discussed in Section 1.4.5 in more detail). Rearrangement of the 1,2-isomer can occur on heating of neat polychloroprene. However, rearrangement occurs much quicker in the presence of certain chemicals, such as ZnO. The rearranged 1,2-isomer is shown in Figure 1.10.

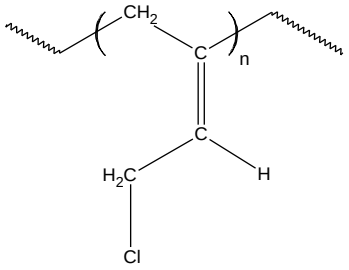


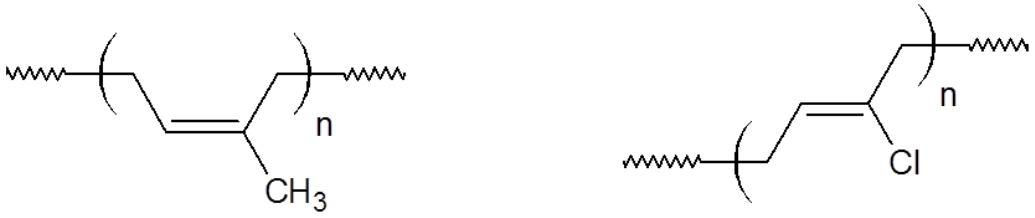
Figure 1.10. The structure of the 1,2-isomer of polychloroprene after undergoing rearrangement.

1.4.4. Properties of Polychloroprene

Polychloroprene has many unique properties, including good heat, oil, ozone and chemical resistance.[2, 45] Its widespread commercial use is due, in part, to its excellent weather resistance when compared to other rubbers under similar conditions.[4, 80] Other properties include better resilience when compared to natural rubber at high filler loadings, and the ability to retain many of its properties up to 120 °C, giving it a good operational temperature range.[81] These properties, which although not as good as some specialised rubbers, combined with its relatively low price, are the main reason why polychloroprene is a popular choice for a wide range of uses.[8]

1.4.5. Polychloroprene Additives

As previously noted, polychloroprene cross-links differently compared with many rubbers. This is due to its unique structure, when compared to *cis*-polyisoprene [the main constituent of natural rubber (NR)] (Figure 1.11) the main difference is the methyl group in NR substituted by a chlorine atom in polychloroprene. In many rubbers cross-linking occurs through an unsaturation in their backbone, however in polychloroprene the electronegative chlorine atom inhibits this,[82] and cross-linking transpires through the 1,2-isomer after rearrangement of the tertiary chlorine. Consequently, different additives to those discussed in Section 1.3.2.1 are used as cross-linking agents. Other ingredients within a rubber formulation (such as fillers etc.) are essentially the same. With polychloroprene, the main cross-linking agents used are ZnO and ETU, either separately, but more typically in combination. As there are many health risks associated with ETU, several papers have been written reporting the quest to find an alternative. One of the earliest cross-linking studies conducted with polychloroprene was using lead (II) oxide (also known as litharge).[83] Litharge was compared to ZnO which was in use at the time as an accelerator and was found to give a comparable cure, but much higher levels (10-20 phr) were required. The study concluded that litharge would not be a suitable replacement for ZnO due to the higher levels required. The mechanism by which both litharge and ZnO cross-linked was thought to be similar, although the actual mechanism was not discussed.



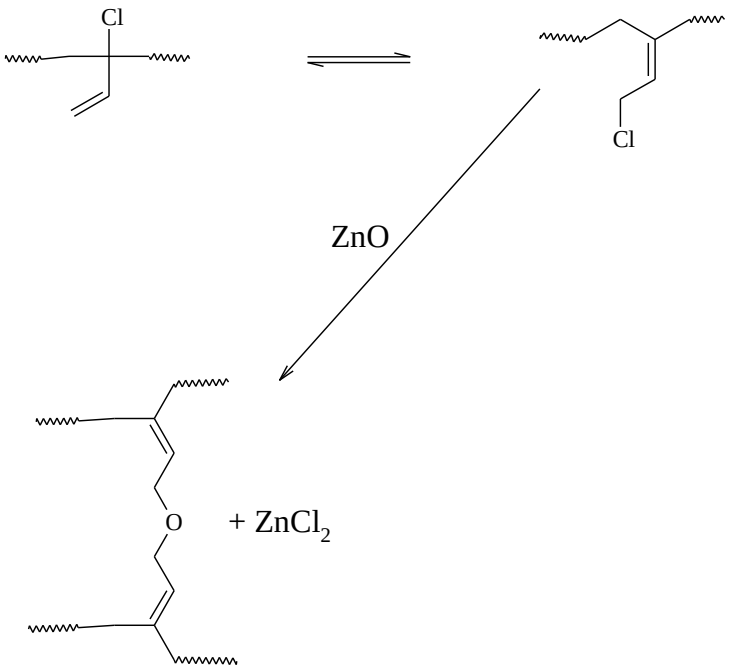
Cis-polyisoprene Trans-1,4-polychloroprene

Figure 1.11. Comparison between the structures of *cis*-polyisoprene and *trans*-1,4-polychloroprene.

1.4.5.1. Zinc Oxide

The major difference with ZnO in polychloroprene (rather than in other rubbers) is that it can cross-link polychloroprene rubber (CR) on its own.[50] ZnO also aids cross-linking when in combination with ETU[75, 76, 84, 85] (see Section 1.4.5.2). The mechanism by which polychloroprene cross-linking occurs with ZnO is not fully understood, and numerous studies and proposals have been presented. In many of the proposed mechanisms for polychloroprene cross-linking, with either ZnO or ETU, the first step is the rearrangement of the 1,2-isomer.[8, 16, 38, 50, 62-64, 73-79, 81, 86-89] One of the earliest theories for cross-linking polychloroprene was through the formation of an ether linkage,[16, 38, 74] with the oxygen derived from ZnO (Scheme 1.5). This theory has subsequently been disproved by several studies through the use of model compounds[86] and NMR spectroscopic studies.[79] Further experiments with halobutyl based compounds have also discounted the cross-linking reaction proceeding *via* a Diels-Alder reaction.[86, 87]

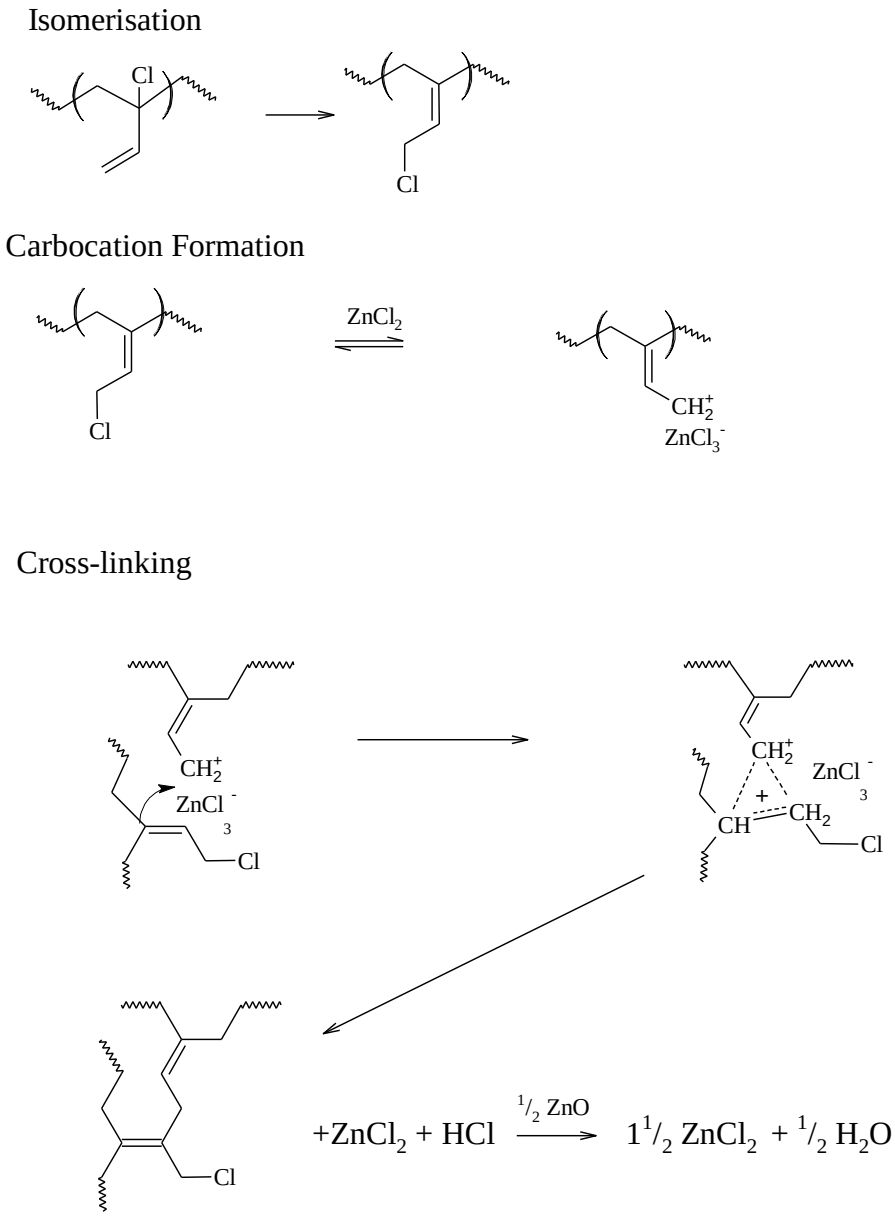
Both Vukov[87] and Desai *et al*.[62] proposed that the cross-linking reaction proceeds cationically. Vukov[87] used model compounds and building upon work with chlorobutyl rubber by Kuntz *et al*,[86] put forth that the major reaction taking place is that of diene formation. The diene then acts as a catalyst for the cross-linking reaction. Desai *et al*.[62] gave evidence for a three stage cross-linking process (Scheme 1.6), - isomerisation of the 1,2-isomer, carbocation formation and then cross-linking. The evidence for this mechanism, however, was obtained using zinc chloride ($ZnCl_2$), not ZnO, and relies on the formation of $ZnCl_2$ for cross-linking to occur.



Scheme 1.5. 'Ether linkage-forming' cross-linking mechanism for zinc oxide in polychloroprene,[16, 38, 74] now discounted due to several papers.[79, 86]

Several studies examining cross-linking polychloroprene with ZnO suggested that model compounds such as chlorinated poly(iso-*co*-butylene) (CIIR or chloro butyl)[62, 86] would help elucidate the mechanism. This approach was adopted by Baldwin *et al*.[88] who used CIIR to propose a cationic mechanism, where $ZnCl_2$ was formed *in situ*. A revised cationic mechanism was then proposed using CIIR over a series of papers by Hendrikse *et al*.[89-91] Both the original and revised mechanisms have similarities to those proposed for polychloroprene by Vukov[87] and Desai[62] respectively. However, the validity of using CIIR as a model compound, due to its structural differences to polychloroprene, is unknown.

A different cross-linking mechanism using ZnO was proposed by Mallon *et al*.[63] From work conducted using Differential Scanning Calorimetry (DSC), two processes were suggested to take place. The first reaction is rapid and involves the unisomerised 1,2-units, the second reaction is slower and only involves the isomerised 1,2-units. No actual reaction mechanisms were given, and the proposed reactions are in disagreement with many other mechanisms, which state that the 1,2-isomer must rearrange before cross-linking can occur.[16, 79, 92] Additionally, the evidence given in the report by Mallon *et al* for the unisomerised 1,2-unit reacting was not conclusive.



Scheme 1.6. Polychloroprene cross-linking mechanism using zinc oxide, proposed by Desai *et al.* [62]

A report by Aprem *et al.*[26] gave two mechanisms for cross-linking with ZnO, the first was that of ether linkage which has previously been discounted. The second involved the insertion of the zinc atom into the cross-link but there is no clear evidence reported for this mechanism.[93]

In addition to their ability to cross-link polychloroprene the ability of metal oxides, in particular ZnO and magnesium oxide (MgO) to 'mop up' acids within a rubber sample have been documented. This enables the metal oxide to form a chloride, which in turn can accelerate the cross-linking process. However, the ability of MgO to act as an activator has

been shown, in sulfur-curing compounds at least, to be worse than ZnO.[94] It has also been shown that MgO-containing samples typically have a lower degree of cross-linking, due to the inability of MgO to form complexes.[94, 95] It is therefore possible that in polychloroprene cross-linked samples there may be a major difference between those samples cured with ZnO and those with MgO.

1.4.5.2. Ethylene Thiourea

The cross-linking of polychloroprene rubber is most commonly achieved using ethylene thiourea (also known as 2-imidazolidinethione) as the accelerator. ETU exists in a tautomeric form (mercaptoimidazoline); the chemical structures of both are shown in Figure 1.12. The levels at which the mercaptoimidazoline is present have been the subject of several papers. Wheatley,[96] expanding on work carried out by Vaughan and Donohue[97] on resonance structures with urea based compounds, found that the tautomeric form accounted for about 78 % of the structure. However, two separate papers produced by the 'Theoretical Chemistry Group' at the McGill University in Canada, concluded differently. [98, 99] Both pieces of work concluded that the level of the tautomeric form would be closer to 58 %. They also placed doubt on the results of Wheatley,[96] claiming that his results would render the nitrogen charge deficient.

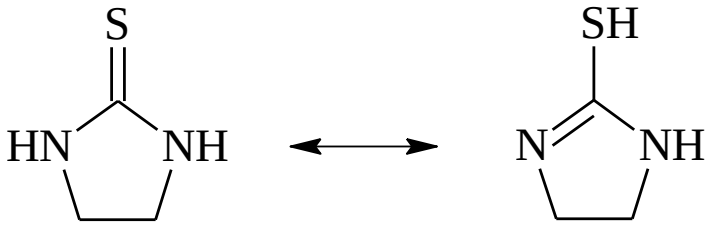
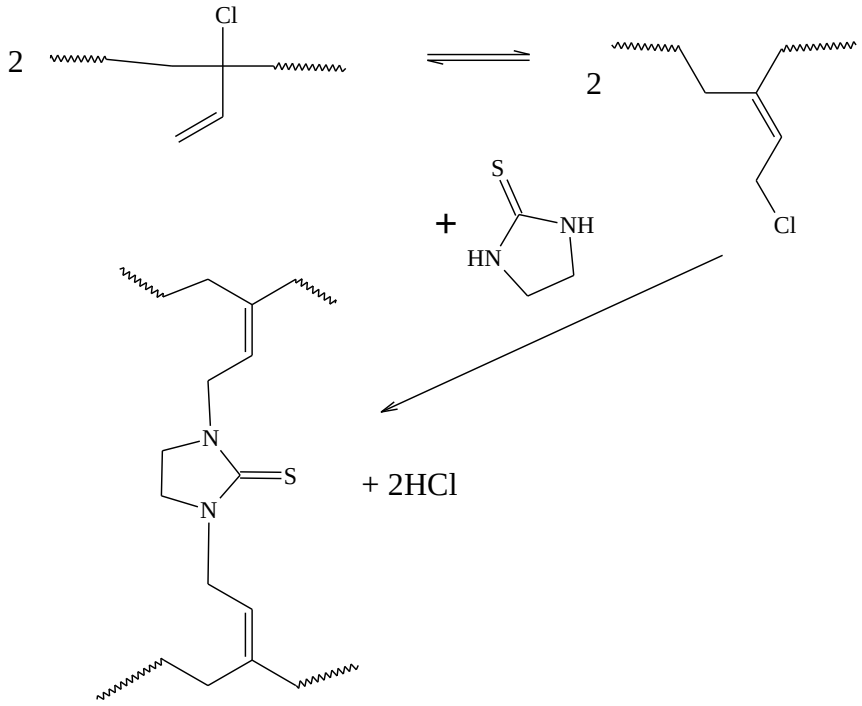


Figure 1.12. Ethylene thiourea and mercaptoimidazoline, the tautomeric forms it can take.

1.4.5.2.1. Cross-linking Polychloroprene with Ethylene Thiourea

A scientific approach to achieve a replacement for ETU involves understanding the mechanism by which ETU cross-links polychloroprene. One of the earliest mechanisms proposed for cross-linking with ETU was put forth by Kovacic.[73] The bis-alkylation mechanism (Scheme 1.7), as it was called, was a general mechanism for a bi-functional diamine, whereby a metal oxide, if present, quenches the acid produced. This theory was purportedly confirmed in work by Hepburn *et al.*[38] but the supporting evidence for this is

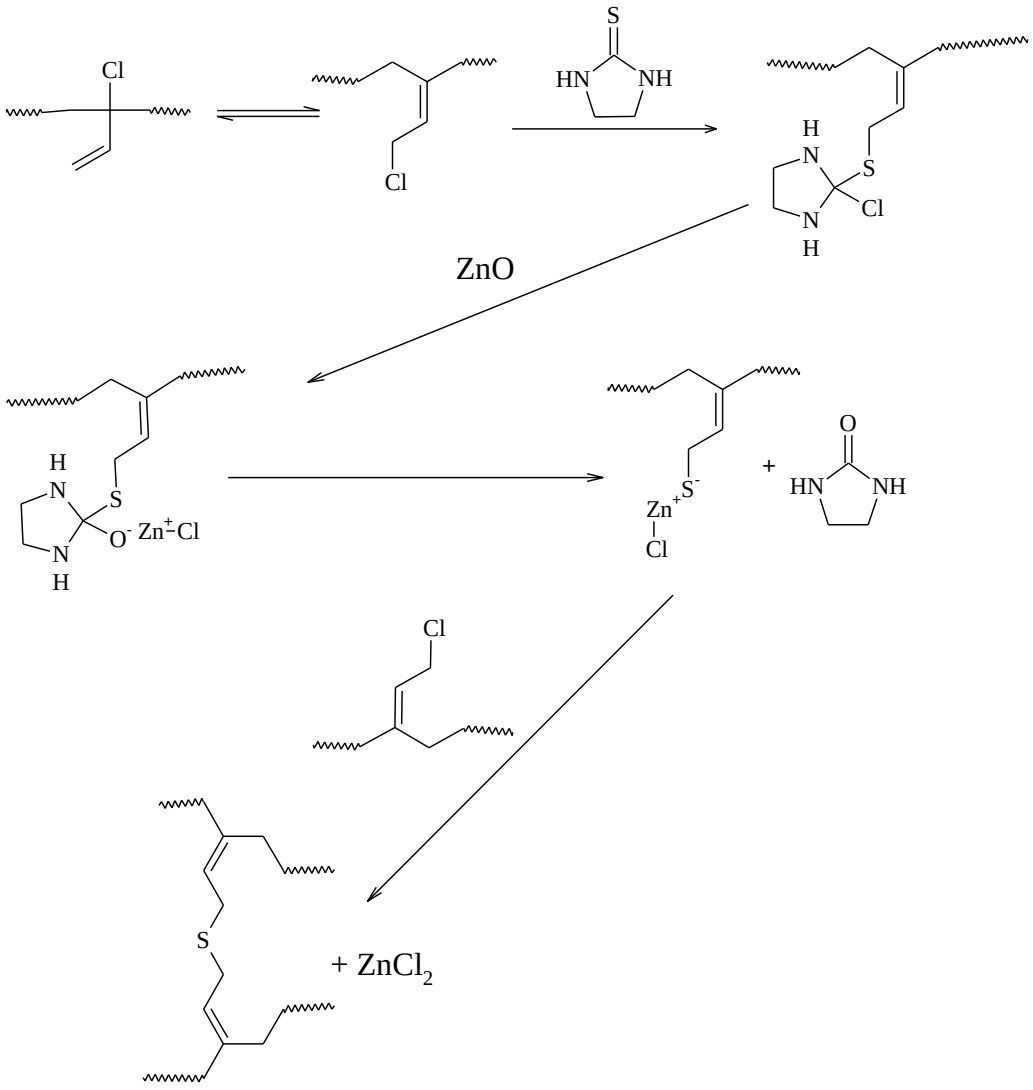
inconclusive. Much work has been based upon the bis-alkylation theory being correct, including work for the use of amines as cross-linking agents.[74]



Scheme 1.7. Kovacic's bis-alkylation mechanism for the cross-linking of polychloroprene. The mechanism is shown here with ETU; however the original report featured piperazine with magnesium oxide present to react with the hydrochloric acid formed to give magnesium chloride.

A cross-linking mechanism with both ETU and ZnO (Scheme 1.8) working together has been reproduced in several books and papers,[16, 25, 100] and has been credited to Pariser.[101] It is the only reported mechanism which includes both ETU and ZnO as necessary components; therefore, it is widely quoted as the accepted mechanism for joint cross-linking.

The bis-alkylation mechanism generates hydrochloric acid as a by-product, if no metal oxide is present,[73] while the Pariser mechanism evolves $ZnCl_2$ and ethylene urea.[101] In theory it should therefore be possible to study the derivatives of these cross-linking reactions for evidence of each of these mechanisms occurring, but this, to date, has not been done.



Scheme 1.8. Cross-linking mechanism for polychloroprene with zinc oxide and ethylene thiourea working in unison as first proposed by Pariser.[101]

1.4.5.2.2. Health Risks of Ethylene Thiourea

There have been a number of reports written on the subject of the health risks associated with ETU. Several of these papers have discussed research into the potential carcinogenic nature of the accelerator, [102-105] with some of the research looking at people who have actually worked with ETU. The study found that although thyroid cancers were seen in rats dosed with ETU,[106] this was not seen with humans who had been working with ETU.[102] There are also risks with regards to thyroid function when using ETU, as shown in research conducted with rats.[107-109] A case of hypothyroid, where raised levels of thyroid-stimulating hormones are produced, was also observed in a human subject who worked with ETU.[103, 110] However, this raised hormone level had no clinical effect upon the worker.

Dangers with ETU to the unborn foetus of pregnant humans, have been researched both in studies with rats[111, 112] and with statistical research on women who had previously worked with ETU and subsequently became pregnant.[102, 113] This work shows similar results to that of carcinogenicity, in that though there is a risk seen in rodents, no cases have been seen in humans. Both studies with human subjects, into carcinogenicity and teratogenicity, admitted that the study groups were small as they would be unable to purposefully expose people to ETU. Furthermore, the levels of ETU that the humans were exposed to would have been smaller than those that the rats were exposed to. However the research has led to women of child bearing age being advised not to work with ETU.[102]

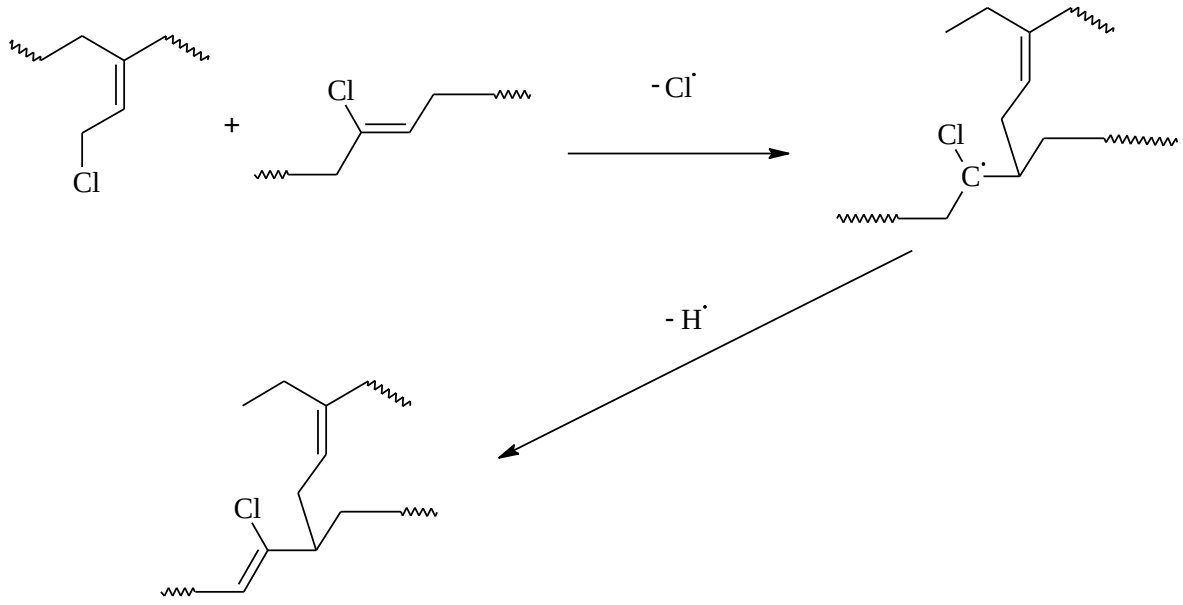
Another potential problem with ETU can arise when it is in contact with skin, where contact dermatitis can occur.[114, 115] This is most often the case in items cured with ETU, where some residual amount of the chemical is still present and when the item is in contact with the skin for a prolonged period. As a consequence studies were conducted to analyse 'workers' that were in contact with ETU on a regular basis at work. New research allowed for the levels of ETU within a worker's system to be monitored. The findings also showed that the half-life of ETU within a human to be 19 to 23 hours following exposure.[116]

ETU is formed by the decomposition of ethylenebis(dithiocarbate) fungicides used on food crops. As there are potential risks with ETU if consumed by humans, the life time of ETU in plants after exposure was studied.[117] It was seen that small traces (1-2 % of initial dose) of ETU were still present in the plants after 20 days. However a degradation product of ETU, ethylene urea (EU) was found to be present in the plants. This shows another potential problem with ETU - if it is allowed to get into the wider environment, any contamination of crops would still be present several weeks later. This coupled with the potential health risks if ingested show the need for a replacement of ETU.

1.4.5.3. Other Cross-linking Mechanisms for Polychloroprene

After examining the cross-linking of polychloroprene with ETU and ZnO, other mechanisms are also present in the literature. Polychloroprene is able to undergo a form of cross-linking as a consequence of thermal degradation.[79, 92] In this mechanism polychloroprene loses a chlorine radical, which enables self-vulcanisation to occur. This mechanism is unique to all of

the other proposed mechanisms as it is the only mechanism in which the 1,4-isomer takes part (Scheme 1.9).



Scheme 1.9. Cross-linking of polychloroprene during thermal degradation, proposed by Miyata and Atsumi.[79, 92]

Cross-linking can occur when polychloroprene has been blended with another polymer; this process greatly alters the properties of the polymers involved.[118-121] As a result, much of the research conducted into this area is concerned more with the change of properties than the mechanisms and reason for cross-linking.

1.4.5.4. Alternative Accelerators for Polychloroprene

As a consequence of the issues discussed in Section 1.4.5.2.2 with ETU, a safer accelerator has long been sought for cross-linking polychloroprene. Many studies, for example those concerning tribasic lead sulphate,[122] were unsuccessful. Others, however, were more effective. In a study that Kato *et al.* conducted, 2,2,4,4-tetrahydroxydiphenyl sulfide (AD-9) (Figure 1.13) was tested as an accelerator to directly replace ETU.[77] It was found to give similar results to ETU in the presence of ZnO. However, AD-9 is considerably more expensive than ETU.

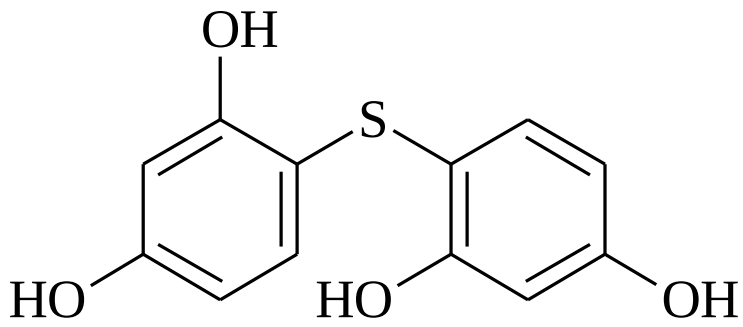


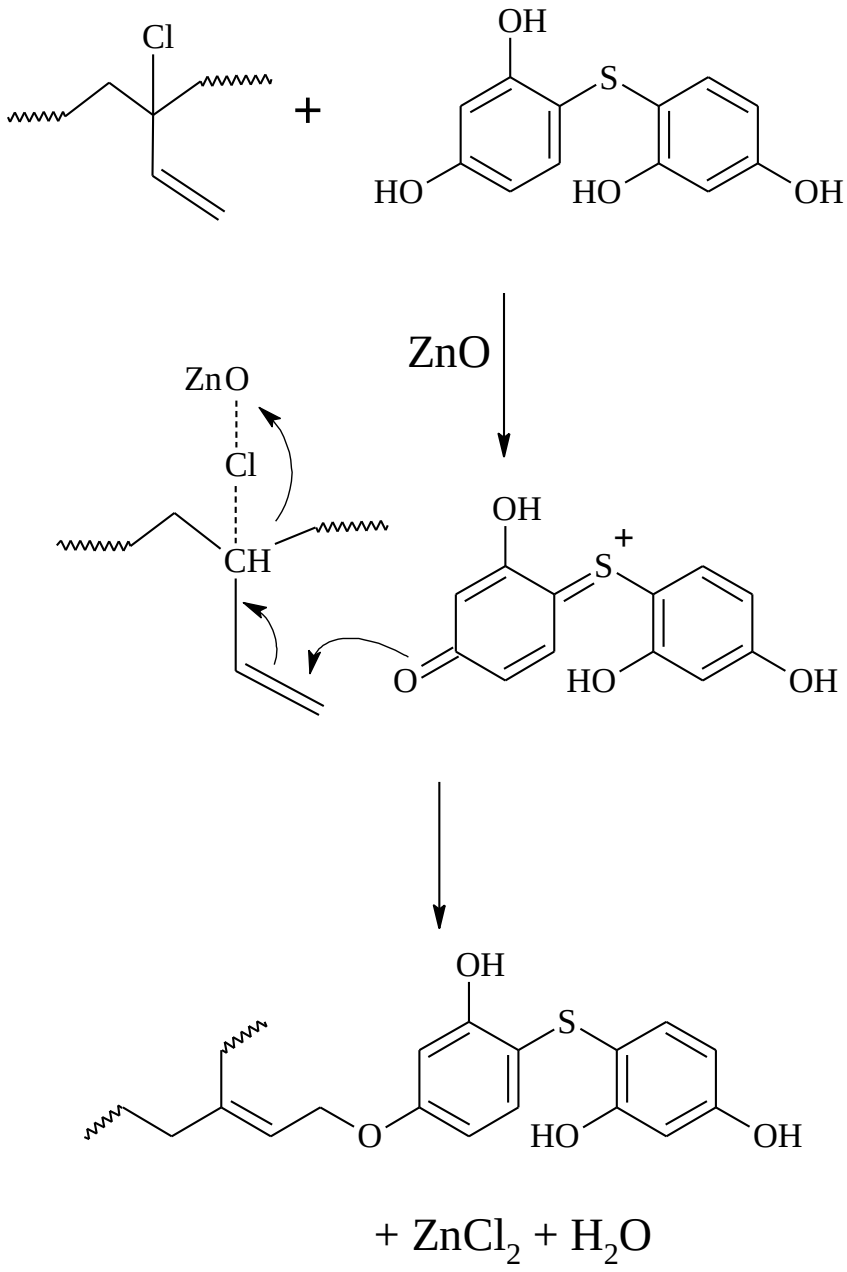
Figure 1.13. Structure of AD-9, a proposed replacement for ethylene thiourea.[77]

A mechanism by which AD-9 cross-links polychloroprene (Scheme 1.10) was proposed in the same paper.[77] From the outcome of this proposed mechanism, Kato went on to test a dicatechol polysulfide as an accelerator for polychloroprene.[123] The paper concluded that dicatechol polysulfide was able to cross-link polychloroprene, but only in the presence of TMTD, which acts as a sulfur donor.

A series of reports on the moisture curing of halogenated rubbers was reported by Yamashita *et al.*,[124-127] where polychloroprene was reacted with 3-aminopropyltriethoxysilane (APS) in hot water. There is no comparison between the moisture curing system used and a standard curing system, however. For this reason, and the different technology employed compared to standard curing it is difficult to see this as a potential replacement for ETU.

Several papers have reported the ability of one compound to cross-link several different rubbers. These reports are generally more concerned with the ability of the compound to cross-link, rather than finding a potential replacement for ETU. Minoura *et al*.[128] studied aldehydes and acidic compounds in combination to cross-link rubbers (including polychloroprene), and a general rubber cross-linking mechanism was given. The characteristics of 1-(*N*-oxydiethylenethiocarbamyl)-2-(*N*-oxydiethylene thio) benzimidazole (MBSPT), were studied.[129] Its ability to act as both an anti-oxidant as well as an accelerator in polychloroprene was reported, but no comparison with ETU was given, nor was a mechanism provided. Similarly, a study of dicumyl peroxide in many rubbers was reported.[130] It was found that although dicumyl peroxide was able to cross-link polychloroprene; it was not very active compared to its use in other rubbers. The dicumyl peroxide produced on average half a cross-link for each for each molecule of peroxide, which

is very low, particularly when compared to styrene-butadiene-rubber (SBR) where over 12 cross-links were produced per molecule of peroxide. This means that on average half the molecules of dicumyl peroxide were wasted in polychloroprene.



Scheme 1.10. Initial stage for cross-linking polychloroprene with AD-9, the next stage requires one of the remaining alcohol groups to react with a chlorine in the polychloroprene chain and complete a cross-link in a similar manner.[77]

Several thiophosphoryl disulfides and structurally similar chemicals were tested as accelerators in polychloroprene rubber.[76] They were found to be able to cross-link polychloroprene, but with a higher cure time than the standard ETU system, a problem that would have to be overcome for them to have a practical application. Thiophosphoryl

disulfides were also examined in blends of polychloroprene with EPDM,[131] with more emphasis on their ability to help filler dispersions rather than the curing characteristics.

Many other potential replacements have been studied but shown to have flaws. Cetyltrimethylammonium maleate (CTMAM) was examined first in NR[132] before being tested in polychloroprene.[133] It was shown that higher concentrations were needed to achieve similar cure times to ETU, and that the resilience of CTMAM compounds was reduced compared to standard curing systems. Blends of polychloroprene with phosphorylated cashew nut shell liquid (PCNSL) pre-polymer were also studied and compared to a conventional cure system[134]. However, it was shown that the ETU cured system had a higher cure rate and maximum torque. The naturally occurring amino acid dimethyl $_{L}$-cystine, was found to work well as a cross-linking agent in polychloroprene, especially in the presence of sulfur.[75] It is acknowledged that a more detailed study would need to be performed to fully understand the chemistry of the process that is occurring. 2,5-dimercapto-1,3,4-thiadazole was suggested as a potential replacement[135] for ETU. It was claimed to produce a better curing system, due to a higher scorch time and flatter cure plateaux, compared to the marching modulus of an ETU system (see Section 1.5.1.1 for explanation of scorch time cure curves). It was also shown, however, to give a longer elongation at break and lower tensile strength compared to the ETU system.

One of the closest studies to providing a replacement for ETU is that by Fuchs *et al*.[84] The use of 3-methyl-thiazolidine-thione-2 (MTT) (Figure 1.14) as a replacement showed promise, but for a small window of optimum cure brought about by a longer scorch time and shorter overall cure. This combined with the fact that MTT is sensitive to the activity of ZnO (whereas ETU is not), and that a health risk assessment was not carried out leads to the conclusion that more work is required in the search for a replacement for ETU.

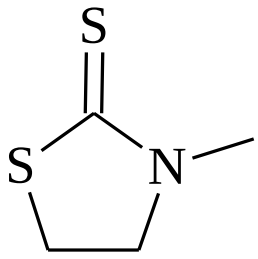


Figure 1.14. Structure of 3-methyl-thiazolidine-thione-2 (MTT), a proposed alternative accelerator to ETU.[84]

In 1950, before ETU had widespread use as an accelerator for polychloroprene, ZnO was trialled with several 'rubber-type' accelerators.[136] It was assumed that polychloroprene cross-linked in a similar fashion to other rubbers, so it was believed that sulfur was necessary for cross-linking. This is in part due to some grades of Neoprene containing sulfur, which were believed to decompose to give free sulfur, and thus aid in cross-linking.[4] To this end either accelerators which can act as sulfur donors or those that could not with the addition of sulfur were trialled. It was found that some accelerators such as tetramethylthiuram monosulfide (TMTM) were able to cross-link polychloroprene when in the presence of ZnO. Additionally, traditional rubber accelerators were examined in polychloroprene rubber and the rheological and mechanical properties studied using mathematic models based upon quantitative structure-property relationship (QSPR).[137] These studies were concerned with mathematic models ability to predict of physical properties, rather than the mechanisms of cross-linking.

1.5. Characterisation Techniques for Rubbers and Polymers

Many different techniques can be used in the characterisation of rubbers and polymers. Some of these techniques are specific to polymers or rubbers and others are more general analytical techniques. This section examines the mechanical testing of rubbers, looking in detail at the rheological and tensile tests utilised. The spectroscopic tests most commonly performed namely nuclear magnetic resonance (NMR) and Fourier transform infrared (FTIR) are then also reviewed.

1.5.1. Physical and Mechanical Property Determination

There are many physical and mechanical tests that can be used to characterise rubbers, such as hardness and compression set. Perhaps two of the most useful are rheological testing, which can impart knowledge of how well cured the rubber is, and tensile testing which will allow the ultimate tensile strength of the cured rubber to be acquired. Both of these techniques are discussed in more detail in this section.

Physical testing is one of the most common ways to directly compare one cured compound with another. Typically, physical testing is used as a quality control test (to ensure that either samples of the rubber or additives contained therein meet the appropriate standard), but it is also used as a research tool, identifying certain properties of the rubber. As well as producing

data such as how hard or how high the tensile strength is, other factors can also be gleaned from the results. Such as how cross-linked the sample is. Additionally, information on the cross-links can be obtained which is important in sulfur curing as the difference in characteristics between something with mono-sulfidic cross-links and poly-sulfidic cross-links can be quite large. This leads to the researcher looking for different ideal results depending upon the application of the final product.

Hardness measurements of polymers can be done in several ways. The most common of which is the resistance to penetration by an indentor under a constant load.[138] There are several different scales used, the most common being Shore A or D[139] and international hardness.[140] They are therefore usually used as a comparative test to compare to previously measured samples. The level of hardness in all cases increases as the degree of cross-linking increases.[16]

The compression set of a material is a measure of the amount of plasticity within the cured rubber. This is measured as the amount of deformation remaining in the material after a load has been removed.[6, 141] There are several variables that can be altered, depending upon the final use of the cured rubber article, these include,[142-144] the amount of compression achieved either through (i) samples compressed to a measured thickness, usually measured as a percentage of the original thickness, (ii) a constant load placed upon the samples to be tested. The length of time under compression, and the temperature compression occurs at can also be varied.

1.5.1.1. Rheological Studies

For a rubber, the rheology (or flow) of matter when under an applied force are currently measured by rheometers, sometimes called in the rubber industry curemeters. Originally developed in the 1950s and 60s[145] the most commonly used ones today are moving die rheometers (MDR), oscillating disc rheometers (ODR) and Mooney rheometers. Each of these instruments measures the rheology slightly differently, thus results will vary from method to method. This means that many rubber technology laboratories are equipped with more than one type of rheometer. In MDR, a sample is placed between two heated platens, the bottom platen oscillates and the torque required for the oscillation is measured (Figure 1.15A). Alternatively, ODR has a heated disk embedded in the rubber sample; this is placed between

two heated dies (Figure 1.15B). The disc then oscillates and the torque required for continued oscillation is measured. In a Mooney rheometer a heated rotor or spindle is placed into the rubber sample, this is then located between two heated dies (Figure 1.15C). The spindle is then rotated at a constant speed and the torque required for constant rotation is measured. In all three cases as the rubber cures the torque required will increase, up to a point where the rubber is fully cured.

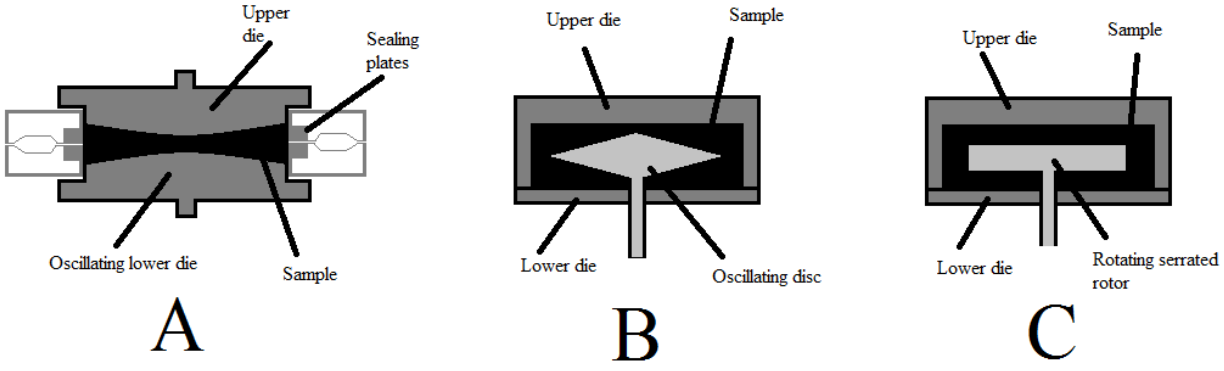


Figure 1.15. Cross-sections of the three rheometers A) moving die rheometer, B) oscillating disc rheometer and C) Mooney rheometer.

The results from these rheometers will be in the form of a trace, from which several important factors can be ascertained. A typical rheometer trace is shown in Figure 1.16, highlighting the three regions of curing; the induction or scorch (region 1) , curing (region 2) and over cure or post cure (region 3).[146] Induction marks the region before curing starts. The length of induction also called the scorch time, TS1 or TS2, and is marked when the torque has increased either 1 or 2 points from the minimum torque. The choice between using TS1 or TS2 as the choice of scorch time is usually made depending upon the cure system. A material with a low scorch time may be known as a scorchy material, this property in a rubber would have implications in industry as it would cause problems with samples beginning to cure before being fully moulded. Hence the use of certain accelerators in sulfur cured systems (such as CBS) which are deliberately employed to increase the scorch time.

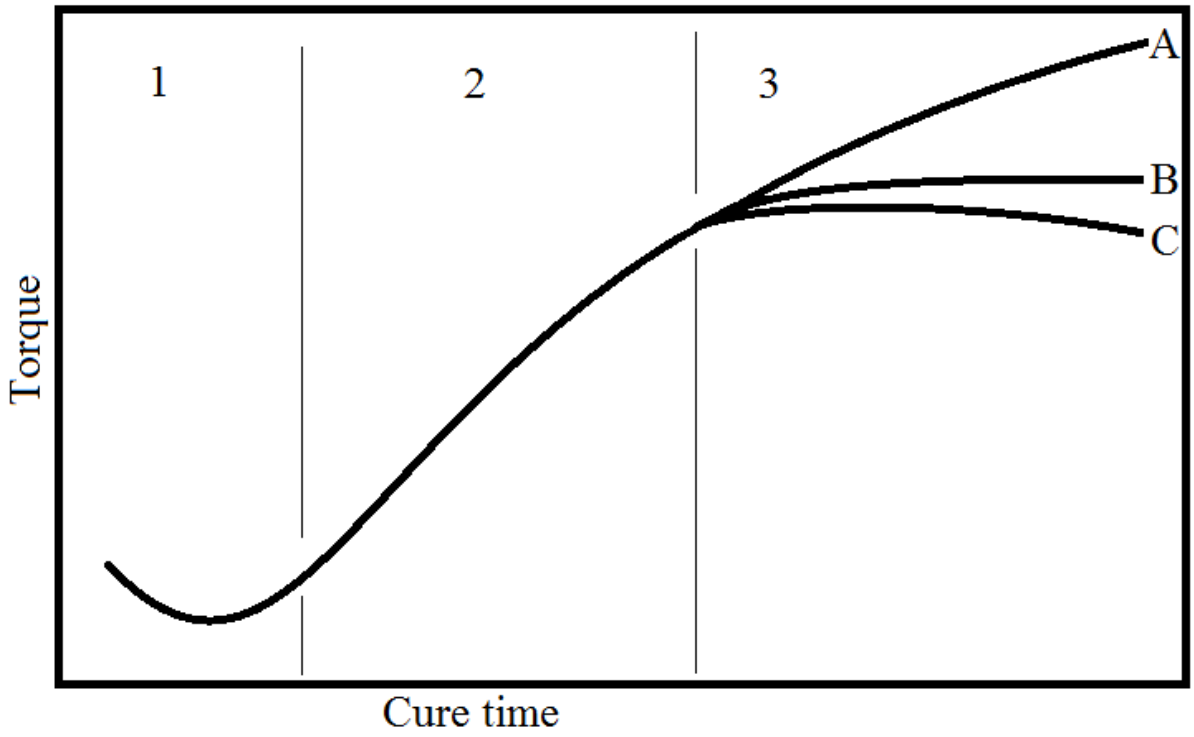


Figure 1.16. Typical rheometer trace, where regions; 1) induction, 2) cure and 3) over cure, and curves A) marching modulus cure B) normal cure and C) reversion cure are indicated.

The curing time indicates the time taken for the full, or optimum, cure to be reached, often indicated by a T90 time (the time to reach 90 % of the maximum torque). During this period the maximum rate of increase in torque and the MH (maximum torque reached) is also measured. The MH can impart the level of cross-linking present within the sample, but does not provide details concerning the types of cross-links present (mono-sulfidic, poly-sulfidic etc., in a sulfur cure). For example, if a sample has a low MH it will have poor physical properties, due to lack of cure, however, high MH does not imply better physical properties as the cross-links present may be weaker.

There are three states that can be seen in the post cure in a rheometry trace; (i) plateau – where the final torque remains roughly constant (ii) marching modulus where the torque continuously gradually increases and (iii) a reversion cure (which is occasionally observed) where after reaching its maximum level the torque starts to drop.

1.5.1.2. Tensile Testing of Rubber

Tensile testing of cured rubber samples is achieved using a tensometer. Dumbbell shapes are cut out of the rubber sample, clamped within jaws of the tensometer and pulled apart at a constant rate. The force required to pull the jaws apart at this constant rate is measured.[147] Knowing the dimensions of the dumbbell before testing allows the modulus at various stages of extension to be calculated. It is also possible to work out the yield strength, ultimate tensile strength, elongation at yield and elongation at break. The speed at which the jaws move apart, and the size of the samples being tested will alter the final results; it is therefore imperative that like for like samples are compared.[6] A typical curve produced from a tensile test is shown in Figure 1.17, and the various points are marked upon it.

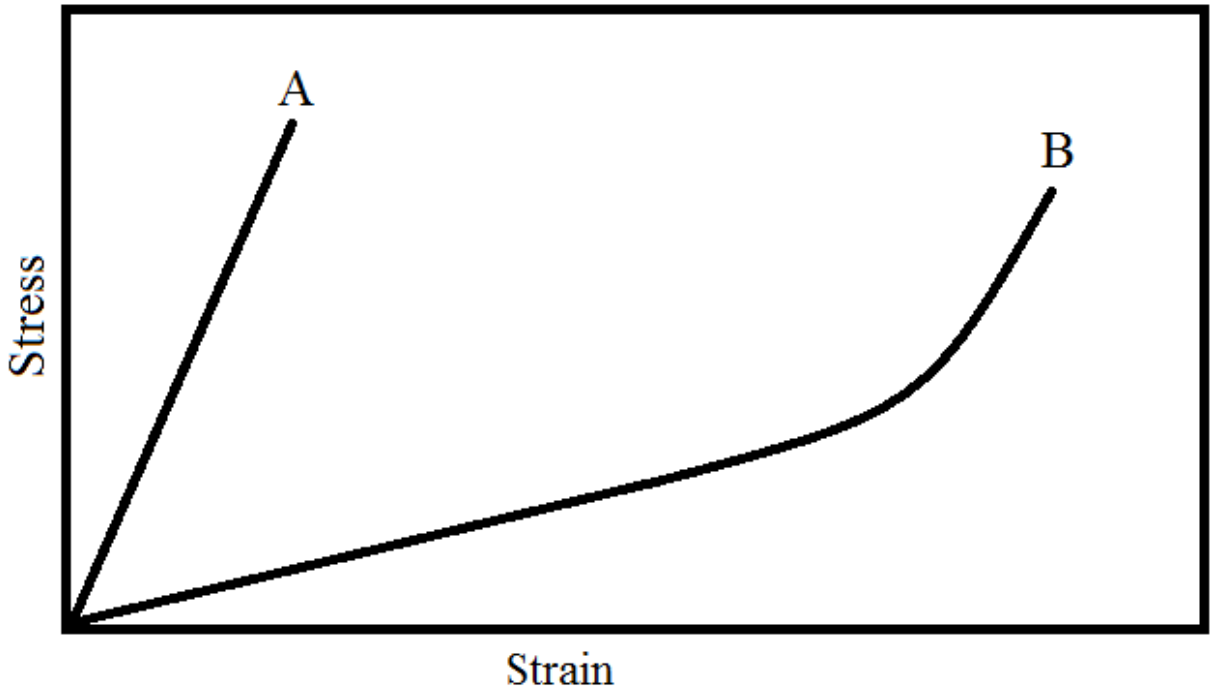


Figure 1.17. Typical tensile test curves, where A) highly cross-linked sample, B) lightly cross-linked sample. The stress and elongation at the fracture point can be established from this data.

From the ultimate tensile strength a gauge of the number of cross-links is possible, but only up to a point. After an optimum number of cross-links has been reached if more cross-linking occurs the ultimate tensile strength will fall.[16] However, the tensile stress at a particular elongation will continue to rise with increasing cross-links. It is therefore possible to measure the extent of cross-linking from tensile results, but only by looking at the modulus at

consistent elongation, rather than the ultimate tensile strength. A rubber with a high tensile strength, which, in part, will be due to a high degree of cross-linking, will have a low elongation and so be a higher viscosity rubber. As a result the rubber will suffer from poor flow, and so when moulding takes place cracks and fissures may appear. If this occurs the moulded item suffers from weaknesses which would clearly be disadvantageous to the final product. Consequently it is easy to deduce that a higher tensile strength is not necessarily the most desirable result.

1.5.2. Spectroscopic Studies

Spectroscopic analysis of polymers can be done using several different techniques, depending upon the information required. Two of the most commonly used techniques (FTIR and NMR) are described in more detail in Sections 1.5.2.2 and 1.5.2.3, but there are a wide range of other analytical tools that can be used as briefly discussed herein.

1.5.2.1. Gel Permeation Chromatography

Gel Permeation Chromatography (GPC) is also known as Size Exclusion Chromatography (SEC). This technique can separate a polymer sample based upon its radius of gyration in solution which is dictated by the molecular chain length. The time taken for various chains to travel through a column is measured, with larger chain lengths travelling through the column quicker. A schematic of a GPC instrumentation is shown in Figure 1.18.

Within the columns are porous gel beads; smaller polymer species are able to enter these pores and become temporarily ‘trapped’ taking a longer time to travel through the system. The important information ascertained from GPC concerns the molecular mass of the polymer.[148] Most commonly reported molecular masses; include the number-average molecular mass (M_n, which is the arithmetic mean of molecular weights found) and the weight-average molecular mass (M_w, which uses the weight fraction of each polymer chain, to enable a weighted average to be calculated). From these two averages, the polydispersity index (PDI) can be calculated, by dividing M_w by M_n. The PDI describes the distribution of chain lengths within the sample; where a value of 1 (i.e. $M_w = M_n$) would show that all the chain lengths are the same length (although this value would be impossible to achieve with a real polymer sample).

Figure 1.18. Schematic diagram of GPC apparatus. This schematic diagram was provided by the original author, Dr. A. Pryke.[149]

To enable the calculation of the different molecular masses for a polymer solvent system, several standards with known molecular masses must first be run. This allows the Mark-Houwink parameters (Equation 1.1) **a** and **K** to be ascertained *via* a calibration curve. The calibration curve allows the relative molecular mass of any polymer within the same solvent to be measured in that instrument. However, the calculated molecular masses will not be exact; they will only be with reference to the standard. The closer the architecture of the standard to the polymer being tested the more accurate the resultant molecular masses will be.

$$[\eta] = K M^{a} \qquad \textbf{(Equation 1.1)}$$

Whereby η is the intrinsic viscosity (dL/g), a and K (dL/g) are the Mark-Houwink parameters which are dependent upon the polymer and solvent system in use, respectively, and M is the molecular mass.

1.5.2.2. Optical Spectroscopy

This section deals with spectroscopic methods that employ light as a tool to elucidate structures within the chemicals under scrutiny. The methods discussed are infra-red spectroscopy, in which the absorbance of infra-red radiation by the bonds within the sample is measured. Next discussed is Raman spectroscopy, whereby the scattering of light by the structures within the chemical under observation are measured and ultraviolet-visible spectroscopy where the transmission of light in the ultra-violet to visible range is measured through a diluted sample. Each of these techniques is examined in detail, and any literature pertaining to their use with polychloroprene is scrutinised. The infra-red and ultra-violet-visible light systems rely upon the Beer-Lambert Law (Equation 1.2) which relates the transmission (or absorbance) of light through a material to the properties of that material. As Raman spectroscopy relies on the scattering of light the mathematics behind that technique are different, as discussed in Section 1.5.2.2.2.

$$\mathbf{A = \varepsilon c l} \qquad \textbf{(Equation 1.2)}$$

Whereby A is the absorbance, **ε** is the molar absorptivity or extinction coefficient (m^2/mol), c is the concentration of sample (mol/L) and l is the path length through material (m).

1.5.2.2.1 Infra-red Spectroscopy

Infra-red spectroscopy (IR) is one of the most widely used spectroscopic techniques, and makes use of the electromagnetic spectrum with wavelengths in the region of 0.8-1000 μm. The most useful range is generally in the region of 2.5-20 μm. More commonly the wavelength is referred to in its reciprocal form, in units of cm^{-1} and thus the most useful range is from 500 to 4000 cm^{-1}.[150] In this region the resonant frequencies of many chemical groups or bonds exist, and when subjected to their resonant frequencies these chemical structures will absorb this energy. The resonant frequency is determined by the mass of the atoms involved, and the mode of deformation that the bond is undergoing. There are many different ways that an atom can deform, these include: symmetrical and non-symmetrical stretching, bending or scissoring, rocking, wagging and twisting (Figure 1.19).[151] Functional groups and specific bonds undergoing certain types of deformation will therefore have specific frequency bands associated with them.

Early spectrometers worked by an infra-red light-source capable of emitting the entire infra-red spectrum. The light would be split into two beams, of equal intensity, at a single frequency. An exact frequency of the beam could be obtained by use of a prism and by movement of the prism the frequency could be altered. Only one of the beams would pass through the sample being tested, and then the two beams would be compared. If the sample contained a structure which absorbs light at that frequency, this would be seen in the difference between the two beams. A plot of absorbance against the wavelength of the infra-red radiation was given.

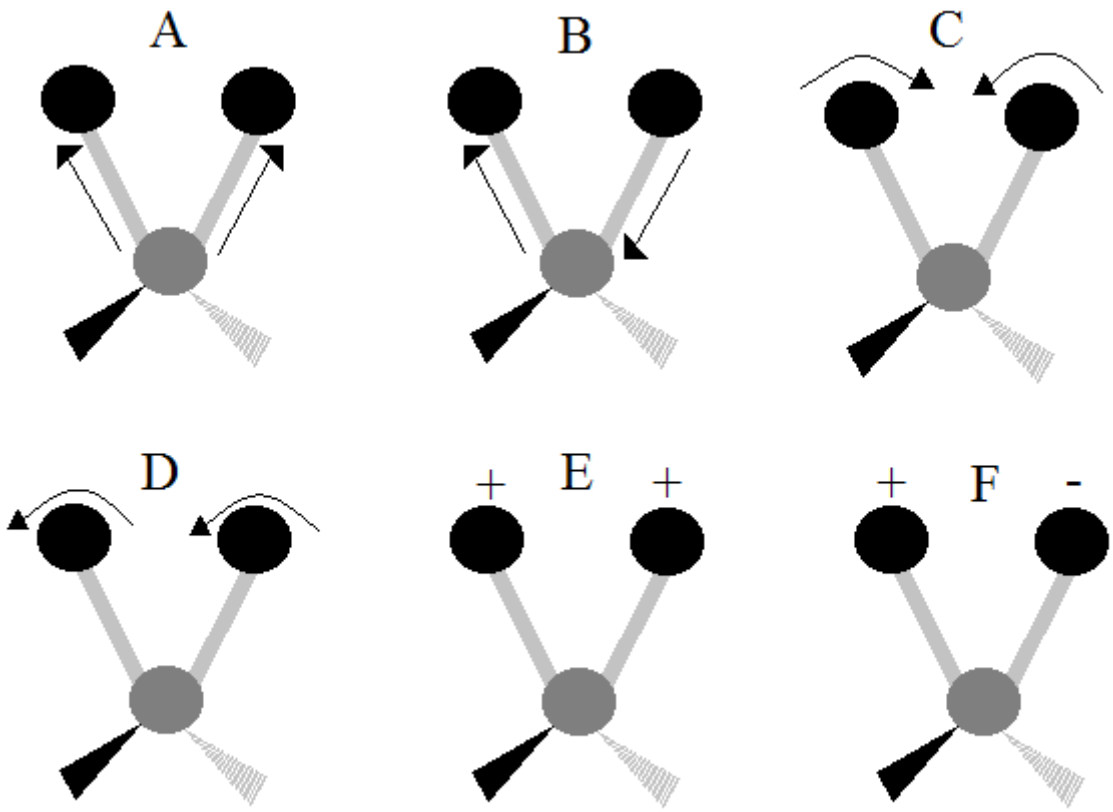


Figure 1.19. Modes of deformation in infra-red spectroscopy; A) symmetric stretching, B) non-symmetric stretching, C) bending or scissoring, D) rocking, E) wagging and F) twisting.

Fourier transform infra-red spectroscopy (FTIR) is a more modern method for collecting an IR spectrum and is more commonly used. It also involves two beams of light which cover the entire spectrum desired. Either both beams, one with a slight delay, or one beam are passed through the sample being tested. The beams are then re-combined; this produces an interference pattern, which is the sum of all of the interference at each wavelength of the beam. As the difference between the two paths is altered, a different interference pattern is

produced. This change of interference pattern with different path lengths is called an interferogram. It is this interferogram to which the Fourier transform occurs, so producing an IR spectrum. The same as would be seen if the older method of shining monochromatic light was used. There are many advantages to using FTIR over that of the older monochromatic method. As the whole spectrum is scanned at once, it is much quicker to obtain a spectrum. Weakly absorbing samples can be measured by adding together several scans. It is also possible to more easily manipulate the data as it is obtained digitally. This means that spectra can be subtracted and compared more easily.

The sample preparation for IR spectroscopy can be very important, as can the collection method. There are several different ways in which the sample can be prepared, such as sodium chloride discs, which are invisible to infra-red radiation and thus do not produce any peaks within the IR spectrum. If the sample is a liquid it can easily be placed between two discs and tested. For solid samples, a suitable solvent is often used to dissolve the sample; typically this is carbon tetrachloride or chloroform. It can then be possible to compare a sample of pure solvent with that to the sample containing solvent. Other ways of testing solids include grinding the solid with a liquid hydrocarbon or hexachlorobutadiene, and this is pressed between sodium chloride discs. Alternatively the solid can be ground with potassium bromide (KBr) and then pressed into a disc which is examined.[151] These techniques use the transmission of the IR beam through the sample. An alternative procedure for the collection of spectra is through the use of attenuated total reflectance (ATR). ATR relies on the total internal reflectance of a crystal – infrared light reflects off the internal surfaces of the crystal. This occurs in a way that allows the beam to reflect off the surface the sample is in contact with at least once. The beam penetrates a fraction beyond the reflecting surface and the beam can then be detected as it exits the crystal.[152] Fourier transform can then be performed on the beam as would happen if it were a transmission beam. One of the main advantages to this system is that there is no need for sample preparation; the sample can be placed directly onto the crystal as long as good contact is made. This is true for solids as well as liquids. The main disadvantage to this technique is that as the beam only penetrates a short distance (0.5-2 μm) and therefore only the surface of the sample is examined.

1.5.2.2.2 Raman Spectroscopy

Raman spectroscopy was named after Sir C. V. Raman.[153] The technique works by examining the scattering of a monochromatic light beam in the infra-red, visible or ultra-violet region. When a sample is illuminated, the atomic vibrations within the sample can produce two types of light scattering, Rayleigh scattering, which is elastic, and inelastic Raman scattering. It is this second weaker form of scattering that is important in Raman spectroscopy. Raman scattering occurs when the photons within the light interact in such a way that they either gain or lose energy (called Stokes and Anti-Stokes shift respectively), this change in energy causes a shift in frequency.[154] The shift in frequency can then be measured for different initial illumination frequencies.

In providing information due to vibrational frequency of bonds, Raman spectroscopy has some similarities with IR spectroscopy. However, the information provided differs with some bonds providing more information in one technique than the other. Generally, covalent bonds are stronger in Raman and ionic bonds stronger in IR.[153] Raman spectroscopy is also able to provide spectra of molecules which do not have a permanent dipole moment, unlike in IR spectroscopy, where a dipole must be present.[155] Raman and IR spectroscopy are very complimentary techniques as any mode within a molecule which is not present in the spectra of one technique will be present in the other (although many modes are present in both).

The set-up for Raman spectroscopy would normally consist of (i) an excitation source (most commonly a laser); (ii) a sample illumination and collection system (such as an achromatic lens system); (iii) wavelength selector (the simplest being an interference filter) and (iv) a detection, control and processing system (computer).[154]

1.5.2.2.3 Ultraviolet-visible Spectroscopy

Ultraviolet-visible (UV-vis) spectroscopy uses light with wavelengths normally in the region of 200-700 nm. This technique relies upon the absorption of differing wavelengths of light by chemical structures when in a dilute solution. Chemical groups which give this electronic absorption are known as ‘chromophores’.[150] The absorption of light determines the colour that the chemical is perceived to be – differently coloured chemicals will have a different absorption wavelengths.[156] This absorption is due to a transition between electronic energy levels in the orbitals of the concerned chemicals, with the wavelength depending on this separation between energy levels.[151]

When a sample is tested, two equal beams of the same wavelength will be compared, one which has passed through pure solvent and the other which has travelled through the sample diluted in that solvent. The intensities between the two beams are then compared, and a beam of the next wavelength is then passed through both samples. This process is continued until the entire required wavelength range has been assessed.[151] When samples are being tested one of the most important factors to be aware of is the solvent used, as there will be some absorption in the spectra due to the solvent. Thus the solvent chosen must absorb in a region lower than that from the groups in the test sample.[150, 151]

UV-vis spectroscopy is a very good analytical technique for quantitative analysis. This is due to the absorbance being proportional to the amount of material dissolved into the solvent (Beer-Lambert relationship Equation 1.2). If a series of solutions at known concentrations are made up and the absorbance at λ_{max} (wavelength maximum) is plotted against concentration, a calibration curve is obtained. This would allow a sample of unknown concentration to be determined by comparison to the calibration curve.

1.5.2.2.4 Optical Spectroscopic Studies

Many papers have been written on investigations using infra-red to study polychloroprene. The most common theme amongst these papers is the confirmation of the structure of polychloroprene and quantifying the levels of the isomers present (levels are quoted in Section 1.4.3, from these and other sources).[65, 67, 70] Other papers include a series of three papers authored by Coleman *et al* [71, 157, 158] where subtraction techniques are applied to look at the microstructure of polychloroprene. This technique allows the bands associated with the various isomers to be confirmed.[157] IR was also used to look at the mechanism of thermal degradation,[71] a study which was subsequently built upon by Miyata and Atsumi[79, 92]. Both of these studies show the rearrangement of the 1,2-isomer occurring in polychloroprene upon heating. The final area the series of papers by Coleman deals with is that of structural irregularities in the crystalline region of polychloroprene co-polymers.[158] An earlier paper by Tabb *et al.*[66] (which was co-authored by Coleman and Koenig) deals with structural irregularities in the crystalline region of pure *trans* 1,4-polychloroprene. The irregularities arise from the presence of non 1,4-isomers and a comparison is made between polychloroprene synthesised at different temperatures. Their results show that an increase in polymerisation temperature increases the amount of irregularities, and that these irregularities are interspersed through the 1,4-isomer phase randomly.

All of the papers mentioned thus far deal with various aspects of the IR spectra and in each case the nature of several bands are identified or confirmed. Two reports, both analysing the FTIR and Raman spectra of polychloroprene, are concerned with band identification explicitly; one examined the *cis*-1,4-polychloroprene,[69] and the other evaluated the *trans*-1,4-polychloroprene.[72] These papers, along with many general texts[150, 159-163] have enabled the major peaks in polychloroprene gum stock to be identified (Figure 1.20).

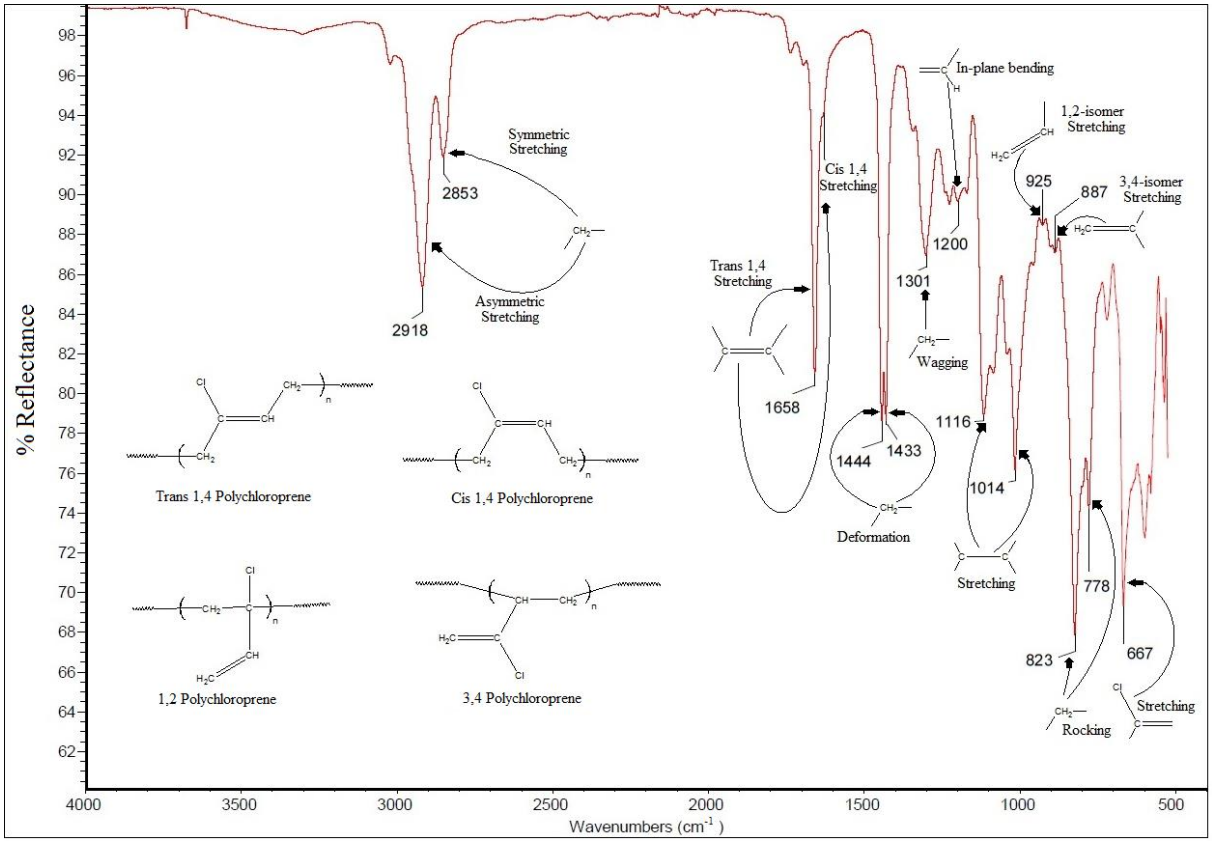


Figure 1.20. Identification of the major peaks in the FTIR spectrum of polychloroprene, through various literature sources.[67, 69, 70, 72, 151, 157, 159, 160, 162, 163]

Raman spectroscopy, as well as its use in identifying and confirming peaks in FTIR, has also been used to study cross-linking of polybutadiene rubber.[164-166] Although polybutadiene cross-links differently to polychloroprene, these papers showed that sulfur cross-links readily show up in a Raman spectrum and the region in which they appear. This could be useful in the cross-linking studies of polychloroprene as there is the possibility that a sulfur cross-link is formed. Thus knowing the bands they appear at will be very beneficial. These studies[164-166] also showed time-resolved curing of polybutadiene. This also contributes to Raman spectroscopy potentially being a useful technique in the elucidation of the cross-linking mechanism, as it shows that the cross-links themselves may be visible *via* Raman spectroscopy.

1.5.2.3 Nuclear Magnetic Resonance

Nuclear magnetic resonance (NMR) spectroscopy is a technique where the nuclei of some atoms exhibit certain magnetic properties that allow the structure of the chemical to be determined. The background to this technique is explored in this section, before studies relating to its use with polychloroprene are examined.

1.5.2.3.1 Background

NMR spectroscopy was first discovered in the mid-1940s, and Bioch and Purcell, received the 1952 Nobel physics prize for this breakthrough.[167] A simple explanation is that the nuclei of some atoms have a nuclear spin and this spin can make each nucleus behave like a magnet.[151] When a nucleus has an odd number of nucleons and it is placed into a magnetic field, its spin will mean it can only take up two orientations; with the applied field, or against the applied field.[151] This is most useful for ^{1}H and ^{13}C atoms although others can also be employed. When certain frequencies are applied, the nuclei change orientation and the frequency at which this occurs can be measured. The magnetic environment in which a given nucleus is contained will minutely affect the frequency at which the change in orientation takes place.[151] Many factors will cause this change. Some effects, such as electronegativity of the surrounding atoms, are referred to as 'through bond' effects. These 'through bond' effects are generally easy to predict, and there are a number of software packages available to this end.[168] Other effects, such as electric and magnetic field effects, or 'through space' effects, will be much harder to predict.[168]

There are two techniques to gather NMR spectra, the first is continuous wave (CW), in which a signal is applied to the sample, the response is picked up by a receiving coil and the frequency of the CW is varied to collect the required range.[150] The second technique uses a Fourier Transform (FT) system, the more common method used today. This method works in a similar fashion to FTIR in that a pulse with a range of frequencies is sent through the sample and the result from this pulse is extrapolated *via* FT to create a plot which would be similar to that obtained *via* the CW route.[168] The latter method has the advantage that a spectrum can easily be obtained within a few seconds; however, there may be problems with signal to noise interference. This can be overcome by performing repeated scans of the sample to allow a clearer spectrum to be obtained; there must be a waiting period between scans as the nuclei must be allowed to return their original state.[169]

1.5.2.3.2 Nuclear Magnetic Resonance Studies

The use of NMR as an analytical technique has been applied to polychloroprene in a similar fashion to that of FTIR, i.e. to study the structure of polychloroprene and the levels of isomers present,[64] in several cases this has been done in conjunction with FTIR.[65, 92] It has also been used to examine the head-to-head, head-to-tail and tail-to-tail confirmations in addition to the various isomer levels.[170] Other uses for NMR in the study of polychloroprene include its use to examine cross-linking with ZnO (discussed in Section 1.4.5.1). Additionally solid state NMR has been used to examine char formation,[171] this was done at much higher temperatures than those associated with vulcanisation, thus any of the by-products formed would not be seen when cross-linking occurs. Using the aforementioned literature sources and more general spectroscopic texts, several of the peaks in the ^{1}H NMR spectrum have been identified (Figure 1.21). The NMR spectrum in Figure 1.21 is of oligochloroprene made using dodecylmercaptan as a chain transfer agent (CTA).

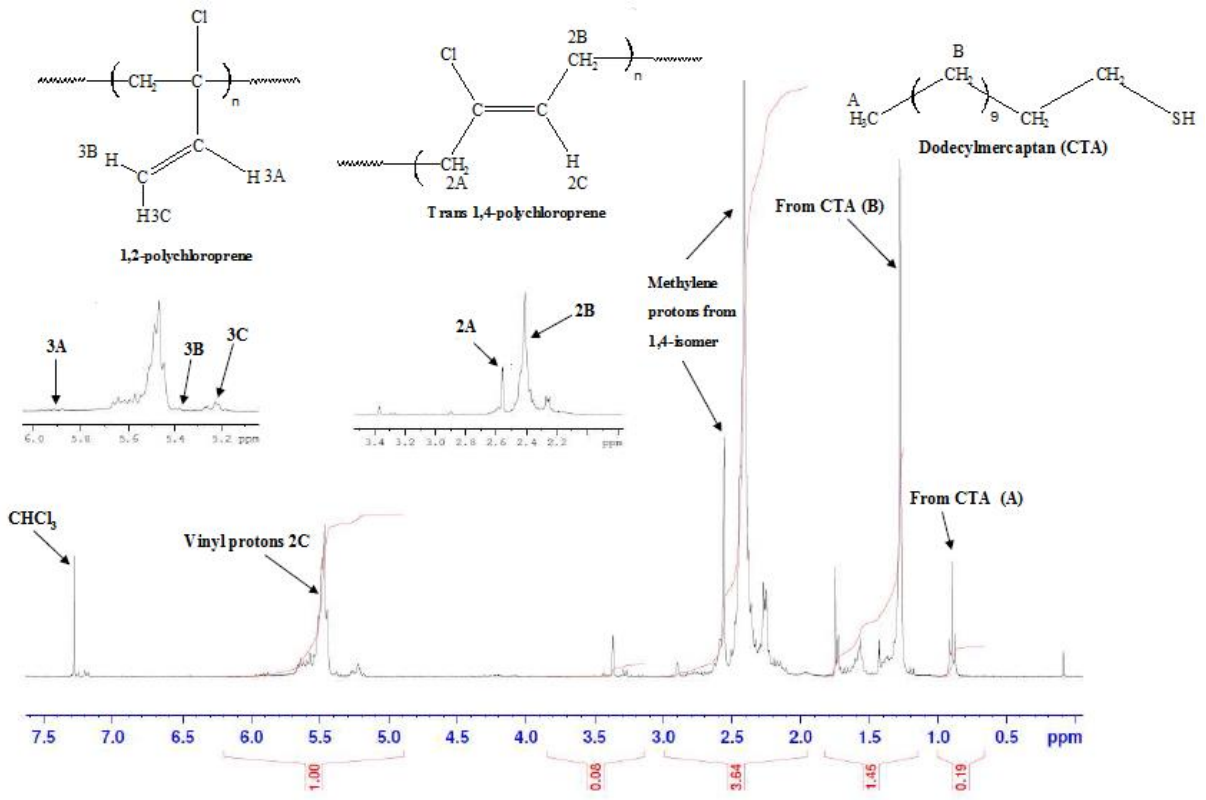


Figure 1.21. Annotated ^{1}H NMR Spectrum of oligochloroprene.

1.6. Aims

Polychloroprene is one of the oldest and most widely exploited synthetic elastomers in use today. The reason for the continued widespread use of polychloroprene is its range of superior properties compared to other elastomers. Many of these properties are obtained when polychloroprene is cross-linked; unfortunately the most effective cross-linking agent, ETU, has health risks associated with its use (as discussed in Section 1.4.5.2.2). Therefore, the main aim for this project is to find a replacement for ETU. The replacement molecule, once found, should have a similar performance to ETU. These properties are required not only in the pure polychloroprene rubber, but also in a commercial filled industrial master batch.

In order to design a new accelerator molecule, the elucidation of the cross-linking mechanism for ETU on its own and jointly with ZnO, in polychloroprene needs to be achieved. The novel approach that this project adopts to elucidate the mechanisms that occur during cross-linking will be *via* the use of not only spectroscopic methods, but also through the use of mechanical and physical testing techniques. By using both of these resources in tandem a new understanding of the curing mechanism is hoped to be achieved.

Through a better understanding of the cross-linking mechanism, it should be possible to propose new potential accelerator molecules. These molecules, once synthesised, will be tested and compared with the exacting standards required for a replacement of ETU. Initially this will be done in pure polychloroprene rubber. However, as the new accelerator may behave differently to ETU in a filled master batch, the formulation of some additives in a master batch will be altered accordingly. To this end, the idealised set of those additives for a master batch formulation will be examined.

As a secondary aim, the use of ZnO within all cross-linking systems for polychloroprene is to be reduced. The main reason to try and reduce the level of ZnO is its inherent environmental toxicity, which has led to the search for prospective replacements. Together with finding a replacement for ETU, this will make the whole cure system for polychloroprene much safer. A potential substitute for ZnO may be realised through the use of a multi-functional additive (MFA). MFAs have the ability to act as both activators and accelerators due to the amine aspect of the MFA. They have also been shown to reduce to amount of ZnO needed in some cross-linking systems, and it is hoped that will be the case with the new accelerator and its cross-linking system.

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CHAPTER 2

MATERIALS AND EXPERIMENTAL METHODS

2. Materials and Experimental Methods

2.1. Materials

Tables 2.1 to 2.4 list the materials used in this project, any abbreviations used, the supplier and the purity as quoted by the supplier.

Table 2.1. Solvents used with chemical name, abbreviation, supplier and purity.

Solvents			
Name	**Abbreviation**	**Supplier**	**Purity (%)**
dichloromethane	DCM	Sigma-Aldrich	99
ethyl acetate		Sigma-Aldrich	99
hexane		Sigma-Aldrich	95
industrial methylated spirit	IMS	Sigma-Aldrich	99
methanol	MeOH	Sigma-Aldrich	99
tetrahydrofuran	THF	Sigma-Aldrich	99
toluene		Sigma-Aldrich	99

Table 2.2. Rubber additives used with chemical name, abbreviation, supplier and purity.

Rubber Additives			
Name	**Abbreviation**	**Supplier**	**Purity (%)**
N-cyclo-2-benzothazolesulfenamide	CBS	Flexsys	96
di-isopropyl xanthogen polysulfide	AS100	Robinson Brothers	99
diphenyl guanidine	DPG	Flexsys	97
ethylene thiourea	ETU	Linkwell	98
magnesium oxide	MgO	Omya	97
2-mercaptobenzothiazole	MBT	Omya	99
methyl-2-mercaptobenzimidazole	MMBI	Bayer	99
polychloroprene gum stock	CR	Denka S40V	95
stearic acid	SA	Croda	99
tetrabenzyl thiuramdisulfide	TBzTD	Flexsys	95
tetramethyl thiuramdisulfide	TMTD	Omya	98
zinc dibutyldithiocarbamate	ZDBC	Flexsys	98
zinc oxide	ZnO	Pharma grade	99
zinc oxide active		Lanxess	93

Table 2.3. Model compounds used with chemical name, abbreviation, supplier and purity.

Model Compounds			
Name	**Abbreviation**	**Supplier**	**Purity (%)**
4-amino-phenyl-ethylamine	4-APE	Robinson Brothers Ltd	99
3-amino-1-propanol		Sigma-Aldrich	99
butylamine		Sigma-Aldrich	99
1,4-diamino butane	DAB	Sigma-Aldrich	99
1,12-diamino dodecane	DAD	Sigma-Aldrich	98
1,7-diamino heptane	DAHp	Sigma-Aldrich	98
1,6-diamino hexane	HAHx	Fisher	99
1,3-diamino propane	DAP	Sigma-Aldrich	99
dibutylamine	DBA	Sigma-Aldrich	99
dibutylthiourea	DBTU	Sigma-Aldrich	97
1,3-dimethyl-imidazolidine-2-thione		Sigma-Aldrich	97
ethylene urea	EU	Sigma-Aldrich	96
1,6-hexanedithiol	HDT	Sigma-Aldrich	96
hexanethiol		Sigma-Aldrich	95
1,8-octanedithiol	ODT	Sigma-Aldrich	97
piperidine		Sigma-Aldrich	96
piperazine		Sigma-Aldrich	99

Table 2.4. All other chemicals used with chemical name, abbreviation, supplier and purity.

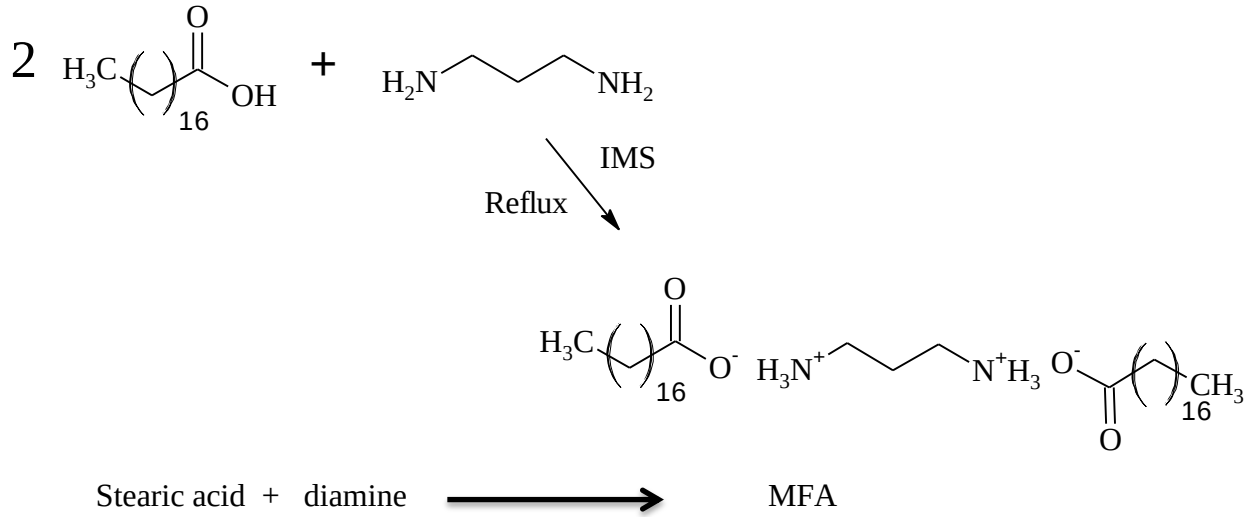
Other Chemicals			
Name	**Abbreviation**	**Supplier**	**Purity (%)**
2-chlorobutane		Sigma-Aldrich	99
3-chloro but-1-ene		Sigma-Aldrich	97
piperazine-1-carbodithioic acid	PCA	Robinson Brothers Ltd.	99
potassium permanganate		Sigma-Aldrich	99

2.2. Experimental Methods

The experimental methods followed and equipment used within this project are outlined in Sections 2.2.1 to 2.5.3. Any other specific experimental methods undertaken not detailed herein are described in the relevant chapters.

2.2.1. Synthesis of the Multi-functional Additive

The multi-functional additives used in this project consist of a linear diamine and stearic acid, typically at a molar ratio of 1:2, respectively and the reaction is shown in Scheme 2.1.



Scheme 2.1. Reaction between stearic acid and 1,3-diaminopropane to create an MFA.

Stearic acid was diluted to 10 % w/v in a suitable solvent (typically IMS) and the solution stirred with a magnetic follower in a three-necked round-bottomed flask fitted with a condenser, a thermometer and a dropping funnel. The appropriate diamine was diluted to 10 % w/v with the appropriate solvent and added drop-wise, to the stearic acid mixture over 15 minutes. In a typical experiment, 6.45 g stearic acid was diluted into 65 ml IMS, to this 1 g 1,4-diaminobutane diluted in 10 ml IMS, was added. After addition, the reaction mixture was heated to reflux for 2 hours. It was noted that the solution went clear between 40 ºC and 55 °C depending upon the solvent used. The mixture was allowed to cool to room temperature and then left overnight at 3 °C before filtering the following day. After filtering the resultant cake was dried at 40 ºC overnight to remove any excess solvent. Yield ~ 80 %.

Characterisation of the MFAs by FTIR, showed that the 1697 cm^{-1} peak associated with C=O stretching in stearic acid[1] was no longer present (a typical spectrum is shown in Figure 2.1). Likewise, neither of the 3360 cm^{-1} and 3281 cm^{-1} peaks associated with NH_2 stretching (two peaks due to symmetrical and asymmetrical stretching) from the diamine were present.[1] Two

new peaks at 1507 cm^{-1} and 1566 cm^{-1} appeared which were not related to the groups in the diamine or stearic acid. These can be attributed to NH_3^+ bending (Figure 2.1),[2] thus confirming the formation of the MFA as described. A DSC study of the MFA synthesised as described above showed a single endothermic peak at 88 °C and is ascribed to the melting point. Unfortunately, due to difficulties in finding a suitable solvent able to dissolve the MFA no NMR studies were performed.

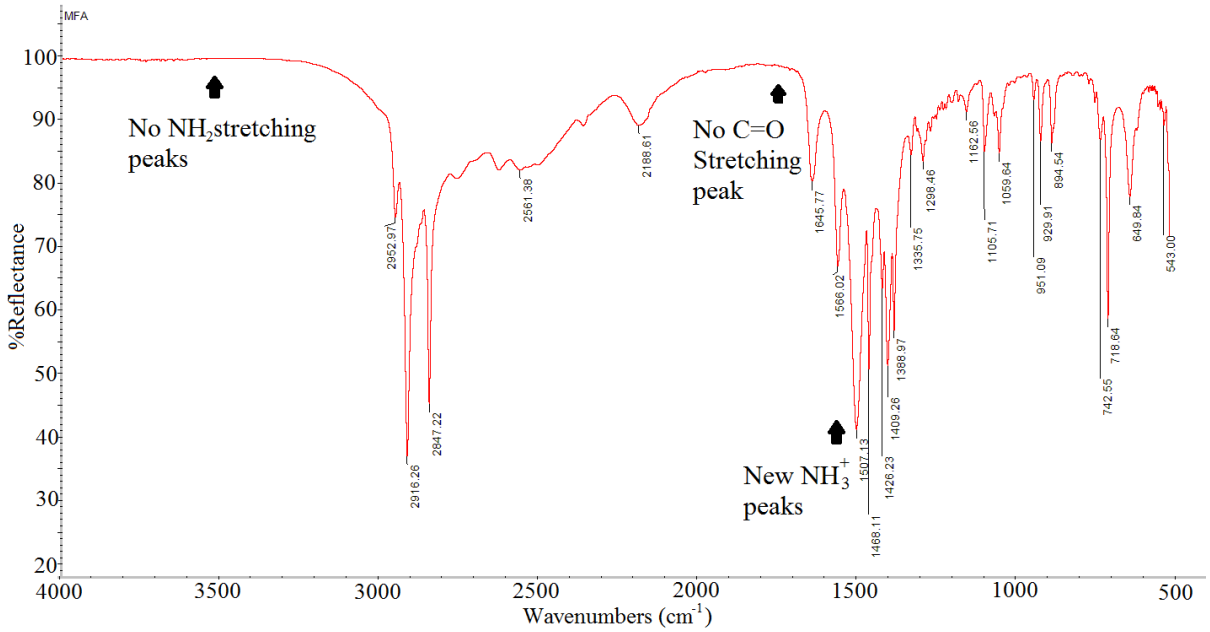
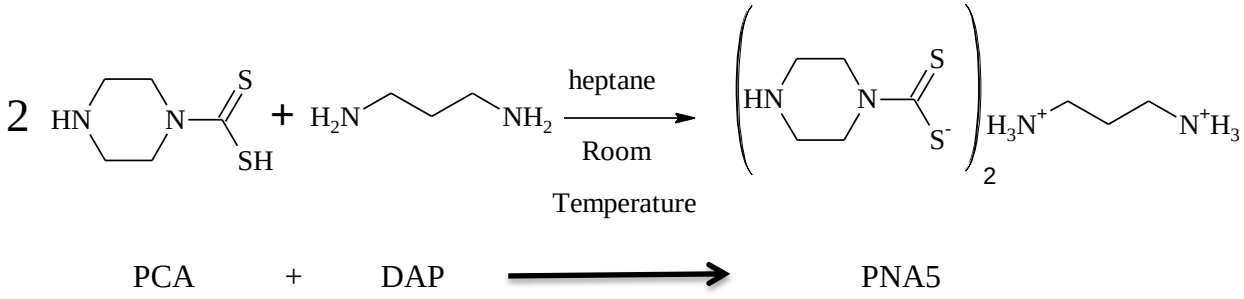


Figure 2.1. FTIR spectrum of a typical multi-functional additive (MFA), shown is stearic acid and 1,4-diaminobutane at a 2:1 ratio.

2.2.2. Synthesis of Proposed New Accelerator 5

All of the proposed 'new' accelerators were initially made by Grand Synthesis Latvia (GSL). Once trials had been completed on the initial samples, the most promising candidate, proposed new accelerator 5 (PNA5), was synthesised in house. PNA5 is a complex of two parts piperazine-1-carbodithioic acid (PCA) to one part 1,3-diaminopropane (DAP). The reaction scheme for the synthesis of PNA5 is shown in Scheme 2.2.



Scheme 2.2. Reaction scheme for the synthesis of PNA5.

A three-necked round-bottomed flask fitted with a magnetic follower and a condenser was charged with PCA at 19 % w/v in heptane. DAP was added over 10 minutes, and the resultant mixture stirred for one hour at room temperature before being filtered. In a typical synthesis, 16.2 g PCA was mixed with 85 ml heptane, to which 3.7 g DAP was added. The resultant powder was dried at 40 ºC overnight to remove any excess solvent. A yield of over 95 % was regularly achievable. Various ratios of raw materials and reaction temperatures were also trialled, with the above method altered accordingly, as discussed in Chapter 5.

Characterisation of PNA5 by FTIR showed the removal of the peaks at 3358 cm^{-1} and 3281 cm^{-1} associated with NH_2 stretching of the diamine (Figure 2.2). Due to the weak bands associated with sulfur-containing bonds, those peaks within the PCA spectrum were unable to be identified. Nevertheless, a small peak was present in the spectrum of PNA5 at 3182 cm^{-1} that is not present in either PCA or the diamine, and which is associated with NH_3^+ stretching (Figure 2.2); confirming the production of the PNA5 molecule. Using DSC to study the PNA5 molecule showed two endothermic peaks one at 109 °C attributed to the melting point, the other at 179 °C ascribed to decomposition. There is also an exothermic peak at 128 °C which may be due to a reaction between unreacted amino groups of the diamine with the dithiol group of any free PCA. This may occur as the initial synthesis is performed at room temperature.

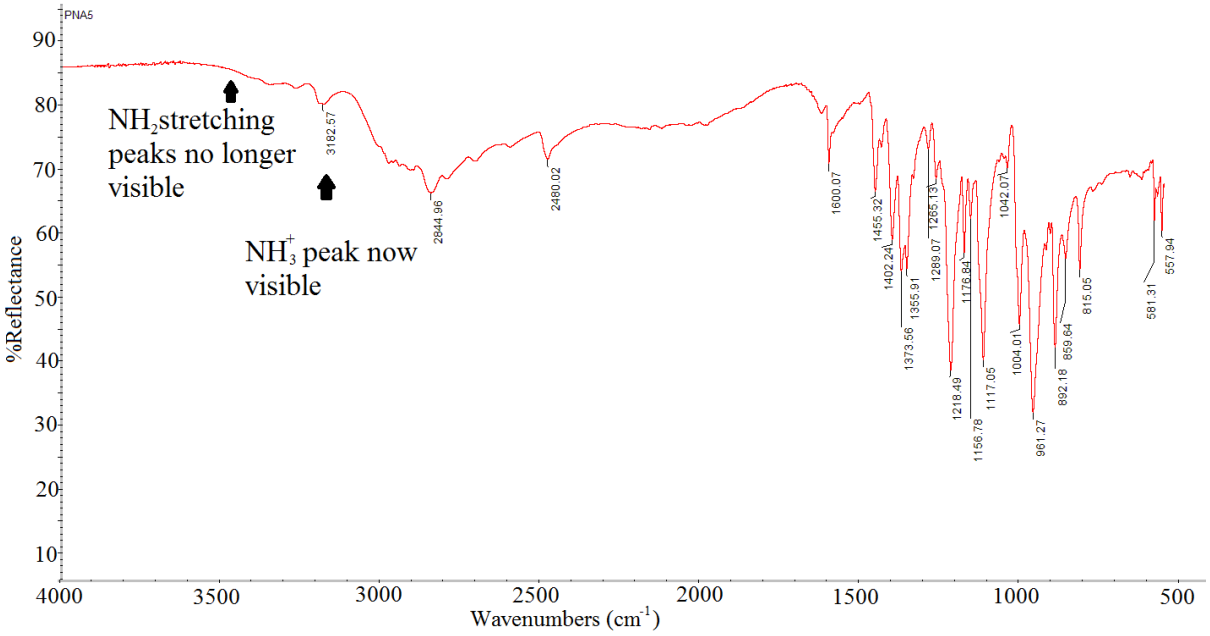


Figure 2.2. FTIR spectrum of PNA5 showing the disappearance of the NH_2 stretching peaks associated with the diamine and showing the NH_3^+ peak formed as part of the complex.

^{1}H NMR studies were performed on PNA5 using deuterium oxide (D_2O) as the solvent. 128 scans were run and a solvent suppression programme was employed to enable the best spectrum to be plotted. Solvent suppression involved the presaturation of the sample with a low power pulse before testing and removal of the largest peak formed – associated with the solvent. The spectrum (Figure 2.3) shows peaks associated with the piperazine-1-carbodithioic acid and 1,3-diaminopropane in PNA5 ^{1}H NMR (D_2O): 4.27 (4H, m), 2.82 (8H, m), 1.73 (2H, quin).[2, 3] The complexity of peak A in Figure 2.3 may be due to piperazine-1-carbodithioic acid creating a salt within itself due to its secondary amine.

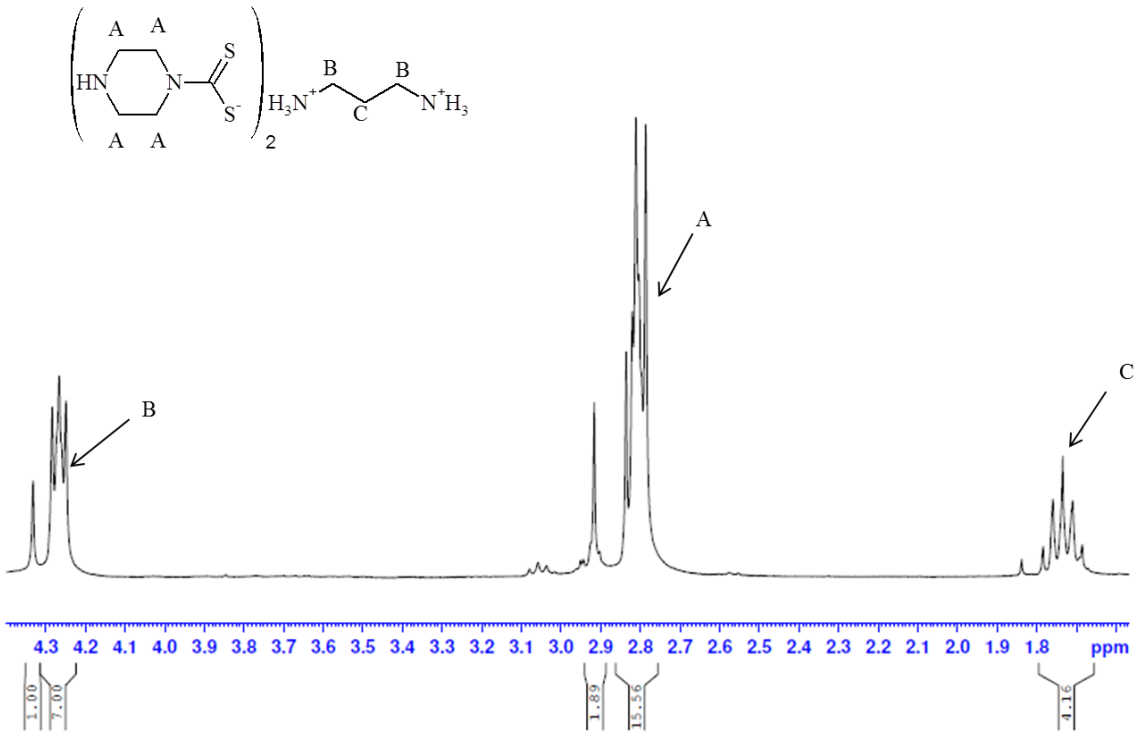


Figure 2.3. ^{1}H NMR spectrum of PNA5.

2.2.3. Compounding of Oligomers

All oligomers used were synthesised by N. Pullan of Aston University and all mixing and testing of oligomers was carried out in conjunction with N. Pullan. Oligomer and additive were weighed out accurately into a test tube and were then roughly mixed with a spatula before a magnetic follower was added. The test tube was sealed and placed into a sonicating bath to ensure complete mixing of materials. Sonicating was performed for various times, depending upon the mixture, with the maximum time being approximately 16 hours.

2.3. Molecular Characterisation Methods

The following characterisation techniques were utilised in this project and are described within this section: Fourier Transform Infra-Red spectroscopy, Raman spectroscopy, Nuclear Magnetic Resonance spectroscopy, Gel Permeation Chromatography, ultraviolet-visible spectroscopy, Gas Chromatography with Mass Spectrometry and Thermogravimetric Analysis with Differential Scanning Calorimetry.

2.3.1. Fourier Transform Infra-Red Spectroscopy

The majority of Fourier Transform Infra-Red (FTIR) spectra were obtained on a Thermo Scientific Nicolet iS10 instrument. Samples were collected for 32 scans using attenuated total reflectance (ATR) in the solid state on a diamond crystal plate. The scanning range was from 550-4000 cm^{-1} with a resolution of 4.0 cm^{-1}.

Prior to testing rubber samples were first pressed on a manual hydraulic press from Specac fitted with temperature controlled electrically-heated platens. Samples were pressed by placing the samples between Melinex sheets and applying a pressure of 5 ton. This was done at 40 °C for two minutes for uncured samples and 160 °C for 1.5 x T90 for cured samples. Melinex sheets were removed in all cases before analysis.

The FTIR spectra that were obtained whilst curing utilised a Thermo Nicolet Nexus instrument, set automatically to collect spectra every 30 seconds using a Golden Gate ATR accessory. Spectra were collected as a single beam of 16 scans with a resolution of 4.0 cm^{-1}, in the range 600-4000 cm^{-1} and then normalised against the background or the initial uncured sample. These samples were not pressed prior to testing.

2.3.2. Raman Spectroscopy

Raman spectra were collected using a Renishaw Raman spectrometer with a near infra-red laser connected to an inVia Raman microscope. The slit was set to 65 µm and the microscope magnification used was x20. Exposure time was 10 seconds and typically 20 acquisitions were collected for each sample.

2.3.3. Nuclear Magnetic Resonance Spectroscopy

A Bruker Avance 300NMR was used at 300 MHz (for ^{1}H) and at 75 MHz (for ^{13}C).

Deuterated chloroform was the most common solvent used, although other deuterated solvents were also used where appropriate. Samples were analysed at approximately 1 % w/v.

2.3.4. Gel Permeation Chromatography

The apparatus used was a PC-GPC plus integrated GPC/SEC from Varian Inc. with an operating temperature of 40 °C and calibrated with narrow polystyrene standards (M_p range of 162 to 6,035,000 g mol^{-1}). A flow rate of 1 ml min^{-1} through three PL gel 5 µm 300 x 7.5 mm mixed C columns was used. The eluent system was THF containing 2 % (v/v) TEA and 0.05 % (w/v) BHT.

2.3.5. Ultraviolet-Visible Spectroscopy

A Secomam Uvikon XL, instrument was used for UV-Vis spectroscopy in this project. Samples were typically scanned from 190 to 700 nm. Various solvents were employed depending upon the sample. Testing was initially completed on samples diluted to approximately 5 mg/ml. Samples were filtered prior to analysis to remove any particulates which had not dissolved. The cell used was a 10 mm quartz cell, and all samples were tested under ambient conditions.

2.3.6. Gas Chromatography – Mass Spectrometry

The gas chromatograph utilised in this project was an Agilent 7890A, and the mass spectrometer was an Agilent 5975B inert XL MSD. A flame ionisation detector was used, with an isothermal oven temperature of 200 °C with injector and detector temperatures of 300 °C. The carrier gas was helium at a flow rate of 1 ml/min, with an injection volume of 2 µl and the column used was a Zebron ZB-5HT inferno, 30 m x 0.32 mm with 0.25 µm film thickness.

2.3.7. Thermogravimetric Analysis/Differential Scanning Calorimetry

A Rheometric Scientific Limited PL-STA 625 and S10 system interface were employed in this project. This instrument provides combined Thermogravimetric Analysis (TGA) and Differential Scanning Calorimetry (DSC). Samples of approximately 10 mg were placed into an aluminium crucible, where the accurate sample weight was measured by the system. Samples were heated from ambient to 250 ºC at 5 ºC/min in air.

2.3.8. Thin Layer Chromatography

Samples were dissolved in DCM at approximately 1 % (w/v). Glass plates with a silica gel covering were used as the stationary phase. A small spot of the solution was applied to the plate 1 cm above the bottom edge. Filter paper was placed in a chamber with 0.5-0.7 cm of ethyl acetate as the eluent. The plate was placed in the eluent, such that the eluent did not reach the sample. Once the eluent had reached approximately 2 mm from the top of the plate, the plate was removed and allowed to dry. When dried the plate was dipped into potassium permanganate to stain the plate, as ETU was not visible under UV illumination.

2.4. Rubber Compounding and Characterisation

A range of instruments were used in the compounding and mechanical and physical testing of rubber during this project. Each technique is described herein in Sections 2.4.1 to 2.4.8.

2.4.1. Two-Roll Mill

All rubber was milled using a two-roll mill from David Bridge & Co. Ltd. with a friction ratio of 1:1.25. The rolls had cooling water running through them at all times and mixing for each sample was completed within 15 minutes. After banding the rubber to be analysed around the front roll, the gap between rolls was adjusted to allow a small amount of rubber to rotate above the nip. All additives were added starting from the least to most active, starting with stearic acid or multi-functional additive, as they both act as processing aids. Following which, the metal oxides were added, with MgO being added before ZnO. Finally the amines, thiols or other model compounds, or the accelerators (ETU or PNA5 etc.) were added. In the event where both a model compound and an accelerator were added, the accelerator was added first. After all additives were added, the rubber was cut and folded 12 times in total from alternate sides to ensure good mixing. All samples were rested for three hours before any further tests were undertaken.

2.4.2. Rheology

A moving die rheometer (Monsanto MDR 2000E), with an oscillating frequency of 1.667 Hz, was used to characterise the rheological properties of the rubbers. Approximately 5-6 g of material was placed between Melinex sheets before being tested. Standard test parameters were 160 ºC for 15 minutes. All samples were rested at ambient temperature for a minimum of 3 hours after mixing before being tested. One of the important results given by the MDR is T90 (where T90 is the time required to reach 90 % of the maximum torque, or optimum cure,

at a specific temperature). The MDR software calculates the torque required to oscillate a sample of rubber between two heated platens. Torque increases as the sample cures or cross-links, until it reaches a maximum when the sample is fully cured. For more information about data obtained from rheological testing see Section 1.5.1.1.

2.4.3. Pressing

Pressing of samples for physical testing was carried out on a 12 inch diameter piston hydraulic press from Bradley and Turton Ltd. A pressure of 100 tonnes was applied, and released quickly, three times, to ensure the removal of air from the sample. For tensile and hardness testing, a mould of 15 x 15 cm with a thickness of 2 mm was used. All unfilled samples were placed between Melinex sheets when cured. The compression set test pieces were cured in small circular moulds with a thickness of 6.3 mm and a diameter of 13 mm.

2.4.4. Tensometer

Tensile testing was undertaken on an Instron 4302. Test pieces were pulled according to BS903: Part 2A: Type 1 Dumbbells (Large). The thicknesses of the test sheets were measured using a Mitutoyo Digimatic multiplexer MUX-10 micrometer. All test pieces were pulled at 500 mm/min. Samples were cured for 1.5 x T90 prior to physical testing. For more information about the data obtained from tensile testing refer to Section 1.5.1.2.

2.4.5. Hardness

The hardness of samples was measured on a Wallace Rubber Hardness Tester. Layers of cured material were placed on top of each other until a depth of 8 mm was reached. All samples were examined using a spherical indentor with a diameter of 2.5 mm. An initial load of 0.3 N was applied to the sample for 5 seconds to provide an initial measurement, after which a force of 5.4 N was applied for 30 seconds before a reading was taken. Three points on each sample were tested 5 mm apart. This instrument records hardness in International Rubber Hardness Degrees (IRHD).

2.4.6. Compression Set

Samples were cured for 1.5 x T90 and rested for 24 hours after curing before compression set testing. A minimum of five test buttons (13 mm ± 0.5 mm in diameter and 6.3 mm ± 0.3 mm thick) were cured for each sample. The samples were compressed to 4.77 mm, a compression of 25 %, with the thickness of each button being measured prior to compression. Test pieces

were then heated to 70 ºC whilst under compression and held in this state for 24 hours. After removal from the heat and releasing from the compression, the samples were allowed to recover for 30 minutes before the thickness of the test button was re-measured. The compression set for each sample was calculated using Equation 2.1.

$[(H_a-H_b)/(H_a-H_s)] \times 100 = CS$ (**Equation 2.1)**

Whereby CS = Compression Set

H_a = Initial thickness of test piece

H_b = Final thickness of test piece

H_s = Compression thickness of test piece (in this case 4.77 mm)

This test conforms to BS903 Part A6 (1992) Method B. ISO 815 (1991) Type B test pieces.

2.4.7. Ageing of Tensile Samples

Tensile dumbbell samples were aged in a multi-cell ageing chamber from Wallace Test Equipment, containing seven cells. After curing, the sample was left for 24 hours under ambient conditions before testing commenced. Samples were then placed in the same ageing cell for seven days at 70 °C. Once ageing had finished, the samples were removed and allowed to rest under ambient conditions for a further 24 hours before being tested. Tensile testing could then proceed as described in Section 2.4.4.

2.4.8. Mooney Viscometer

The Mooney viscometer employed in sample testing was a Negretti type 1 from Prescott Instruments Limited. Samples were tested at 100 ºC for 10 minutes with a 1 minute pre-heat time. A large serrated rotor with a 38 mm diameter was utilised and the torque measurement was conducted in Mooney units (MU). The MU is an arbitrary unit used on all Mooney viscometers to measure the torque required to keep the rotor turning at a constant rate of two revolutions per minute.

2.5. Purification Technique: Soxhlet Extraction

Soxhlet extraction was set up to remove impurities from the rubber (Figure 2.4). The solvent used was methanol and each run was carried out at reflux for 8 hours, unless otherwise stated. Cellulose extraction thimbles 32 x 100 mm were filled with 20 g of rubber. In the distillation flask, 250 ml solvent, enough to allow the top chamber to empty four times (ensuring that

there is enough solvent in the flask at all times), was heated. Following extraction, the system was allowed to cool to room temperature. The rubber was then removed and placed at 40 ºC overnight to remove traces of solvent.

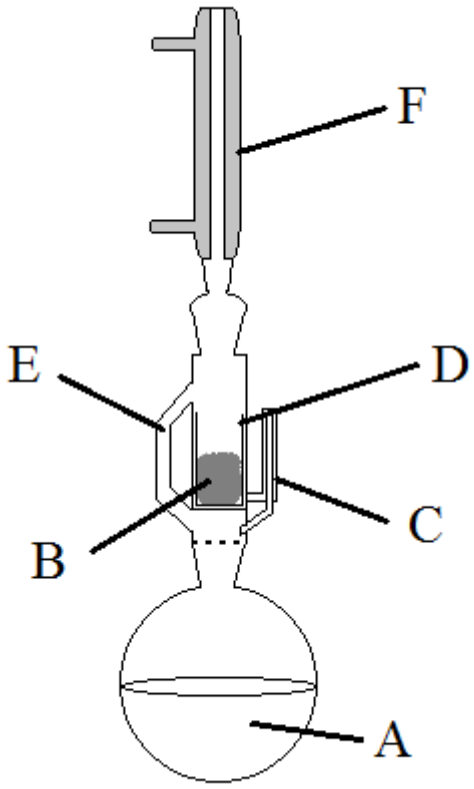


Figure 2.4. Soxhlet schematic where A) still containing solvent, B) sample, C) siphon, D) thimble, E) distillation path and F) condenser.

References

1. L. J. Bellamy, *The Infra-red Spectra of Complex Molecules*, 3rd edn., Chapman and Hall, London, 1975.
2. D. H. Williams and I. Fleming, *Spectroscopic Methods in Organic Chemistry*, 4th edn., McGraw-Hill Book Company, London, 1989.
3. M. Balci, *Basic 1H- and 13C-NMR Spectroscopy*, Elsevier Science and Technology, Amsterdam, Netherlands, 2005.

CHAPTER 3

THE MECHANISMS OF CROSS-LINKING POLYCHLOROPRENE WITH ETHYLENE THIOUREA AND METAL OXIDES

3. The Mechanisms of Cross-linking Polychloroprene with Ethylene Thiourea and Metal Oxides

As described in Chapter 1 (Section 1.4.3) polychloroprene consists of four isomers, *trans* 1,4-, *cis* 1,4-, 3,4- and 1,2-. It is the 1,2-isomer (1.5 % of the total) that is primarily responsible for the cross-linking reaction.[1-3] The presence of the tertiary chlorine in the structure distinguishes it from any other commercial rubber, e.g. natural rubber or styrene-butadiene rubber. As a result, most accepted accelerated sulfur cure systems (Section 1.3.1.1) are not effective with polychloroprene. Moreover, widely used accelerators such as thiurams, benzothiazoles and sulfenamides, are not capable of vulcanising polychloroprene (Figure 3.1). For example rheographs (Figure 3.1) for polychloroprene cured with tetramethyl thiuramdisulfide (TMTD), N-cyclohexyl-benzothiazole-sulfenamide (CBS) or mercaptobenzyl thiazole (MBT) show flat curves indicating little or no cross-linking is occurring. Improved cross-linking occurs when ethylene thiourea (ETU) is used on its own; however, the most effective vulcanisation system is ETU in combination with zinc oxide (ZnO). Nonetheless, the mechanism of cross-linking polychloroprene with ETU and metal oxides is still not fully understood (Section 1.4.5.2.1).

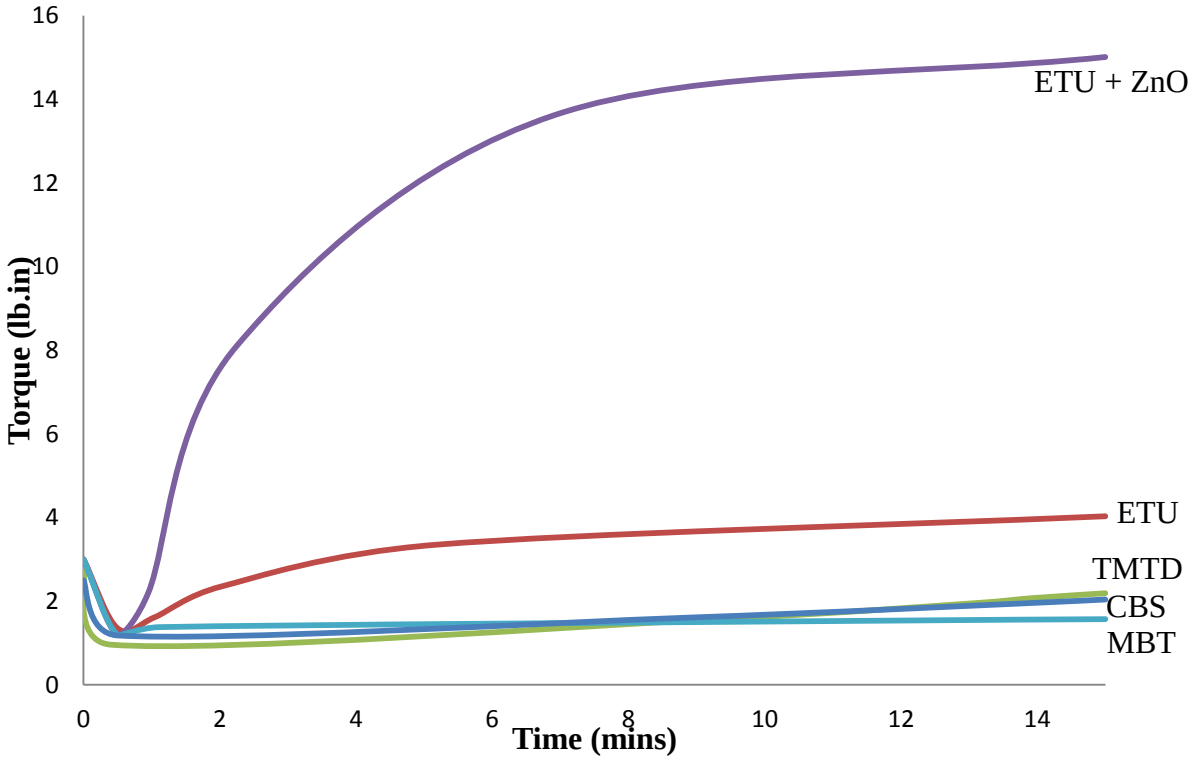


Figure 3.1. Rheographs of polychloroprene cured with 3 phr ethylene thiourea, 3 phr ethylene thiourea with 5 phr zinc oxide, 3 phr tetramethyl thiuramdisulfide, 3phr N-cyclohexyl-benzothiazole-sulfenamide and 3 phr mercaptobenzylthiazole.

This chapter provides new evidence for the mechanisms by which ETU is able to cross-link polychloroprene. Initially, the cross-linking reaction which occurs when ZnO is used on its own is analysed (Section 3.1). ETU alone is then considered (Section 3.2) and finally ETU in combination with ZnO is studied (Section 3.3). This study adopts a novel approach to decipher the mechanisms by examining both physical properties of cross-linked polychloroprene together with spectroscopic analysis. These studies have been performed on the current additives used (ETU and ZnO), traditional rubber accelerators (e.g. TMTD, MBT) and on model compounds (e.g. amines, thiols). Results are compared to existing mechanisms from the literature for cross-linking polychloroprene and the validity of the mechanism or new mechanisms examined. It is worth noting that use of imperial units are widely accepted in rubber technology and as such are used throughout for mechanical property characterisation. Additionally, all additives are measured by weight, as is standard practice in rubber technology, rather than stoichiometrically. All additives were mixed into pure polychloroprene gum stock at stated levels with 0.6 phr stearic acid as a processing aid. No other additives were used unless otherwise noted.

3.1. Cross-linking Mechanisms of Polychloroprene with Zinc Oxide or Magnesium Oxide

To understand how ETU cross-links polychloroprene in the presence of ZnO, the reactions that take place with ZnO alone must first be understood. From rheology data in Table 3.1, the highest torque (MH) of ETU alone and ZnO alone in polychloroprene are very similar. However, when ETU and ZnO are used in combination, the resultant MH is synergistic i.e. higher than the combined total of both. Similarly, the cure, which signifies the highest cure rate achieved during the test, is much higher than the sum of the two individual components. This can be observed more clearly in the rheographs of polychloroprene as it cures (Figure 3.2). These results prove that when used in combination, ETU and ZnO have a synergistic effect. It also proves that a different mechanism is taking place to either of those that occur when the additives are used as cross-linkers on their own. It is evident therefore that the ZnO cross-linking mechanism needs to be studied before that of ETU. This will help elucidate the role ZnO plays in the joint cross-linking mechanism of polychloroprene.

Also noteworthy in Figure 3.2 is the poor performance of magnesium oxide (MgO) in the cross-linking process; it has been stated in some studies that the use of metal oxides in cross-linking is important.[4-6] This statement is however ambiguous, results shown in Table 3.1 and Figure 3.2 indicate that ZnO alone produces vulcanisates with far superior mechanical properties to those of MgO. However, the results also reveal that when MgO is compared to pure polychloroprene rubber gum stock (CR) no cross-linking occurs. Those parts of Table 3.1 not fully discussed here are discussed in more detail in Sections 3.2 and 3.3.

Table 3.1. Mechanical properties of standard gum stock cross-linked with listed additives at 5 phr. For samples that do not reach equilibrium the T90 quoted is that for the test, rather than for equilibrium

		Gum stock[1]	ETU	ZnO	MgO	ETU and ZnO	ETU and MgO
15 mins MDR test at 160 °C	MH (lb.in)	2.04	4.8	5.17	2.53	13.49	4.63
	TS1 (mm:ss)	-	01:33	02:40	13:29	00:53	02:48
	T90 (mm:ss)	12:59	09:09	08:39	13:35	04:38	11:02
	Cure (lb.in/min)	0.16	1.26	1.5	0.18	4.78	0.62

[1]Gum stock contains 0.6 phr stearic acid only and has been milled.

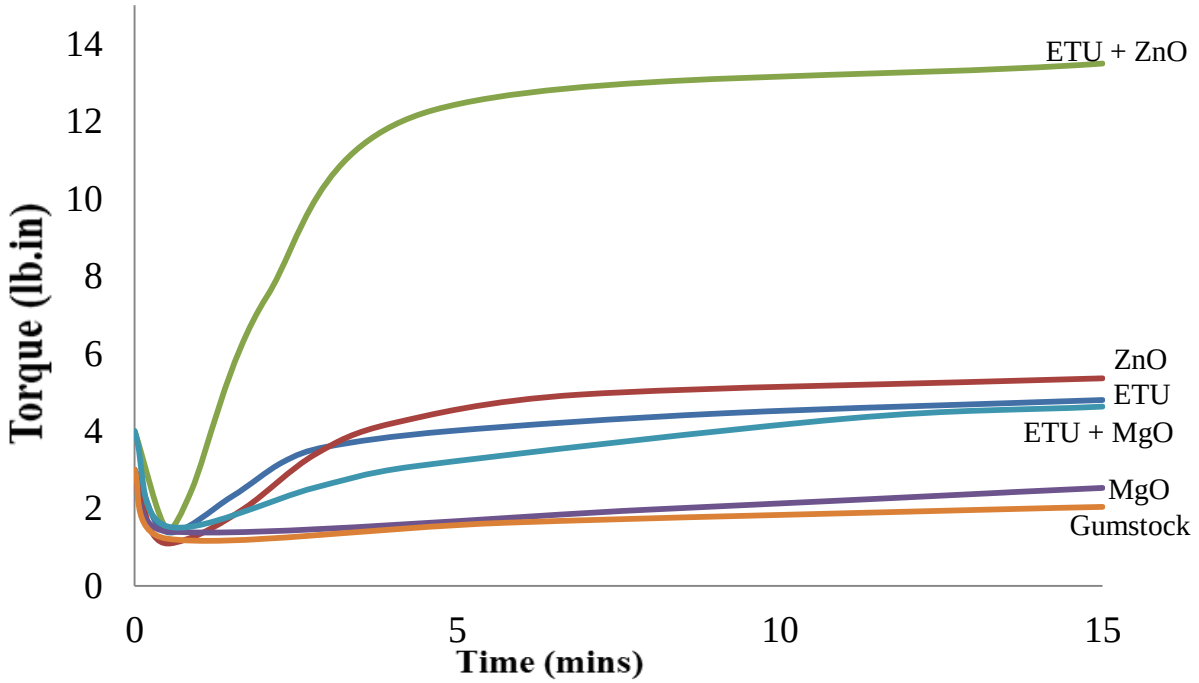


Figure 3.2. Rheographs of polychloroprene with no curatives and cured with 5 phr ETU, 5 phr ZnO, 5 phr MgO, 5 phr ETU with 5 phr MgO, and 5 phr ETU with 5 phr ZnO.

The role of the metal oxide as a hydrochloric acid (HCl) scavenger can be undertaken by either ZnO or MgO. This process does not interfere with the mechanism of cross-linking and is proved through the lack of cure with MgO and reasonable cure seen with ZnO i.e. ZnO can scavenge HCl whilst still able to cross-link. Therefore, ZnO when used in conjunction with ETU cannot solely act as an HCl scavenger otherwise MgO would work as well as ZnO in the presence of ETU. This is discussed further in Section 3.3.

3.1.1. Fourier Transform Infra-Red Analysis

When ZnO alone is used to cross-link polychloroprene, and the resultant rubber is purified *via* methanol soxhlet extraction to remove any impurities, analysis of the cross-linked polychloroprene rubber by FTIR shows a peak at ~1580 cm^{-1} (Figure 3.3) which is not present in the spectrum of the uncured polychloroprene rubber. This region is typical for a C=C stretch[7-9] and would indicate that a carbon-carbon double bond is formed either as part of the cross-link, or elsewhere in polychloroprene, upon vulcanisation.

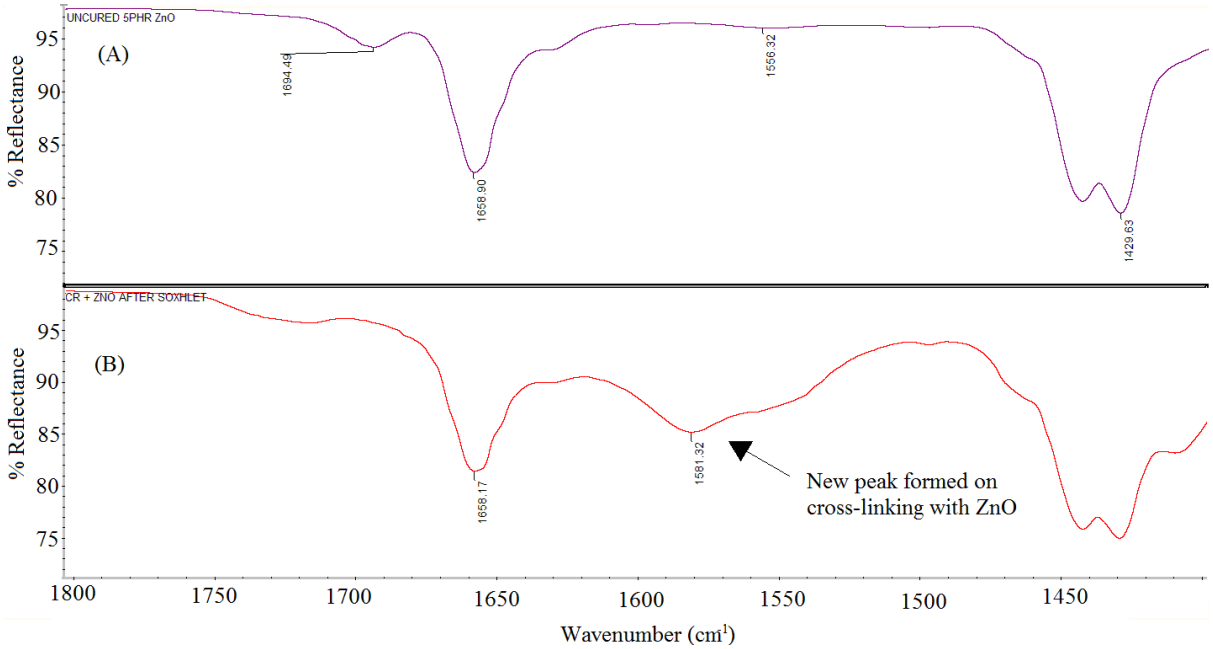


Figure 3.3. FTIR spectra of polychloroprene rubber with 5 phr ZnO; showing (A) uncured ZnO-containing polychloroprene rubber, and (B) after soxhlet extraction. In the region 1400-1800 cm^{-1} showing the formation of a new peak at 1580 cm^{-1}.

As the rubber cures a change in height of the 1580 cm^{-1} peak in the FTIR spectrum is observed. A maximum is reached in approximately four minutes, followed by a steady

reduction in peak height until it levels off (at circa half maximum 'absorbance', yet significantly higher than the starting absorbance) after approximately 20 minutes (Figure 3.4). This suggests that the formation of unsaturation occurs as an initial step in the cross-linking process, but the level of unsaturation is then altered upon full cross-linking.

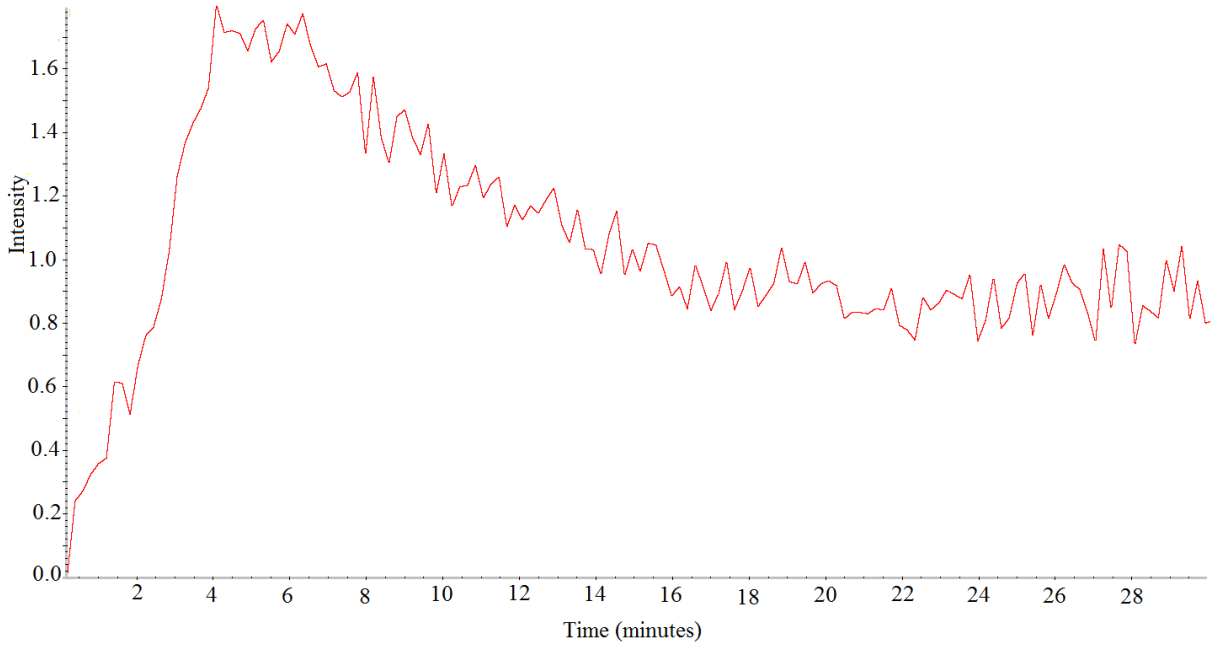


Figure 3.4. Change in intensity of peak height for the 1580 cm^{-1} peak in polychloroprene containing 5 phr ZnO as it cures at 160 °C.

The FTIR spectrum of polychloroprene cross-linked using ZnO indicates that rearrangement of the 1,2-isomer occurs quickly. This was studied by measuring the change in height of the ~925 cm^{-1} band in the FTIR spectrum, associated with C=C stretching in the 1,2-isomer and compared to that of standard polychloroprene rubber without additives when at 160 °C, over time (Figure 3.5). It can be seen that the 1,2-isomer is able to rearrange upon heating over time without any additives, taking approximately 40 minutes, but rearrangement occurs much faster with ZnO. Figure 3.5 shows that with ZnO, the 1,2-isomer undergoes allylic rearrangement very quickly. Approximately 90 % rearrangement occurs within a minute and total rearrangement is complete after 2 minutes.

Polychloroprene containing ZnO takes longer than a minute, when at 160 °C, to begin to cure, which suggests that allylic rearrangement is the first step in the cross-linking mechanism of polychloroprene in the presence of ZnO. These results disprove the theory of Mallon *et al*,[10] in which the authors state that the unrearranged 1,2-isomers take part in the cross-linking

reaction. The scorch time (see Table 3.1) of over 2 minutes for polychloroprene with ZnO indicates cross-linking has not proceeded very far within 2 minutes, while the results in Figure 3.5 show that all of the 1,2-isomer has already rearranged by this time. Therefore only rearranged 1,2-isomer is available to cross-link.

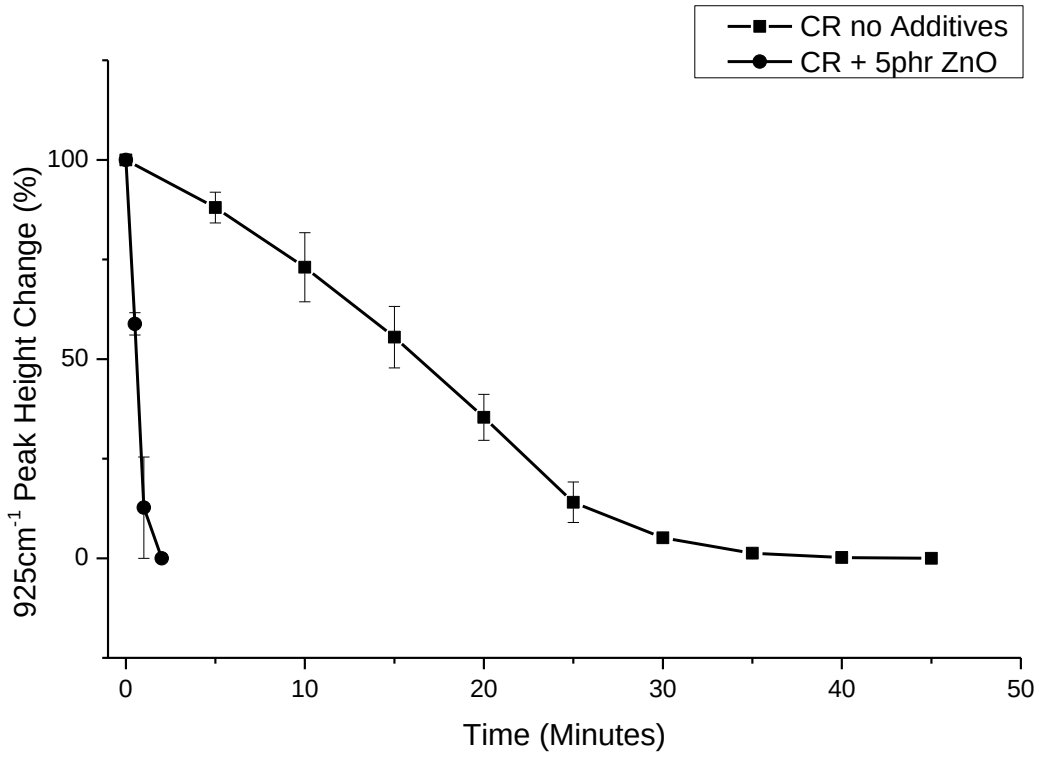


Figure 3.5. Change in height of 925 cm^{-1} peak of polychloroprene containing ZnO with time. Note error bars show one standard deviation and are too small to show above 30 minutes.

Two cationic mechanisms have been reported by Vukov[11] and Desai *et al*[12] to explain the cross-linking reaction between ZnO and polychloroprene. After rearrangement of the 1,2-isomer, Vukov's mechanism[11] proposed diene formation as the major reaction taking place, with the diene reacting to aid cross-linking. The appearance of the 1580 cm^{-1} peak in the FTIR spectrum on cross-linking supports the theory of diene formation. Similarly, Desai's mechanism[12] has formation of an unsaturation within the cross-link; again this is supported by the 1580 cm^{-1} peak in the FTIR spectrum. The reduction in the 1580 cm^{-1} peak after reaching a maximum indicates that the diene created during the process is reacting, suggesting the mechanism postulated by Vukov as more likely to be occurring. However, in the mechanism Desai hypothesised after rearrangement of the 1,2-isomer there are two more steps, carbocation formation and actual cross-linking.

One of the by-products of both Vukov's and Desai's cross-linking mechanisms is zinc chloride. The FTIR spectrum of zinc chloride alone shows two major peaks at 1616 cm^{-1} and 1404 cm^{-1} (Figure 3.6). Unfortunately, both of these peaks are in regions overlapping with peaks on the polychloroprene spectrum (Figure 3.6); and it is therefore difficult to ascertain evidence for zinc chloride by FTIR. Zinc chloride is highly hygroscopic, therefore the large broad peak observed at 3474 cm^{-1} (in the zinc chloride spectrum) is associated with water and would not be present in the cured rubber due to the high curing temperature of 160 °C used.

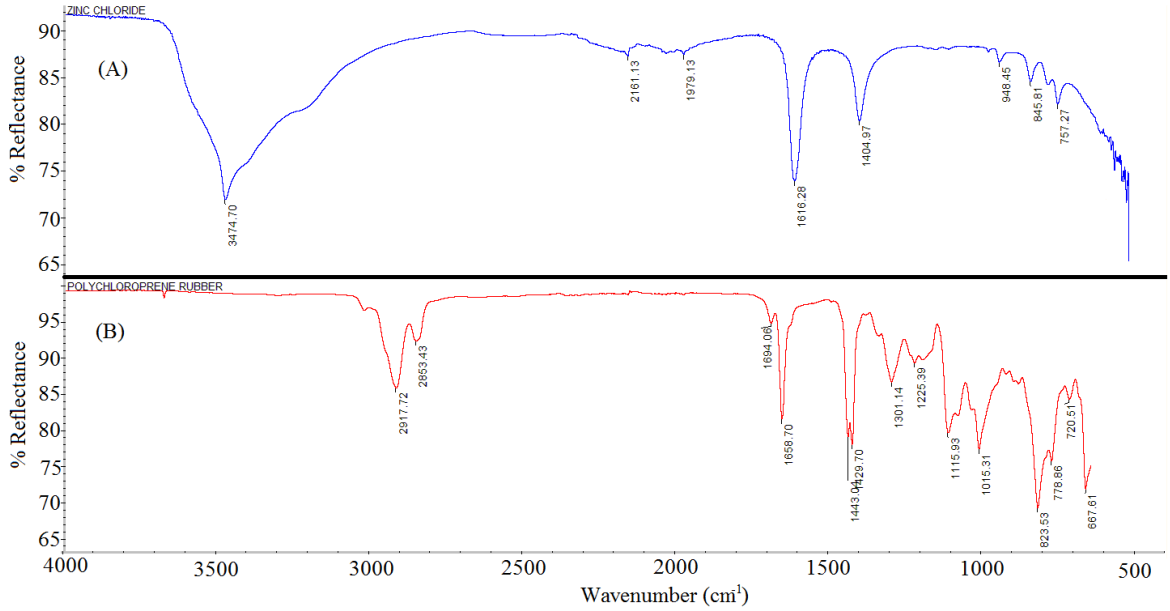
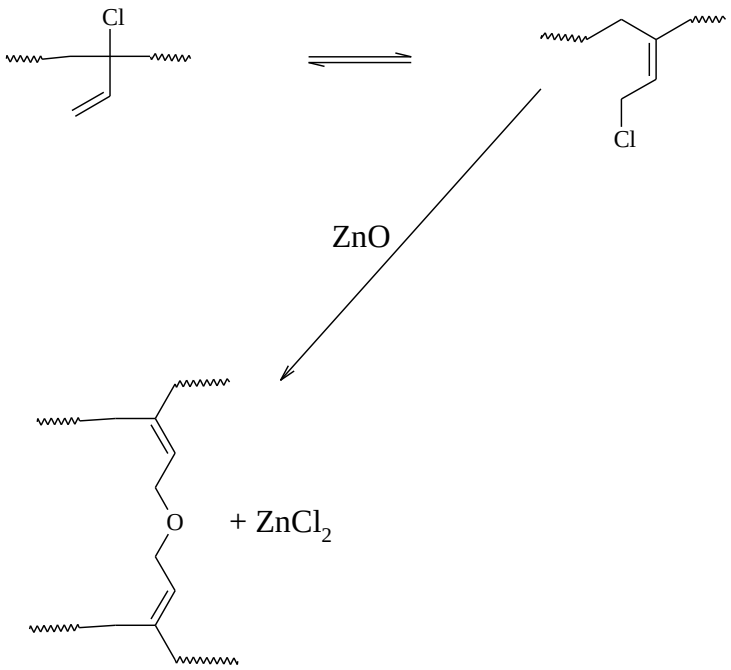


Figure 3.6. FTIR spectra of (A) zinc chloride and (B) polychloroprene rubber, showing peaks in similar positions, thus making the identification of zinc chloride in the rubber difficult.

As reported herein, the only new peak in the FTIR spectrum upon cross-linking polychloroprene with ZnO was at 1580 cm^{-1}. Figure 3.7 shows the spectra of polychloroprene containing ZnO in the region 1000-1300 cm^{-1} before and after curing. No new peaks are observed. The ether linkage cross-linking mechanism (Scheme 3.1),[1, 2, 13] has been disproved by several authors in the literature (see Section 1.4.5.1).[14, 15] If this mechanism were to proceed, a strong band in the 1085-1150 cm^{-1} region would be expected to be observed.[7, 16] These FTIR spectroscopic results further confirm that this mechanism is not occurring when polychloroprene is cross-linked with ZnO alone.



Scheme 3.1. 'Ether linkage-forming' cross-linking mechanism for zinc oxide in polychloroprene,[1, 2, 13] now discounted due to several papers.[14, 15]

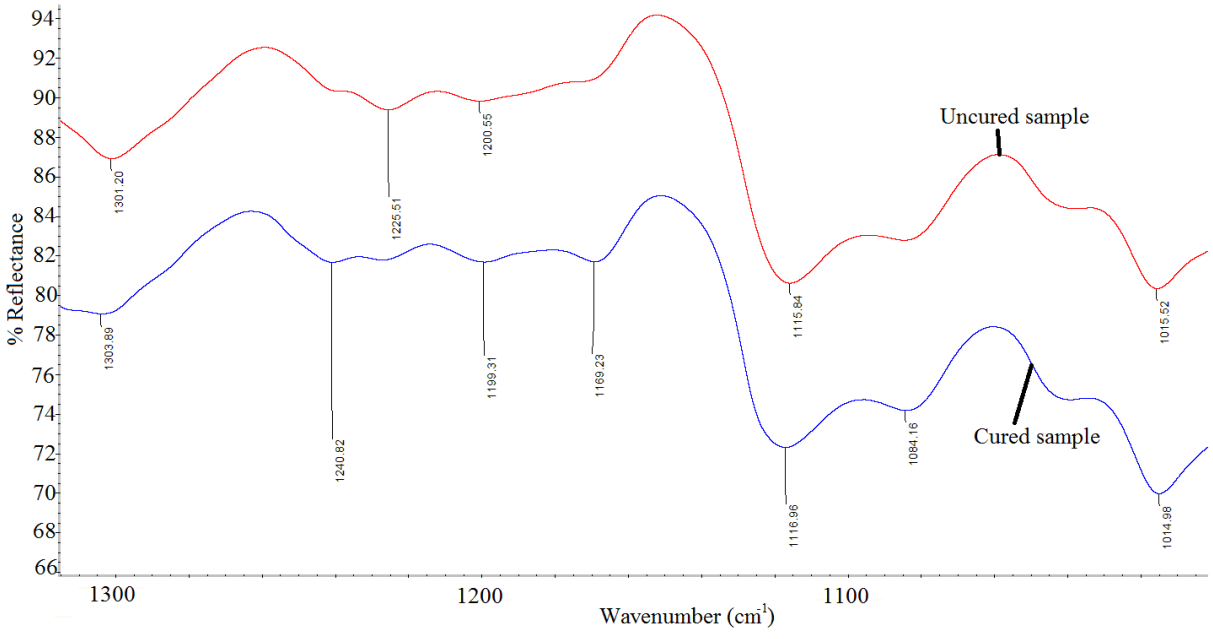


Figure 3.7. FTIR traces of polychloroprene with ZnO cured and uncured in the range 1000-1300 cm^{-1} showing no peaks associated with ether linkages. The plots have been translated along the reflectance axis for greater clarity.

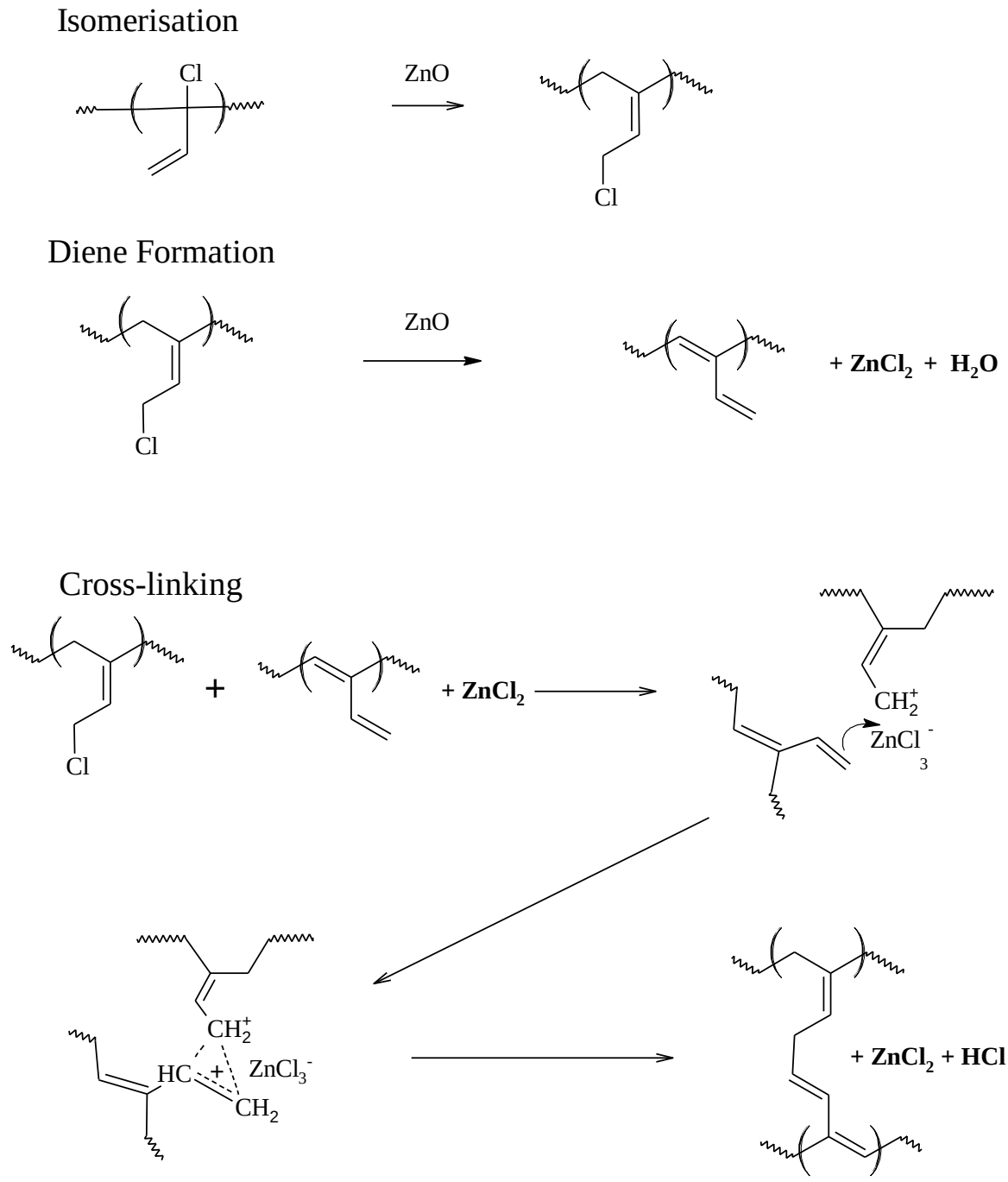
3.1.2. Zinc Oxide Cross-linking Conclusions

From evidence gathered in this study and that from previously published literature, there is proof that the ZnO mediated cross-linking mechanism in which an ether linkage is formed does not occur. This is seen through the absence of the peak associated with an ether linkage in the FTIR spectrum of cured polychloroprene. Additionally, the mechanism put forward by Mallon,[10] whereby the unrearranged 1,2-isomer takes part in the reaction is erroneous. Evidence herein shows the complete rearrangement of the 1,2-isomer of polychloroprene within two minutes with ZnO. Therefore no unrearranged 1,2-isomer remains available to undergo the cross-link reaction. Proof has also been given to show that the effects of metal oxides within the cross-linking reaction are altered by changing the metal oxide. ZnO gives a superior cure to that of MgO. This could be attributed to the fact that magnesium is more reactive than zinc, and it has been shown in the literature that MgO produces more unstable intermediates than ZnO in sulfur cross-linking of natural rubber and so a lower cross-link yield resulted.[17, 18] Additionally, MgO has difficulty in forming the complexes required in a cross-linking reaction.[17, 18]

Evidence herein also suggests that the cross-linking mechanism taking place in polychloroprene with ZnO occurs through one of the proposed cationic mechanisms reported in the literature. Additionally, the cross-links formed are carbon-carbon bonds with an unsaturation created during the cross-linking process. Furthermore, the increase and then reduction in height of the 1580 cm^{-1} peak suggests that diene formation is the initial step in the cross-linking process, as proposed by Vukov. Scheme 3.2 shows the mechanism proposed by Vukov using model compounds. The initial step involves allylic rearrangement of the 1,2-isomer, followed by diene formation, and finally cross-linking, mediated by zinc chloride generated as a by-product from the diene formation step.

3.2. Cross-linking Mechanism of Polychloroprene with Ethylene Thiourea

To understand the mechanism of ETU cross-linking polychloroprene, ETU was compared to traditional rubber curatives and model compounds, in pure polychloroprene rubber and oligomers. Their effect on mechanical properties and spectroscopic differences were then compared and contrasted to results from cross-linking mechanisms suggested in the literature.



Scheme 3.2. Cross-linking mechanism of polychloroprene with ZnO, proposed by Vukov[11] using model compounds, shown here with polychloroprene.

3.2.1. Polychloroprene Rubber Cross-linked with Ethylene Thiourea on its Own and Compared to Widely Used Rubber Accelerators

The analysis herein compares the cross-linking ability of widely used rubber curatives in polychloroprene with that of ETU. Structures of all the various rubber accelerators employed in this study are shown in Table 3.2. All experiments were conducted with 0.6 phr stearic acid present as a processing aid and other additives at levels quoted.

Table 3.3 shows the difference in cure characteristics between ETU and different accelerator classes. Although methyl-2-mercaptobenzimidazole (MMBI) and zinc dibutyldithiocarbamate (ZDBC) show a good cure rate (Figure 3.8), indicating that cross-linking is occurring, the ultimate tensile strength is significantly lower compared to that of ETU (Figure 3.9 and Table 3.4). This indicates that the cross-linking mechanism occurring with ETU in polychloroprene is different to that of other accelerators. It is noteworthy that MMBI shares the isothiourea moiety (Figure 3.10) that the tautomeric form of ETU contains, and ZDBC comprises an N-C=S structure that ETU encompasses. However, tetramethyl thiuramdisulfide (TMTD) which also contains an N-C=S structure is unable to cross-link polychloroprene alone, and is known to require an activator when cross-linking natural rubber,[19] this is investigated further in Section 3.3. Figure 3.8 shows that ETU has a cure rate of less than 1 lb.in/min and this is, in part, due its marching modulus. Marching modulus indicates a continual steady rise in torque after initial curing (see Section 1.5.1.1 for full explanation). This would consequently increase T10 and T90 values (the times when 10 % and 90 % of maximum torque is reached) used to calculate the cure rate. Therefore, the calculation of cure rate would take into account some of the time whilst the marching modulus occurred, thereby reducing the cure rate. It should also be noted that the sample did not break when undergoing tensile testing. This indicates that few cross-links are being created as the polymer chains are able to move more freely (Table 3.4). Therefore it has become a highly branched material rather than a containing a full 3-dimensional network i.e. a 3-dimensional network inhibits movement of the polymer chains due to increase in cross-linking density causing a reduction in extension at break. Another significant aspect of the mechanical properties is the UTS. The UTS of 8 MPa for ETU cross-link polychloroprene is high enough to deduce that the cross-links being formed are strong in nature (Figure 3.9). From the mechanical properties, it can be concluded that ETU does not form many cross-links but those it does form are robust.

Table 3.2. Rubber accelerators employed in this study and their structures.

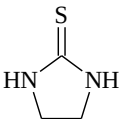
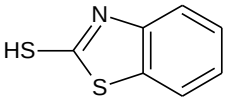
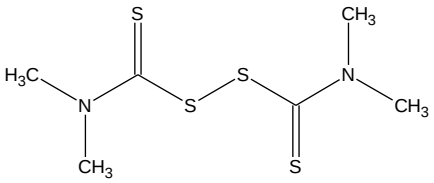
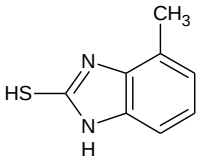
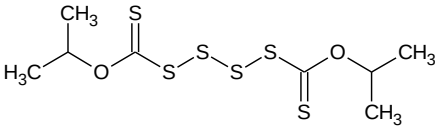
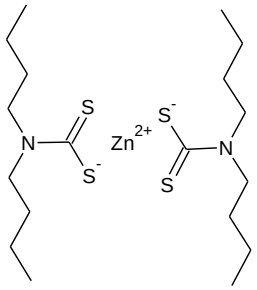
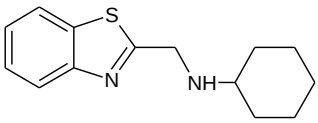
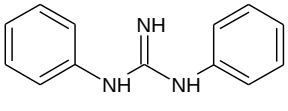
Accelerator Type	Accelerator Used	Structure
Thiourea	ethylene thiourea (ETU)	
Thiazole	mercaptobenzylthiazole (MBT)	
Thiuram	tetramethyl thiuramdisulfide (TMTD)	
Imidazole	methyl-2-mercaptobenzimidazole (MMBI)	
Xanthogen	di-isopropyl polysulfide (AS100)	
Dithiocarbamate	zinc dibutyldithiocarbamate (ZDBC)	
Sulfenamide	N-cyclohexyl-benzothiazole-sulfenamide (CBS)	
Guanidine	diphenyl guanidine (DPG)	

Table 3.3. Rheological properties of polychloroprene cured with different rubber accelerators, with all additives present at 3 phr.

Accelerator	15 minute MDR test at 160 ºC			
	MH (lb.in)	TS1 (mm:ss)	T90 (mm:ss)	Cure (lb.in/min)
ETU	4.03	02:01	10:02	0.8
MBT	1.66	00:00	12:32	0.42
TMTD	2.19	13:09	13:54	0.2
MMBI	4.22	01:17	06:56	1.68
AS100*	2.26	14:18	13:56	0.2
ZDBC	4.22	01:04	08:11	3.94
CBS	2.04	00:00	13:50	0.18
DPG	3.07	08:16	13:27	0.26

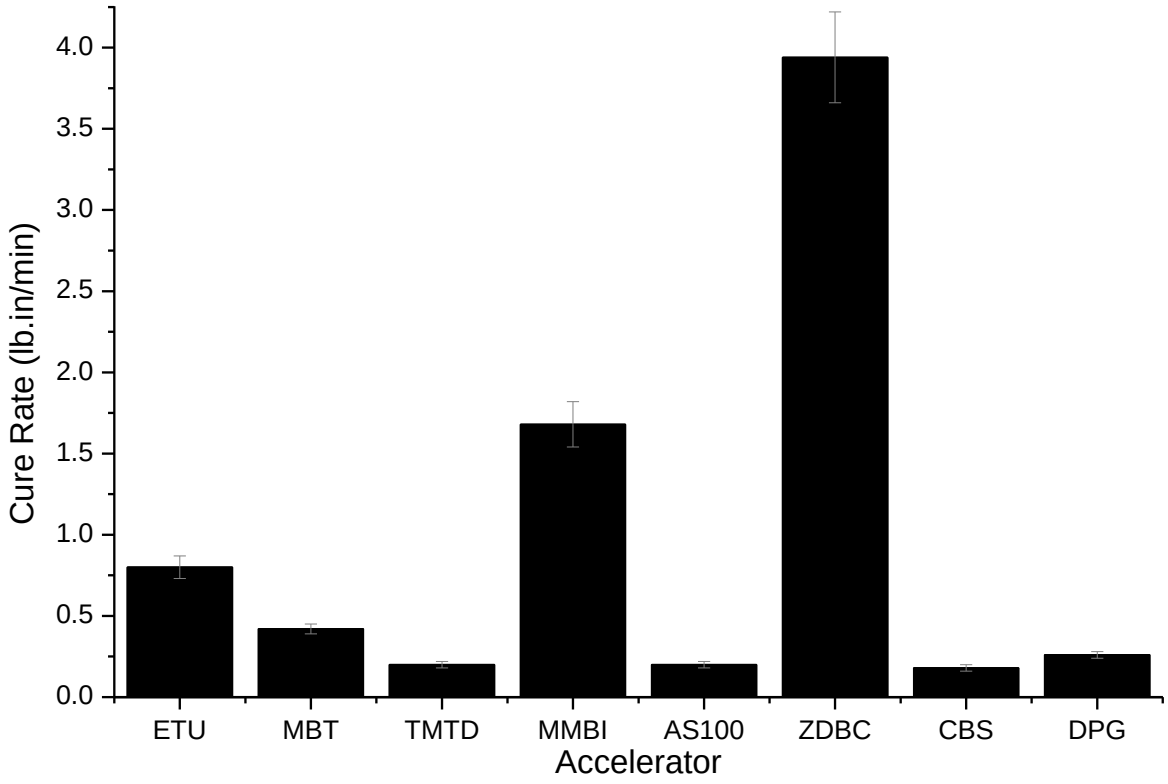


Figure 3.8. Cure rates of polychloroprene cross-linked with 3 phr of different accelerators. Error bars show one standard deviation from three data sets.

Table 3.4. Tensile properties of polychloroprene cured with several rubber accelerators, with all additives present at 3 phr.

Accelerator	Tensile Tests Cured 1.5 x T90				
	100 % Mod (MPa)	**300 % Mod (MPa)**	**500 % Mod (MPa)**	**UTS (MPa)**	**Elongation at break (%)**
ETU	0.67	0.97	1.46	8.0	DNB*
TMTD	0.24	0.2	0.18	0.3	DNB*
MMBI	0.61	0.81	0.99	4.9	1031
ZDBC	0.39	0.49	0.74	4.5	DNB*

*Sample did not break (see Appendix A).

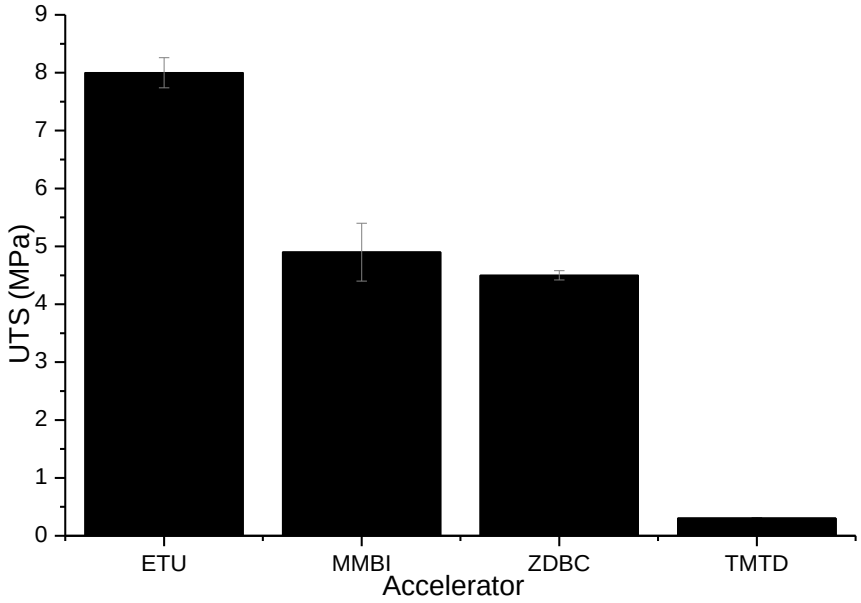
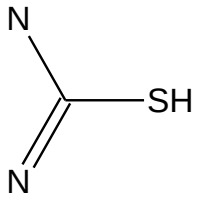


Figure 3.9. Ultimate tensile strength of polychloroprene cross-linked with various accelerators at 3 phr. Error bars show one standard deviation from three data sets and are too small to see with the TMTD sample.



Isothiourea

Figure 3.10. The structure of isothiourea moiety present in both MMBI and the tautomeric form of ETU.

In addition to studying mechanical properties, the use of FTIR spectroscopy to compare cured and uncured polychloroprene samples containing ETU may allow differences in the structure, due to cross-linking, to be identified. One of the most notable new bands after cross-linking polychloroprene with ETU in the FTIR spectrum is the peak formed at ~1550 cm^{-1} (Figure 3.11). This new peak is different to that found when ZnO cross-links polychloroprene alone, which is seen at 1580 cm^{-1} and is consistent with a new C=C bond formed when curing occurs. It indicates that the cross-linked structure of polychloroprene when reacted with ETU is different to that when ZnO alone acts as a cross-linker. Therefore it was envisaged that identification of this peak would help elucidate the cross-linking mechanism. To this end, the FTIR spectrum of model compounds containing nitrogen or sulfur atoms (such as thiols, sulfides, amines etc.), which are also present in ETU, were examined for the presence of the 1550 cm^{-1} peak. None of the compounds studied, however, gave a band in the same region. This suggests that none of groups in the model compounds tested are responsible for producing this peak in the cross-linked structure. Therefore, by assessing model compounds that vulcanise polychloroprene a clearer answer to the cross-linking mechanism of polychloroprene may be provided (discussed in Section 3.2.2).

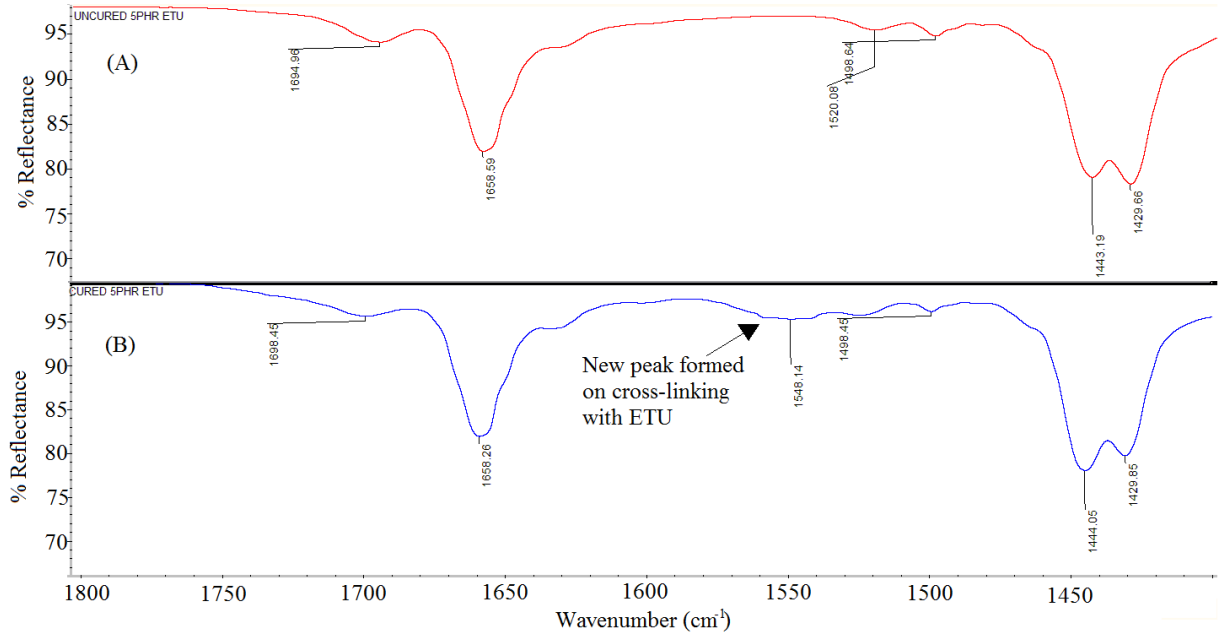


Figure 3.11. FTIR spectra of polychloroprene containing 5 phr ETU, (A) before curing and (B) after curing for the region 1400-1800 cm^{-1}. Showing a new peak in ETU cross-linked sample at ~ 1550 cm^{-1}.

When polychloroprene is cured with ETU, the height of the 1550 cm^{-1} peak in the FTIR spectrum, when tracked over time, initially increases rapidly, followed by a slowdown in the

rate of increase (Figure 3.12). These results indicate a high degree of initial cross-linking activity, and that the rate of cross-linking decreases as ETU reacts. Also, it should be noted in Figure 3.12 the increase in cross-linking activity follows a similar trend to the rheograph of ETU cross-linking polychloroprene. These results suggest that the 1550 cm^{-1} peak is intimately linked with the cross-linking activity of ETU. In contrast to when polychloroprene is cured with ZnO where the peak associated with cross-linking (~1580 cm^{-1}, showed an initial increase followed by a decrease), was associated with an intermediate species, the ~1550 cm^{-1} peak appears to be associated with a final cross-linked product.

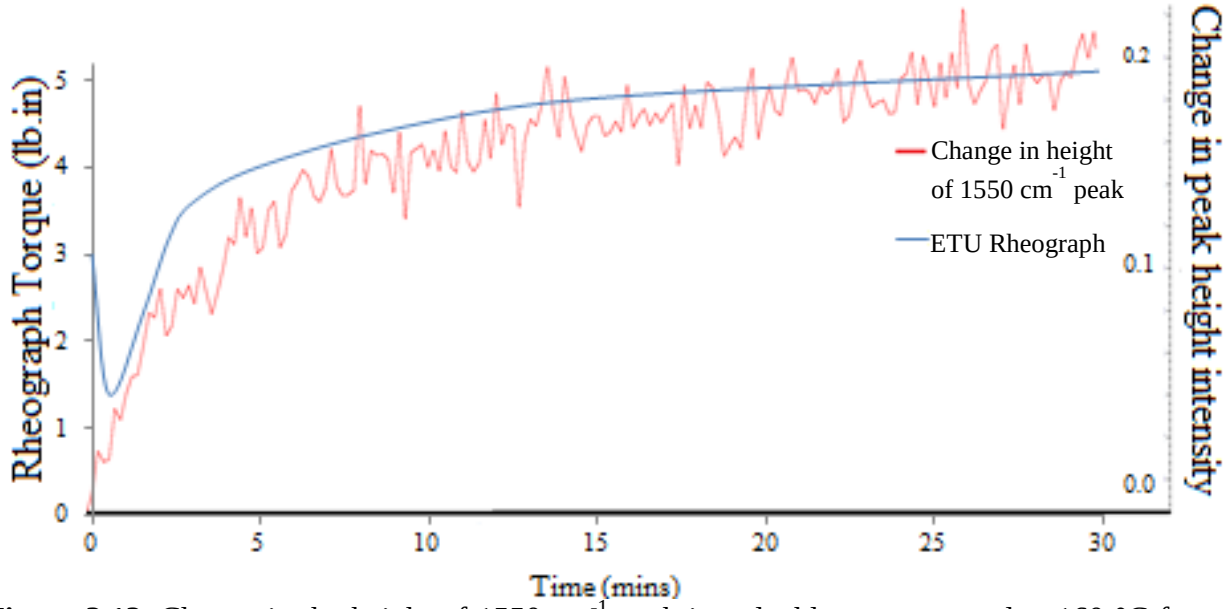


Figure 3.12. Change in the height of 1550 cm^{-1} peak in polychloroprene cured at 160 °C for 30 minutes with 2 phr ETU compared to a rheograph of 2 phr ETU cross-linking polychloroprene at 160 °C.

The mechanism of cross-linking polychloroprene rubber has been investigated by FTIR spectrometry with rubber accelerators capable of cross-linking polychloroprene. ZDBC gives two new peaks at ~1540 cm^{-1} and ~1519 cm^{-1} and the disappearance of a peak 1496 cm^{-1} (Figure 3.13). The latter peak is associated with N-C=S group in ZDBC,[8] and its disappearance over time indicates that ZDBC has undergone a reaction as part of cross-linking process. If the peak at ~1550 cm^{-1} with ETU is due to a structural feature in cross-linked polychloroprene, it is also possible that the two new peaks obtained by cross-linking polychloroprene with ZDBC are due to similar, but slightly different, new arrangements within the polychloroprene structure after cross-linking. Cross-linking polychloroprene with MMBI, on the other hand does not appear to produce any new peaks in the FTIR spectrum.

These results suggest that cross-linking polychloroprene with MMBI does not produce the same resultant structure to that of polychloroprene cross-linked with ETU, or any structure that produces a peak within a similar region.

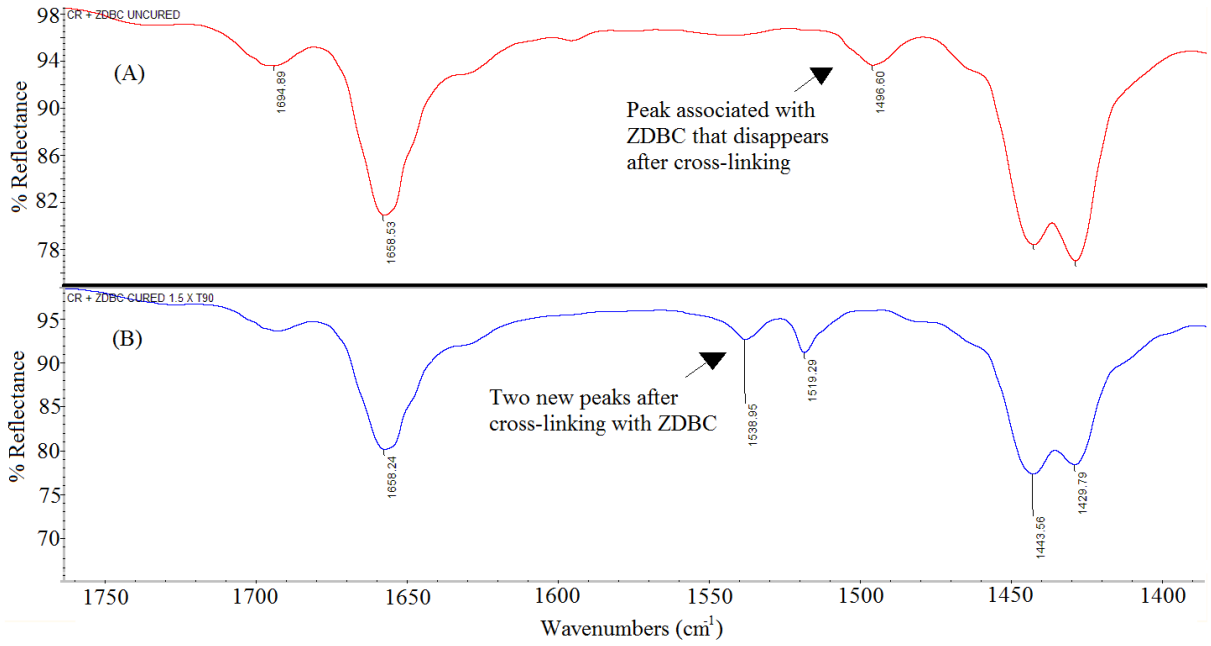


Figure 3.13. FTIR spectra of polychloroprene containing 3 phr ZDBC (A) before and (B) after cross-linking.

As with ZnO-cured polychloroprene, the 925 cm^{-1} band in the FTIR spectrum associated with the 1,2-isomer disappears over time when polychloroprene is cured with ETU. The disappearance of the 925 cm^{-1} peak for ETU-cured polychloroprene is compared to that of pure polychloroprene gum-stock with no additive present in Figure 3.14. As previously mentioned the reduction of the 925 cm^{-1} peak represents a diminishing of 1,2-isomer.[20-22] When ETU is used, over 60 % of the 1,2-isomer is shown to disappear within the first minute, after this a steady decline is seen until all 1,2-isomer has rearranged after 30 minutes. There are two aspects of note. Firstly, using 2 phr ETU gives a scorch time of about 2 minutes (Table 3.3), therefore ETU starts to rearrange the 1,2-isomer before crosslinking begins. Secondly, as cross-linking is said to be 90 % complete within 10 minutes (a T90 of about 10 minutes is seen in Table 3.3 with 2 phr ETU), it would indicate that some 1,2-isomer remains after cross-linking has completed. This would explain the large extension at break observed in ETU-cured polychloroprene tensile samples (see Table 3.4), due to a low extent of cross-linking. As cross-linking is thought to occur through the 1,2-isomer after rearrangement, and a

small amount of un-rearranged 1,2-isomer remains after cross-linking is completed, not all possible sites of cross-linking will have been utilised.

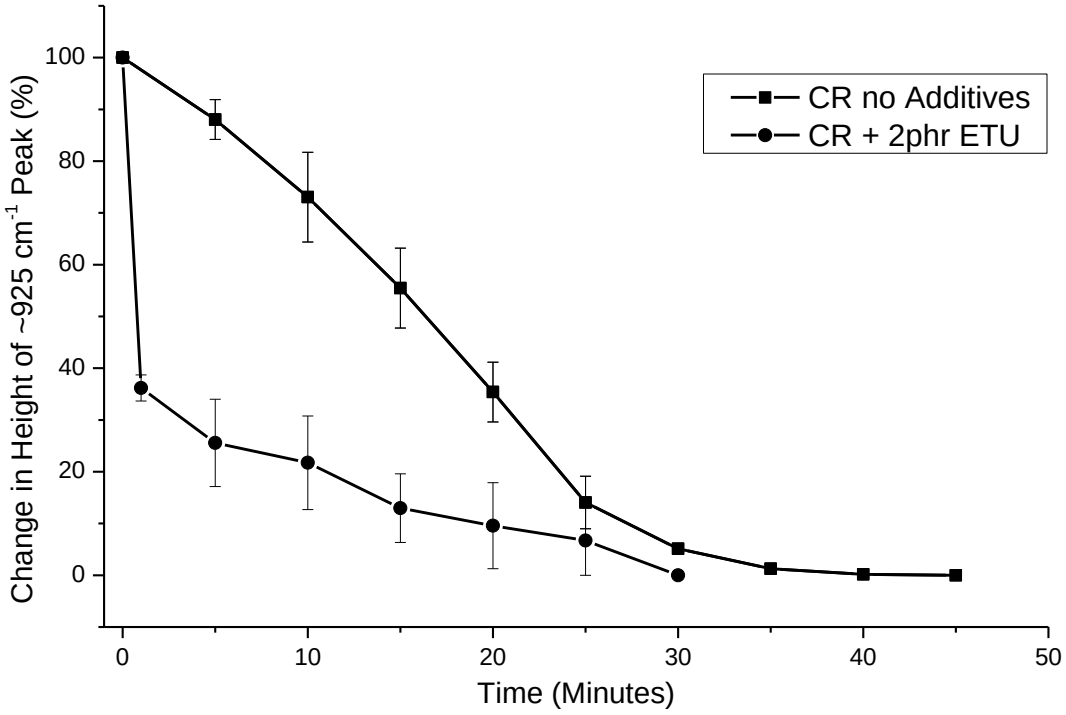


Figure 3.14. 925 cm^{-1} band disappearance with ETU-cured polychloroprene compared to pure polychloroprene with no additives. Error bars are one standard deviation and after 30 minutes are too small to see.

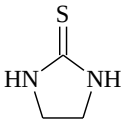
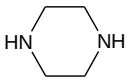
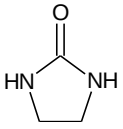
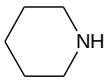
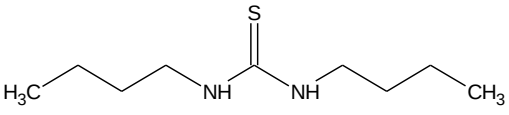
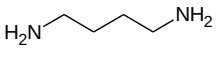
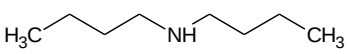
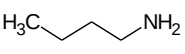
To determine whether the new peak at 1550 cm^{-1} was due to a new cross-linked structure, a product of cross-linking or a side reaction, soxhlet extraction (in methanol) on polychloroprene cured for 1.5 x T90 and 5 x T90 was performed. 2 phr and 5 phr of ETU were used for both cure times and all results showed that the peak at ~1550 cm^{-1} was still present after extraction; this was also true for a sample extracted for an extended period of time (3 days). The results strongly suggest that the 1550 cm^{-1} peak is due to a new cross-linked structure. After evaporation of methanol, it was found (through FTIR and GC) that some ETU was present. Again, this was true in all samples examined, showing that a small quantity of ETU remains after cross-linking. Earlier results herein indicate that some 1,2-isomer also remained after cross-linking polychloroprene with ETU. These results suggest that cross-linking polychloroprene rubber with ETU is not 100 % efficient, as the two components of cross-linking, namely the 1,2-isomer and ETU, are still present at the end of the cross-linking reaction.

3.2.2. Cross-linking Polychloroprene Rubber with Model Compounds as a Comparison to Ethylene Thiourea

Having examined the reaction of polychloroprene with ETU, further study has been made to enable the elucidation of the cross-linking mechanism. A comparison between the physical and spectroscopic attributes of model compounds in polychloroprene and those of ETU will enable the mechanism to become clearer. The model compounds that have been tested are those that contain nitrogen- or sulfur-based groups, and should help in understanding the mechanism by which ETU cross-links (i.e. by which functional groups).

Several different types of amine-containing model compounds have been studied (Table 3.5); some with a similar structure to ETU, such as dibutyl thiourea (DBTU) and ethylene urea (EU). Other amine-containing compounds tested include a linear primary amine (butylamine), linear primary diamine [1,4 diamino butane (DAB)], cyclic secondary amine (piperidine), cyclic secondary diamine (piperazine) and linear secondary amine (dibutylamine). Comparing how these model compounds cure polychloroprene with that of ETU, would allow the role that the nitrogen plays in cross-linking to be more positively identified.

Table 3.5. Structures of amine-containing additives used as model compounds.

Compound	Structure	Compound	Structure
ethylene thiourea (ETU)		piperazine	
ethylene Urea (EU)		piperidine	
dibutyl thiourea (DBTU)		1,4-diaminobutane (DAB)	
dibutylamine		butylamine	

Initially, the cure characteristics of polychloroprene containing 2 phr of the various amine model compounds were compared (Table 3.6) to enable their efficiency to cross-link polychloroprene to be established. All formulations contained 0.6 phr stearic acid as a processing aid. The primary result of interest was the model compound EU; this compound is the most structurally similar to ETU, with the sulfur atom substituted by oxygen. Table 3.6 and Figure 3.15 clearly show that EU does not cross-link polychloroprene to any extent and this is attributed to the electronegativity of oxygen compared to sulfur. As oxygen is more electronegative, it 'withdraws' electron density from the nitrogen atoms, rendering the nitrogen atoms less nucleophilic (i.e. it is more difficult for the lone pair on the nitrogen to attack an electrophilic site). Effectively this deactivates the ability of the nitrogen atoms to react and take part in the cross-linking reaction. Conversely, in ETU, the sulfur atom is less electronegative and does not 'withdraw' electron density from the nitrogen atoms leaving them able to attack an electrophilic site on the polymer chain.

Table 3.6. Rheological properties of polychloroprene with 2 phr of the amine-containing model compounds.

	ETU	**DBTU**	**EU**	**butyl-amine**	**DAB**	**pipera-zine**	**piperi-dine**	**dibutyl -amine**
MH (lb.in)	4.40	3.33	1.56	8.91	13.64	13.77	4.19	5.51
TS1 (mm:ss)	02:05	03:26	-	02:41	01:27	00:44	05:41	07:06
T90 (mm:ss)	10:05	11:21	12:54	12:29	11:33	08:37	13:25	14:02
Cure (lb.in/min)	0.84	0.52	0.14	0.82	2.00	4.86	0.27	0.50

Table 3.6 and Figure 3.15 show that DBTU and dibutylamine both have poor cure rates of about 0.5 lb.in/min. The low cure rates could be due to the steric hindrance of the two butyl groups in both compounds, which retard the cross-linking process. Additionally, Table 3.6 and Figure 3.15 show that both butylamine and piperidine can act as cross-linking agents, although each of these additives only contain a single nitrogen atom. Butylamine is able to cross-link to a level similar to that of ETU, whereas piperidine only gives partial cross-linking with a cure of 0.27 lb.in/min (signifying a poorly cross-linked structure). Despite the poor cure, however, these results show that a compound with a single amine group is able to cross-link polychloroprene. This could be due to the functionality of amines whereby the each nitrogen is able to achieve three bonds, four in the case of a quaternary ammonium salt.

Therefore the nitrogen in butylamine could still be attached to its alkyl chain and form two more bonds thus linking two polymer chains, with dibutylamine able to cross-link by forming a quaternary ammonium salt. Table 3.6 also shows that the cure rates of DAB are twice as high as that observed with butylamine and since DAB has two amino groups, this indicates that the amine itself is reacting to create cross-links, as DAB contains two amino-groups it could create cross-links at both ends of its alkyl chain. The basicity of each amine compound affects its ability to react. Steric and electronic effects will influence the basicity, and means secondary amines are more basic than the primary amines and amines are more basic than a urea or a thiourea. Although changing the media in which the amine is will alter its absolute basicity, i.e. an amine in a solvent will have a different basicity to an amine in the polymer matrix. It should be noted that the relative order of basicity from one amine to another will remain unchanged.[23]

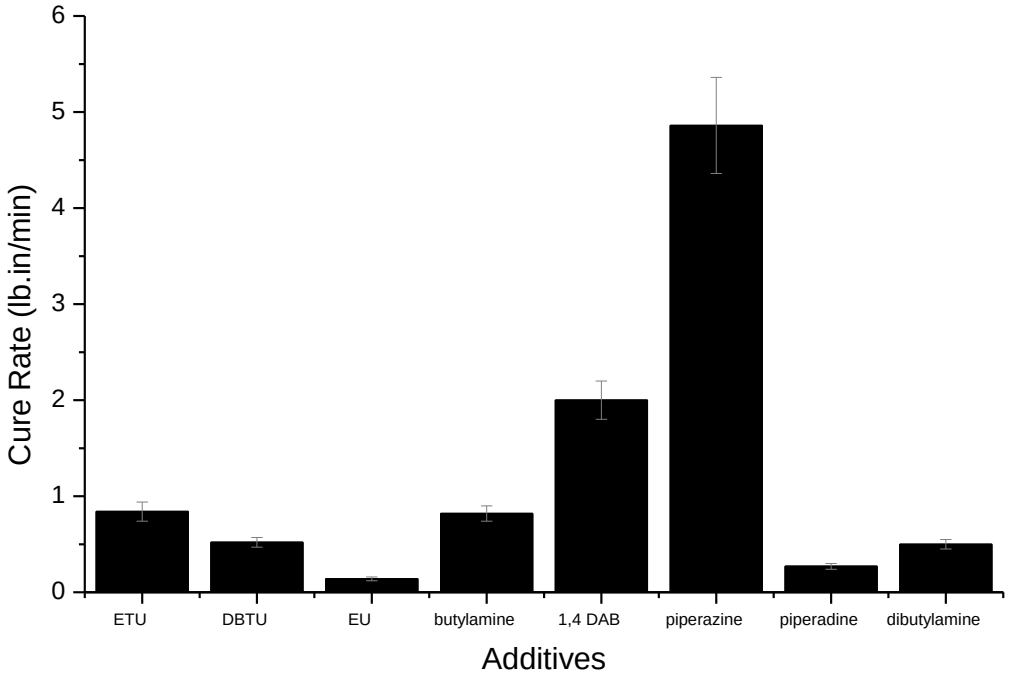
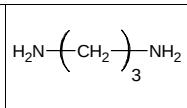
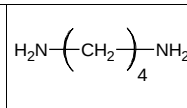
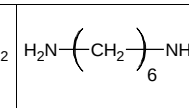
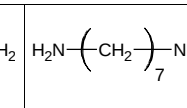
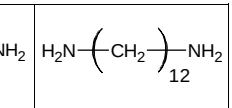


Figure 3.15. Cure rate of various amine-containing model compounds used to cure polychloroprene, all present at 2 phr. Error bars show one standard deviation from three data sets.

To examine the cross-linking of polychloroprene with linear diamines different chain length diamines was studied. If the diamines were ‘slotting’ in to create a bridge between polymer chains a change in the physical and rheological properties of the cured polychloroprene would

be expected. However this is not the case (Table 3.7 and Figures 3.16 and 3.17), with all linear diamines tested from 1,3- to 1,7- producing similar results. 1,12-diaminododecane did not cross-link polychloroprene as well as the other diamines as indicated by the increase in scorch time and T90, and the reduction of MH and cure rate. Similarly tensile results show an increase in extension at break which is also an indicator for fewer cross-links in the network structure. However, in the rubber industry additives are added by weight rather than stoichiometrically and therefore the difference in the 1,12-diamine result can be explained by a lower ratio of amine present to undergo curing compared to lower alkyl length diamines. This can be confirmed by examining the rheological properties when 0.017 moles of 1,12-diamine are used, i.e. equimolar stoichiometric amount as was used for 1.5 phr of DAB (Table 3.8). The results are almost identical, confirming that the level of functional molarity determines cross-linking rather than alkyl length. This suggests that each amine group is creating a cross-link bridge between two polymer chains, and these cross-links are responsible for the physical properties of the cured material.

Table 3.7. The mechanical properties of different amines with varying alkyl lengths tested in polychloroprene rubber at 1.5 phr, with no other additives.

						
100 % Mod (MPa)		0.84	0.85	0.94	0.92	0.71
300 % Mod (MPa)		1.36	1.38	1.55	1.56	1.17
500 % Mod (MPa)		2.99	3.56	4.82	3.69	2.10
UTS (MPa)		6.5	7	8.4	6.7	7.8
Elongation at break (%)		560	559	552	571	685
15 min MDR test at 160 °C	**MH (lb.in)**	13.98	14.03	14.2	13.28	11.91
	TS1 (mm:ss)	01:34	01:32	01:35	01:40	02:04
	T90 (mm:ss)	12:00	11:51	12:03	12:04	12:40
	Cure (lb.in/min)	1.74	1.84	1.74	1.48	1.10

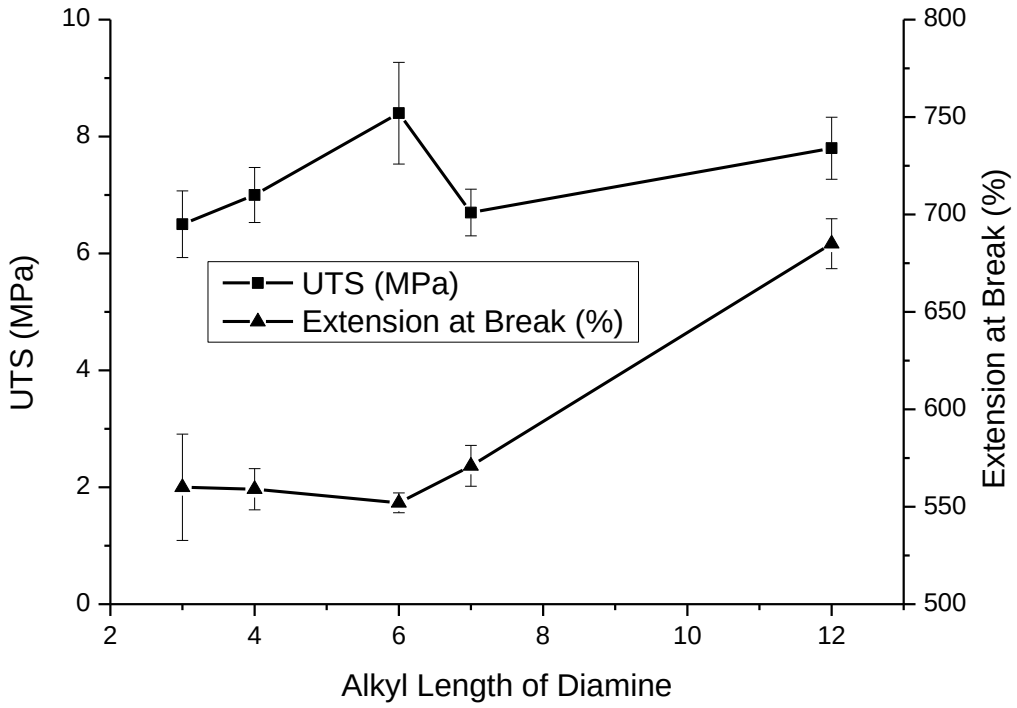


Figure 3.16. Extension at break and UTS of polychloroprene cured with different chain length diamine. Error bars show one standard deviation from three data sets.

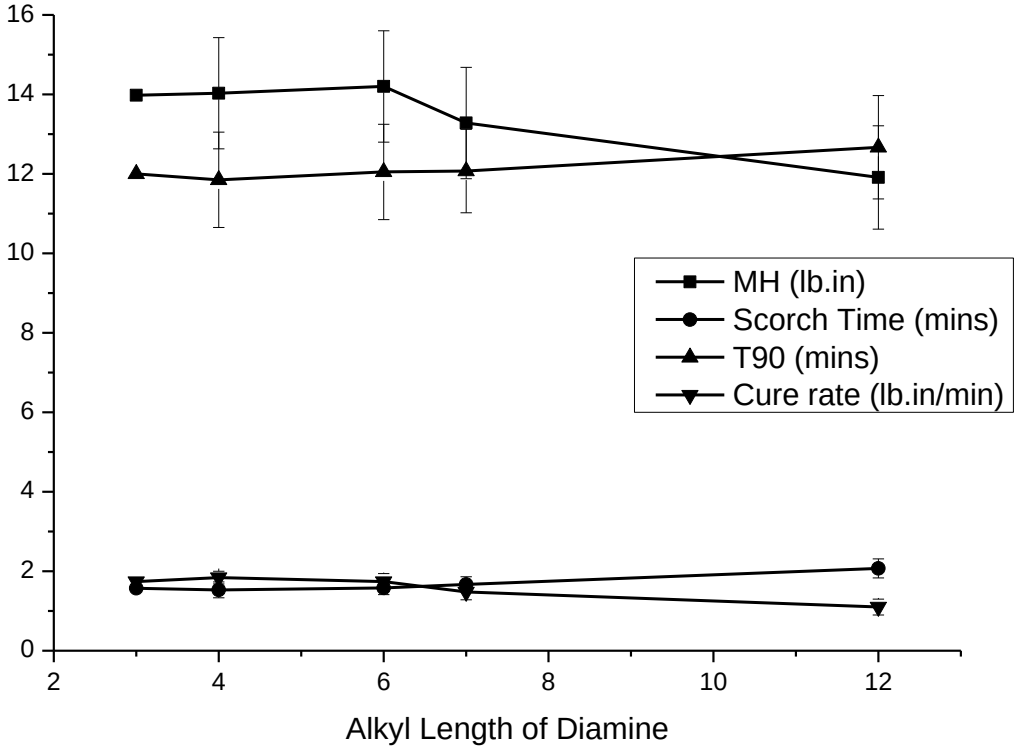


Figure 3.17. Rheological properties of polychloroprene cross-linked with 1.5 phr of linear diamines of various alkyl length. All error bars show one standard deviation from three data sets.

Table 3.8. Rheological results when stoichiometrically identical amounts (0.017 mol) of 1,4- and 1,12- linear diamine are used to cross-link polychloroprene.

		$H_2N-(CH_2)_4-NH_2$	$H_2N-(CH_2)_{12}-NH_2$
15 min MDR test at 160 ºC	**MH (lb.in)**	14.03	14.69
	TS1 (mm:ss)	01:32	01:24
	T90 (mm:ss)	11:51	11:31
	Cure (lb.in/min)	1.84	1.93

Examination of a cyclic diamine, namely piperazine, was then studied in an attempt to elucidate the effect on cross-linking polychloroprene with cyclic diamines. Rheological results in Table 3.9 show that piperazine has a higher cure rate and lower scorch time than ETU i.e. piperazine cures faster with a higher MH and suggests that the resultant cured rubber should be mechanically stronger. This, however, is not the case. Tensile tests show that ETU has a higher UTS and the sample does not break on elongation. These results indicate that polychloroprene rubber cured with piperazine has shorter, weaker, cross-links. To aid in the understanding of its cross-linking mechanism an investigation of polychloroprene cross-linked by piperazine, using FTIR spectrometry was undertaken.

Table 3.9. Comparison of mechanical properties of polychloroprene containing 2 phr of piperazine or ETU.

	Tensile Tests cured 160 °C for 1.5 x T90				**15 minute MDR test at 160 °C**			
	100 % Mod (MPa)	**500 % Mod (MPa)**	**UTS (MPa)**	**Break (%)**	**MH (lb.in)**	**TS1 (mm:ss)**	**T90 (mm:ss)**	**Cure (lb.in/m)**
ETU	0.61	0.99	6.0	DNB*	4.40	02:05	10:05	0.84
Piperazine	0.85	-	2.6	455	13.77	00:44	08:37	4.86

* Sample did not break (see Appendix A).

The FTIR spectra of piperazine or DAB compounded with polychloroprene gum stock has a peak at ~1555 cm^{-1} before curing. This peak is absent in pure polychloroprene gum stock but remains present after curing with piperazine or DAB (Figure 3.18). The height of the peak increases on cross-linking and in both cases this peak is not associated with any of the raw

materials used. Unfortunately this band masks whether or not a new peak at 1550 cm^{-1} has formed as a consequence of cross-linking, as occurs with ETU. The dibutylamine-containing formulation also gives a peak at 1555 cm^{-1} before curing but this disappears after cross-linking has occurred. Butylamine with polychloroprene has no peaks in this region, either before or after cross-linking. Therefore, these results suggest that polychloroprene cross-linked with ETU may produce a different vulcanisate.

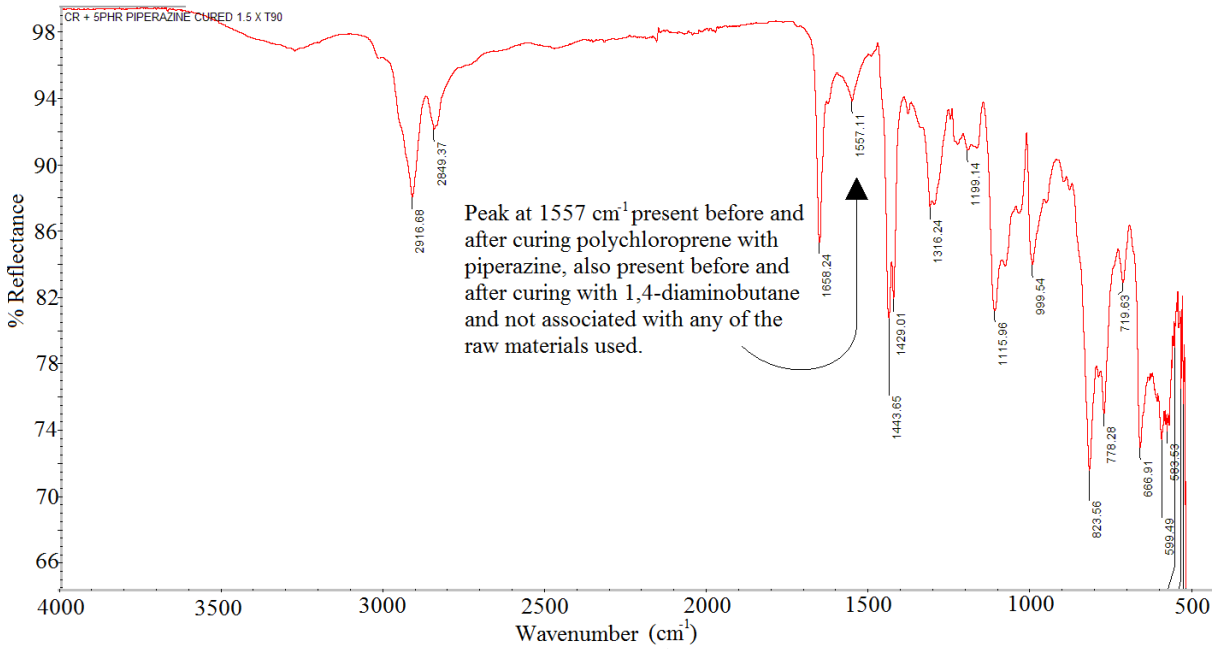


Figure 3.18. FTIR spectrum showing the 1557 cm^{-1} peak in polychloroprene cured with 5 phr piperazine, this peak is also visible before curing. Note a band appears in the same position in polychloroprene with 1,4-diaminobutane, in both the cured and uncured state.

The identification of the ~1555 cm^{-1} peak in the FTIR spectra of polychloroprene cross-linked with amine-containing compounds is challenging. Previously tested model compounds were re-examined, but failed to produce a viable explanation for the new peak. Soxhlet extraction with methanol was performed on polychloroprene cross-linked with piperazine to ascertain if the peak was part of a newly formed cross-link structure or part of a by-product. The FTIR spectra of the piperazine cross-linked polychloroprene after soxhlet extraction showed a very much reduced ~1555 cm^{-1} peak, in terms of both height and area. One of the most compelling arguments that these results advocate is that this represents a salt formed by a reaction with HCl.[7-9] As soxhlet extraction removed most of the materials causing this peak it indicates that it is not part of the actual cross-link. Excess amine will react with the HCl as it is formed during cross-linking. There is no reduction in the 1550 cm^{-1} peak formed in ETU mediated

cross-linking of polychloroprene after soxhlet extraction, therefore this peak is not due to a salt formed.

To aid the understanding of the cross-linking mechanism of polychloroprene with amines, observation of the change in height of the 925 cm^{-1} peak (indicative of the 1,2-isomer) in the FTIR spectra of polychloroprene with a linear primary diamine and a linear primary mono-amine was performed (Figure 3.19). The disappearance of the peak associated with the 1,2-isomer is almost identical between both types of amine, even though the diamine has a faster scorch and higher cure rate than the mono-amine (Table 3.6). It can therefore be deduced that although the rearrangement of this isomer is important for cross-linking, in the case of the amines it does not determine how quickly the rubber will cross-link. However, this is also the case with other additives. In the presence of ZnO the 1,2-isomer has been shown to rearrange very quickly (Figure 3.5), and the cure times are similar to polychloroprene cured with other additives (Table 3.1). All these results therefore suggest rearrangement as the first step in the cross-linking mechanism for these additives in polychloroprene.

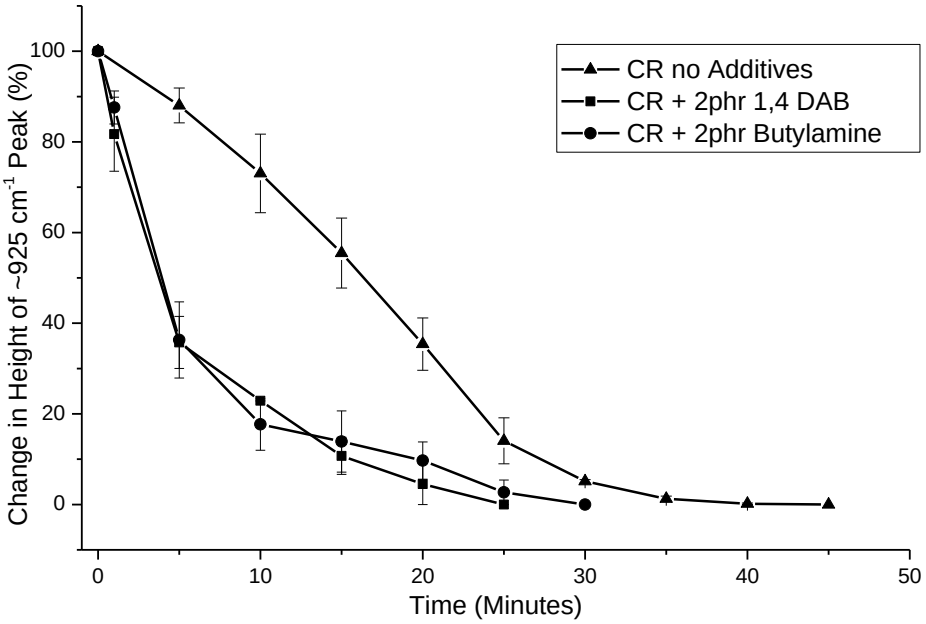


Figure 3.19. Change in height of 925 cm^{-1} peak in polychloroprene rubber cured with 2 phr 1,4-diaminobutane or butylamine compared to CR with no additives. Error bars show one standard deviation and are too small to see above 30 minutes.

Similarities are observed when the change in height of the 925 cm^{-1} peak in the FTIR spectra of polychloroprene with piperazine and ETU are examined (Figure 3.20). This data suggests that the way in which they both rearrange the 1,2-isomer is similar.

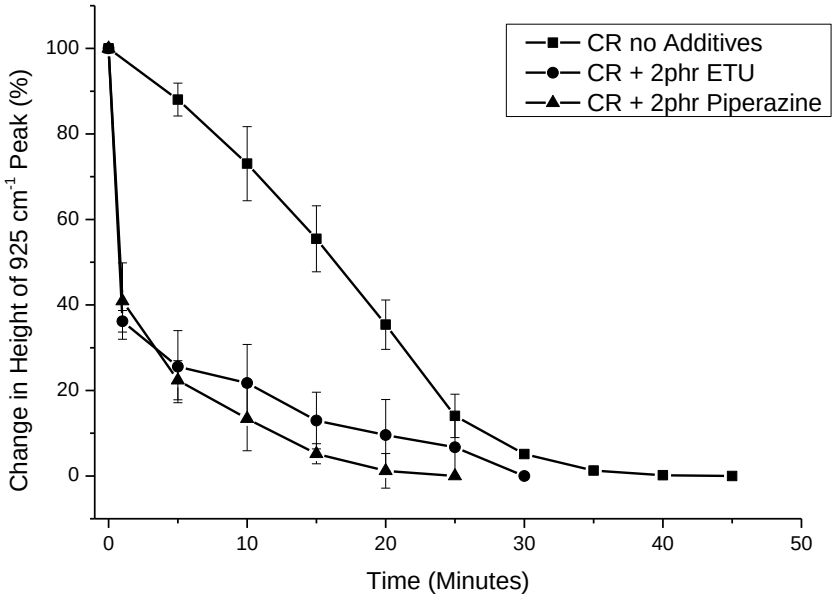


Figure 3.20. Change in peak height of 925 cm^{-1} in polychloroprene rubber cured with 2 phr piperazine or ETU. Error bars show one standard deviation and are too small to see above 30 minutes.

Figure 3.19 shows that both linear primary amines take about five minutes for 60 % of the 1,2-isomer to rearrange, regardless of whether they are mono- or di-amines, despite the molar quantity of amine being doubled in the diamine. On the other hand, both cyclic secondary amine-containing species rearrange 60 % of the 1,2-isomer within one minute (Figure 3.20). This result indicates that cyclic species are able to promote rearrangement of the 1,2-isomer. It is possible that this is due to the cyclic amines being secondary amines, and so should therefore produce more stable intermediates in the allylic rearrangement. More stable intermediates would lower the energy required for the transition and therefore increase the speed of the reaction.

Mechanical and spectroscopic results from cross-linked polychloroprene rubber suggest that all amines cross-link similarly to each other and that this is *via* the bis-alkylation mechanism. The evidence collected also indicates that this is the mechanism by which ETU cross-links. There is no reduction in the 1550 cm^{-1} FTIR peak formed on cross-linking polychloroprene

with ETU after methanol soxhlet extraction, suggesting this peak is part of a cross-link and not a salt. So far, there is no evidence to refute that the cross-linking mechanism proposed by Kovacic,[24] with the bridge through the nitrogen atoms, is untrue for ETU.

Analogous with the amine-containing model compounds, several different model compounds containing sulfur were compared to ETU in polychloroprene in an effort to elucidate the cross-linking mechanism in polychloroprene. These included a linear mono-thiol (hexanethiol) and a linear dithiol (1,6-hexanedithiol). A study of these compounds was envisaged to assist in the identification of the role that sulfur plays in the cross-linking mechanism. All compounds tested had carbon-sulfur single bonds, whereas ETU contains a carbon-sulfur double bond. However, the level of the tautomeric form of ETU that contains a carbon-sulfur single bond, may be as high as 60 %,[25, 26] and thus, they were viewed as suitable model compounds.

Rheological properties of the model compounds indicated that they were unable to cross-link polychloroprene. This was true for the mono-thiol (hexanethiol) and the two different chain lengths dithiols, 1,6-hexanedithiol (HDT) and 1,8-octanedithiol (ODT) (Table 3.10). This result is unsurprising as thiols have been seen in the literature to be unreactive to chlorine-containing species.[27] Unfortunately, due to the level of compounds needed in rubber and the health and safety implications, several other sulfur-containing model compounds were unable to be tested.

Table 3.10. Rheological properties for polychloroprene containing 2.5 phr thiol or dithiol.

		hexanethiol	**1,6-hexanedithiol**	**1,8-octanedithiol**
15 Minute MDR test at 160 °C	**MH (lb.in)**	1.33	1.86	1.81
	TS1 (mm:ss)	00:00*	00:00*	00:00*
	T90 (mm:ss)	13:30	11:38	12:07
	Cure (lb.in/min)	0.10	0.22	0.22

* Increase in torque was too small to measure a TS1 time.

As expected because the polychloroprene did not cure, no change was observed in the FTIR spectra (after allowing to ‘cure’ under similar conditions to other tested samples). Therefore, the change in height of the 925 cm^{-1} peak was not examined in detail with the sulfur-

containing compounds. In summary, sulfur-containing compounds alone (i.e. terminal thiols) do not cross-link polychloroprene. From this, one could lead to the conclusion that it is not possible for ETU to react with the polychloroprene chain *via* its sulfur (e.g. in the creation of a sulfur bridge). However, due to the limited number of compounds tested, further work would be needed for confirmation, particularly with compounds which contain the sulfur-carbon double bond. Additionally, it should be noted that the sulfur is in a different chemical environment in ETU than in primary thiols.

3.2.3. Oligomers with Ethylene Thiourea and Model Compounds

The results reported in the previous sections have been obtained through curing polychloroprene rubber gum stock with various additives. This section discusses the results acquired when additives were tested in oligochloroprene with molecular weight in the region of 3000 g/mol. The use of low molecular weight oligochloroprene enables a wider range of test methods to be utilised. Additionally, the reactions are able to be analysed whilst cross-linking is occurring, this allows reaction products to be monitored. Furthermore, oligomers have greater solubility due to lower molecular weight, which enables tests such as gel permeation chromatography (GPC) and nuclear magnetic resonance (NMR) to be completed. As the sulfur-containing compounds do not cross-link polychloroprene rubber, cross-linking reactions were initially performed on oligochloroprene using ETU and piperazine. Piperazine is seen as a close analogue of ETU, thus a comparison between the two may help shed light into their cross-linking mechanisms.

One of the by-products from the cross-linking mechanism proposed by Kovacic[24] (Section 1.4.5.2.1) is HCl. It is difficult to monitor the formation of by-products when cross-linking in polychloroprene rubber, but simpler to do so with low molecular weight oligomer. These differences arise for several reasons. Firstly the polychloroprene rubber is solid due to a high molecular weight (~500,000 g/mol) and therefore reactions occurring in the polymer matrix are difficult to monitor, whereas oligomers with lower molecular weight are easier to study. Additionally, the polychloroprene rubber is cured in a heated press to ensure uniform curing throughout the sample, again making examination during cross-linking difficult. Oligomers can, however, be cured in a test tube and can be more easily observed. One of the simplest methods of studying the evolution of HCl formation during the curing reaction of oligomers is by examining the pH of the fumes released during the cross-linking process. To achieve this the pH of the headspace above the reaction mixture in the test tube containing

ETU and oligochloroprene was monitored whilst being heated up. It was found that the headspace became acidic almost immediately. The most likely explanation is that HCl is being released during the cross-linking process. When the experiment was repeated with piperazine in place of ETU, the headspace above the reaction was found to be alkaline. The alkaline headspace indicates that either, no HCl is produced as a by-product from the reaction or, a more likely explanation may be that any HCl generated undergoes another reaction to produce a salt with the amine. Also excess amine is likely to be present in this reaction to keep the headspace environment alkaline.

As mentioned previously the results using rubber gum stock studies suggest that the peak formed in the FTIR of polychloroprene cured with piperazine was due to a salt with HCl being formed. To test this hypothesis, the oligochloroprene sample cured with piperazine was washed with water and then re-examined by FTIR spectroscopy. Figure 3.21 shows that after water washing the new peak at ~1560 cm^{-1} disappears proving that this band is not part of the cross-link architecture but from a by-product of the cross-linking reaction.

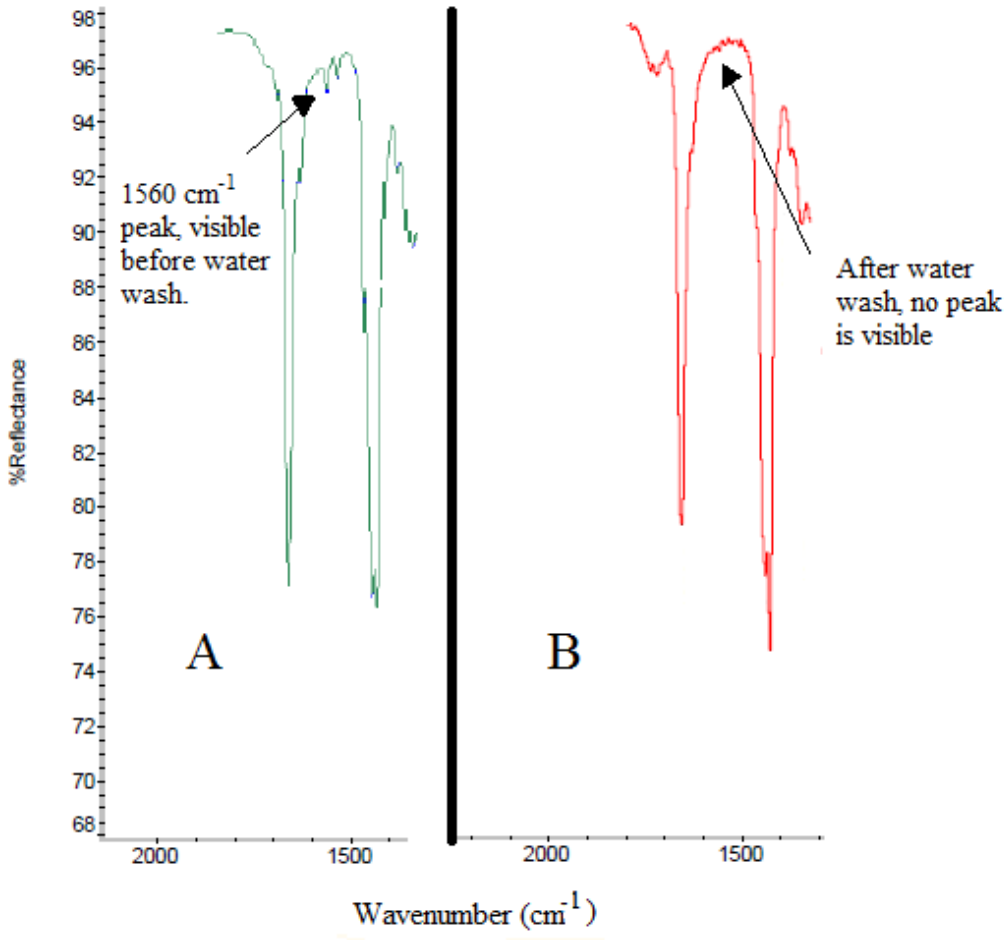


Figure 3.21. Oligochloroprene cured with 2 phr piperazine A) before washing and B) after water washing, showing the removal of the 1560 cm^{-1} peak.

Analysis of the FTIR spectrum of water washes used to wash the oligomer did not show the peak at ~1560 cm^{-1} which would have given more evidence for the formation of a salt. However, this peak may be masked by the broad double peak at 1656 and 1630 cm^{-1} (Figure 3.22). As oligochloroprene is slightly soluble in water, new peaks in the FTIR spectrum of the water washes may be attributed to C=C stretching in the oligomer. The peaks at 1442 cm^{-1} and 1430 cm^{-1} associated with CH_2 deformation in the oligomer are also clearly visible in this spectrum, demonstrating the presence of oligochloroprene in the water. In a different experiment where a small quantity of HCl was reacted with piperazine, examination of the FTIR spectrum revealed a new peak in the 1500-1600 cm^{-1} region. This evidence, couple with the lack of acidity detected in the headspace when curing, suggests that piperazine forms a salt with the HCl evolved during the curing process.

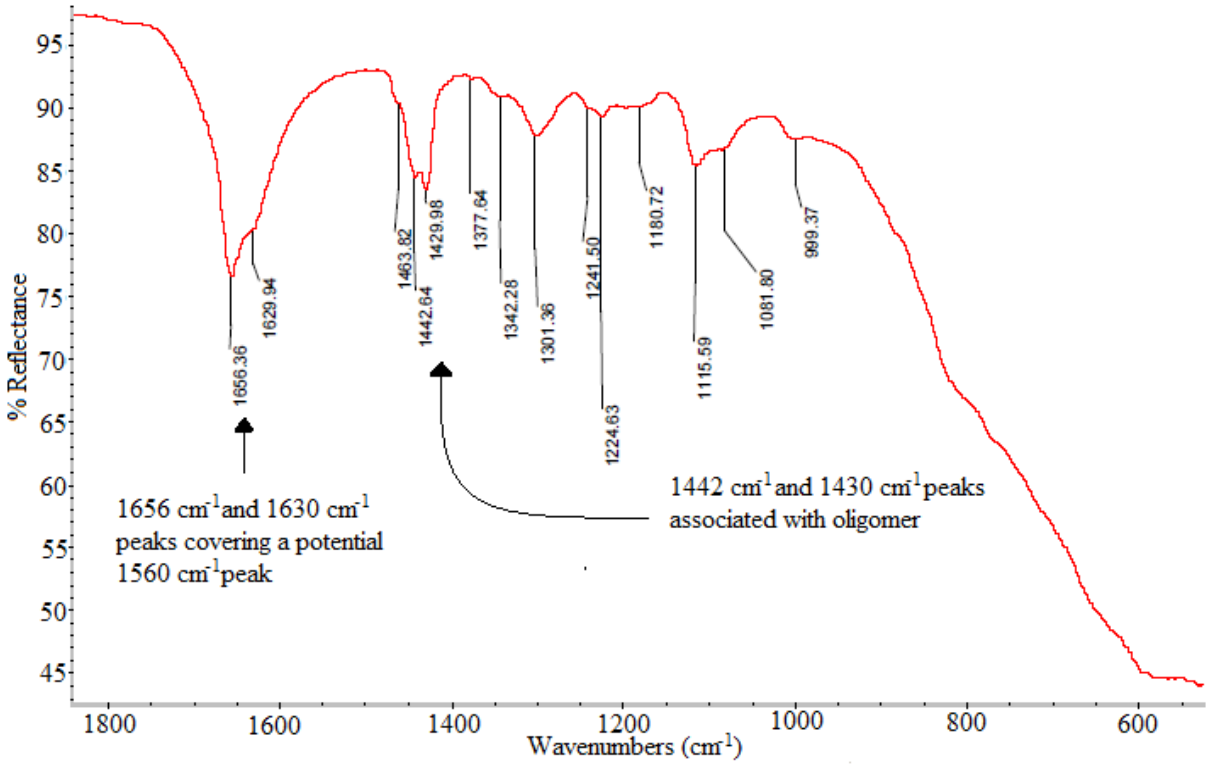


Figure 3.22. FTIR spectrum of material dissolved into water used to wash oligomer cured with 2 phr piperazine after removal of water. Spectrum shows the presence of peaks associated with oligochloroprene.

When a similar water washing experiment was performed on oligochloroprene cured with ETU, it was found that the peak at ~1550 cm^{-1} remained visible after washing. This correlates with findings in polychloroprene rubber where the peak also remained, even after soxhlet

purification. This evidence, coupled with the acidic environment of the headspace when the oligomer was heated leads to the conclusion that ETU does not form a salt with HCl.

Unfortunately GPC and NMR experiments run on oligochloroprene cured with ETU and piperazine provided no additional information (see Appendix B). However, the use of oligomers has enabled examination of reaction products of the cross-linking process to be analysed, thereby allowing HCl evolved from the cross-linking reaction of ETU to be observed. This would not have been possible to detect with rubber gum stock.

3.2.4. Comparison of Results with Existing Cross-linking Theories

One main mechanism often quoted in the literature for cross-linking polychloroprene with ETU alone is that of bis-alkylation proposed by Kovacic.[24] From the evidence gathered so far there is much agreement with this mechanism including; (i) the acidic environment created when ETU was used to cross-link oligochloroprene, signifying the production of HCl; (ii) a new peak in the FTIR spectrum is formed which does not disappear on soxhlet extraction, indicating that a new type of bonding is created during the curing process, and; (iii) evidence that the cross-link bridge must be through the nitrogen atoms as the sulfur-containing compounds used were unable to react with the polymer chain on their own. Although this last point is not conclusive as the chemical environment of the sulfur in the sulfur-containing model compounds was different to that of sulfur in ETU. However, the thiuram-based accelerator was unable to cross-link polychloroprene and dibutyl thiourea could only cross-link polychloroprene inefficiently and both contain sulfur in a more similar chemical environment to that found in ETU.

Kovacic used piperazine as a model compound to study ETU, and consequently arrived at the bis-alkylation mechanism. Evidence gathered in this study suggests that piperazine cross-links polychloroprene in a manner similar to that of ETU. However, piperazine is also able to form a salt with HCl, which ETU is unable to do. The result to support this is the new 1560 cm^{-1} band in the FTIR spectrum that appears on cross-linking in a similar region to the one found in the FTIR spectrum when piperazine is mixed with HCl which is removed from the oligomer and rubber samples after washing.

3.3. Cross-linking Polychloroprene with Ethylene Thiourea and Zinc Oxide

Having examined how ETU and ZnO cross-link polychloroprene separately, this section scrutinises the cross-linking reaction that occurs when both are used in combination in polychloroprene. Again the novel approach using mechanical and spectroscopic techniques was utilised. Firstly, polychloroprene cured with ETU in combination with ZnO is examined. These results were compared with the results obtained by curing polychloroprene with widely used rubber accelerators in the presence of ZnO. Model compounds are trialled in combination with ZnO in both polychloroprene rubber gum stock and oligomers. All results were compared with existing mechanisms in the literature and a judgement made upon their veracity. From this conclusions were drawn about the mechanisms taking place during cross-linking. Using this knowledge several new accelerators were designed to take forward as potential curing agents that could replace ETU in polychloroprene for further trials, and discussed in Chapter 4. The standard formulation used for this work utilised additives at levels quoted, with 0.6 phr stearic acid as a processing aid and 5 phr ZnO.

3.3.1. Polychloroprene Rubber with Zinc Oxide Cross-Linked with Ethylene Thiourea or Traditional Rubber Accelerators

When ETU is used as a cross-linking agent for polychloroprene it is primarily done so in conjunction with ZnO. It has already been established that ETU alone cross-links polychloroprene in a different manner to that of other rubber accelerators (see Section 3.2.1) and that an alternative mechanism takes place when ETU and ZnO are used in combination. ZnO is widely used as an additive in other rubbers and acts as an activator; the mechanisms by which this occurs are known.[28, 29] To ascertain if ZnO acts as an activator in polychloroprene, several traditional rubber accelerators were used to cure polychloroprene in combination with ZnO (see Table 3.11 for results and see Table 3.2 for accelerator structures). This would establish their ability to cross-link polychloroprene after activation of the polymer chain by ZnO, and give an insight into the mechanism by which ETU and ZnO cross-link polychloroprene.

Table 3.11. Rheological properties of polychloroprene with 5 phr ZnO cured with standard accelerators at 3 phr.

Accelerator	Accelerator type	15 minute MDR test at 160 ºC			
		MH (lb.in)	TS1 (mm:ss)	T90 (mm:ss)	Cure (lb.in/min)
ZnO	-	5.17	02:40	08:39	1.5
ETU	Thiourea	14.66	00:56	05:41	5.41
MBT	Thiazole	3.2	02:26	10:23	0.74
TMTD	Thiuram	7.6	00:55	06:01	6.6
MMBI	Imidazole	5.59	00:48	06:15	4.4
AS100	Xanthogen	11.24	01:18	09:32	3.64
ZDBC	Dithiocarbamate	5.01	00:53	05:39	4.12
CBS	Sulfenamide	3.27	06:22	12:35	0.34
DPG	Guanidine	3.88	06:01	13:26	0.34

Rheological results in Table 3.11 and in particular the low cure rate and MH show that the sulfenamide, guanidine and thiazole do not cross-link polychloroprene in the presence of ZnO. The results of these accelerators are less favourable than when ZnO is used alone (Figure 3.23). Both MMBI and ZDBC are able to cross-link polychloroprene with or without ZnO. However, both the xanthogen and thiuram, which were not able to cross-link polychloroprene alone, were able to do so with ZnO, and with better results (higher MH, cure) than with ZnO alone. The accelerators that are capable of cross-linking polychloroprene (thiuram, xanthogen and imidazole) gave vulcanisates with tensile properties (Table 3.12) comparable to that of the ETU and ZnO formulation (Figure 3.24). By considering the chemical structures of both thiurams and xanthogens (Figure 3.25), it can be seen that ZnO cleavage of the disulfide bond generates similar active species. This has been predicted to occur theoretically with thiurams,[19] and is also plausible for xanthogen compounds. Activation by ZnO in this manner generates the dithio-functional group. ZnO may then ‘activate’ the polychloroprene polymer chain and allow this dithio group to cross-link. The possibility of ZnO activating the polymer chain and a sulfur group reacting at these active centres to create a sulfur cross-link is examined later in Section 3.3.2.

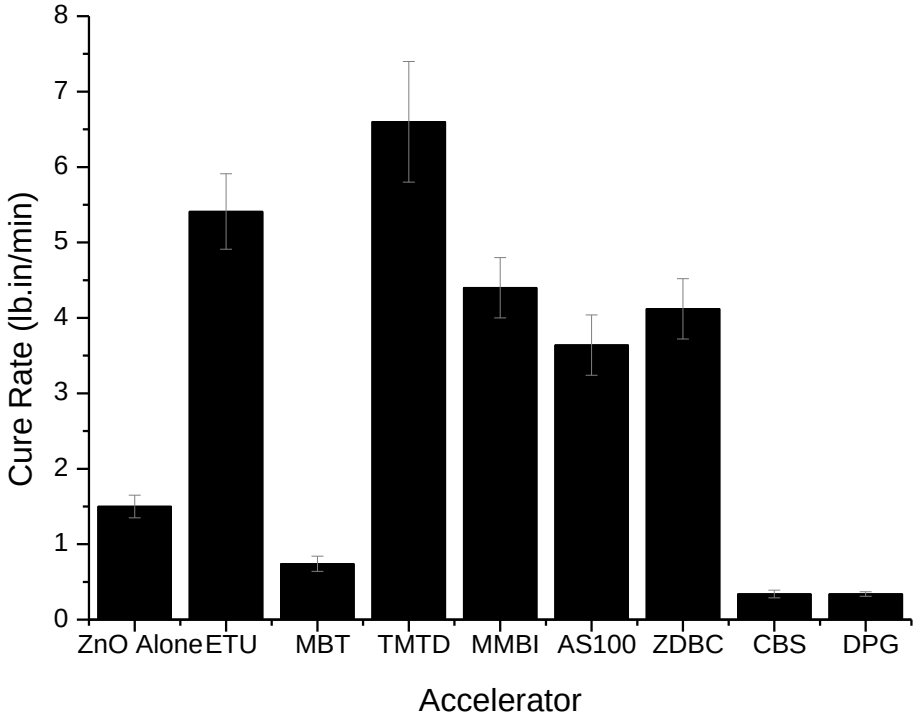


Figure 3.23. Cure rates of polychloroprene with 5 phr zinc oxide and 3 phr of various accelerators. Error bars show one standard deviation from three data sets.

Table 3.12. Tensile results of polychloroprene cross-linked with standard accelerators at 3 phr and ZnO at 5 phr.

Accelerator	Accelerator type	Tensile Tests 1.5 x T90				
		100 % Mod (MPa)	300 % Mod (MPa)	500 % Mod (MPa)	UTS (MPa)	Elongation at break (%)
ZnO	-	0.48	0.6	0.82	4.5	DNB*
ETU	Thiourea	1.12	2.02	5.71	11.1	582
TMTD	Thiuram	0.58	0.7	0.81	10.5	DNB*
MMBI	Imidazole	1.09	1.86	2.98	12.1	928
AS100	Xanthogen	0.73	1.29	2.47	14.2	823
ZDBC	Dithiocarbamate	0.46	0.64	1.06	7	DNB*

*Sample did not break (see Appendix A).

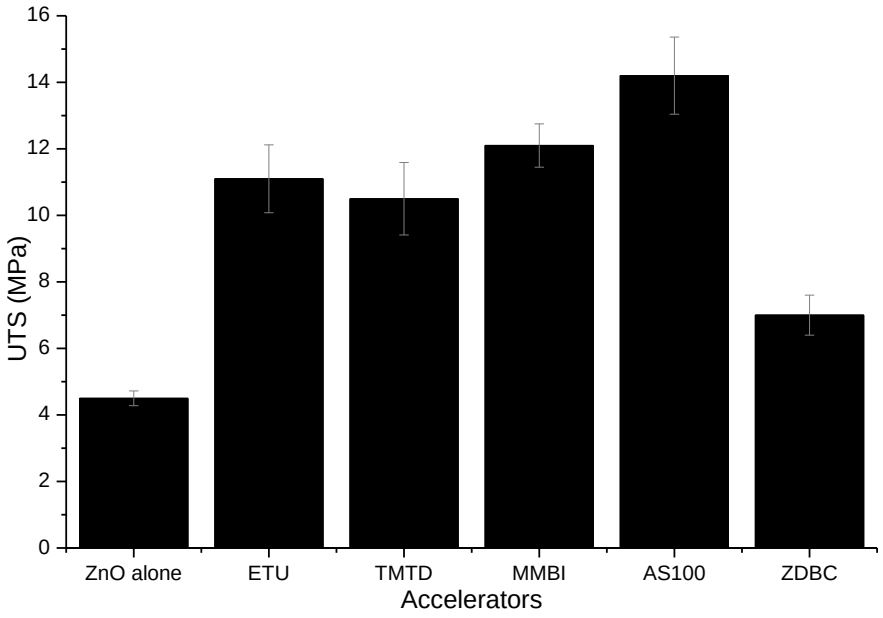
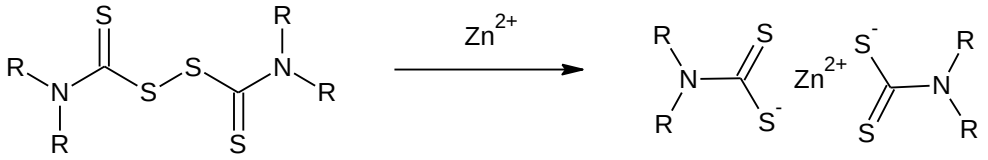


Figure 3.24. Ultimate tensile strength of polychloroprene with 5 phr zinc oxide and 3 phr of various traditional accelerators. Error bars show one standard deviation from three data sets.

(A) Thiuram cleavage by zinc ion



(B) Xanthogen cleavage by zinc ion

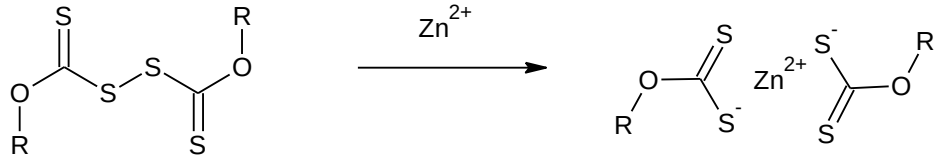


Figure 3.25. Cleavage of thiuram and xanthogen by a zinc ion.

The above results suggest that the sulfur atom of ETU is involved in cross-linking polychloroprene when ETU is used in combination with ZnO. This has been demonstrated by the fact that thiuram- and xanthogen-based accelerators are unable to cross-link polychloroprene alone, but are able to do so in conjunction with ZnO. It is known that ZnO activates thiurams to form a complex and this complex further reacts to liberate a sulfur atom which becomes the cross-link in natural rubber.[19, 30] The knowledge that the thiuram and

xanthogen cross-link natural rubber by creating sulfur bridges indicates that in the presence of ZnO, ETU can potentially act in the same manner.

In an attempt to understand the mechanical properties of the cross-linked polychloroprene, the changes in the FTIR spectra occurring when ETU and ZnO are used in combination to cross-link polychloroprene have been examined. These changes were then compared with variations that transpire in the FTIR spectra when traditional accelerators are used in conjunction with ZnO to cross-link polychloroprene. The spectra obtained when amine- and sulfur-containing model compounds are used in conjunction with ZnO to cross-link polychloroprene are examined later (Section 3.3.2).

When ETU and ZnO are used to cross-link polychloroprene separately, changes were noted in the 1500 to 1600 cm^{-1} region of the FTIR spectra between the cured and uncured polychloroprene samples. The system comprising ETU produced a peak around 1550 cm^{-1}, whereas the ZnO-containing formulation produced a peak around 1580 cm^{-1}. Unsurprisingly, when both are used together to cross-link polychloroprene both of these new peaks are formed, and are both still visible after the rubber has been through soxhlet extraction with methanol (Figure 3.26). The 1498 cm^{-1} peak seen in Figure 3.26 is associated with ETU, and its disappearance is due to the reaction of ETU during cross-linking and removal of any excess ETU by soxhlet extraction. The appearance of the peaks at 1550 cm^{-1} and 1580 cm^{-1} on cross-linking indicates that the mechanisms by which each of these two additives (ETU and ZnO) cross-link polychloroprene are also taking place when both are used together. Table 3.1 shows that mechanical properties of the vulcanisate are significantly improved when ETU and ZnO are used in combination compared to if the two curatives were working separately. This can be seen through MH, cure rates and 500 % modulus values which are greater than a purely cumulative result; i.e. a synergistic effect during the cross-linking reaction of polychloroprene with ZnO and ETU is in place. As a consequence, at least a third mechanism must be taking place.

When TMTD is used in combination with ZnO to cross-link polychloroprene a new broad peak is observed in the FTIR spectrum at ~ 1530 cm^{-1}. After the cured rubber has gone through soxhlet extraction in methanol, this peak becomes much sharper and narrower and centres on 1540 cm^{-1} (Figure 3.27). TMTD is known to act as a sulfur donor to produce sulfur cross-links in NR,[19] however this peak at 1540 cm^{-1} is in the incorrect region for C-S bonds. It is, nevertheless, in the correct region for carbon-sulfur double bonds which is present within

TMTD[8, 9] and therefore the C=S from TMTD may have been incorporated into the cross-link structure. Equally however is the possibility that the C=S from TMTD is part of a by-product from the reaction that does not dissolve in methanol.

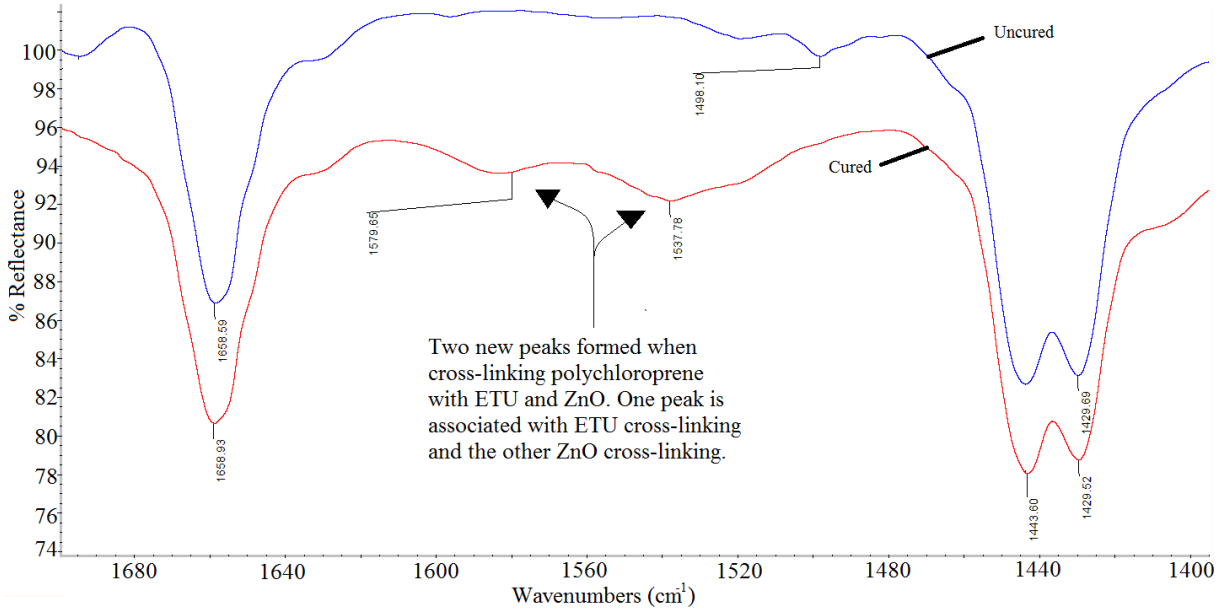


Figure 3.26. FTIR spectra showing new peaks at ~ 1540 and 1580 cm^{-1} when ETU and ZnO are used to cross-link polychloroprene. Spectra are shown from 1400-1700 cm^{-1} and are translated along the reflectance axis for clarity.

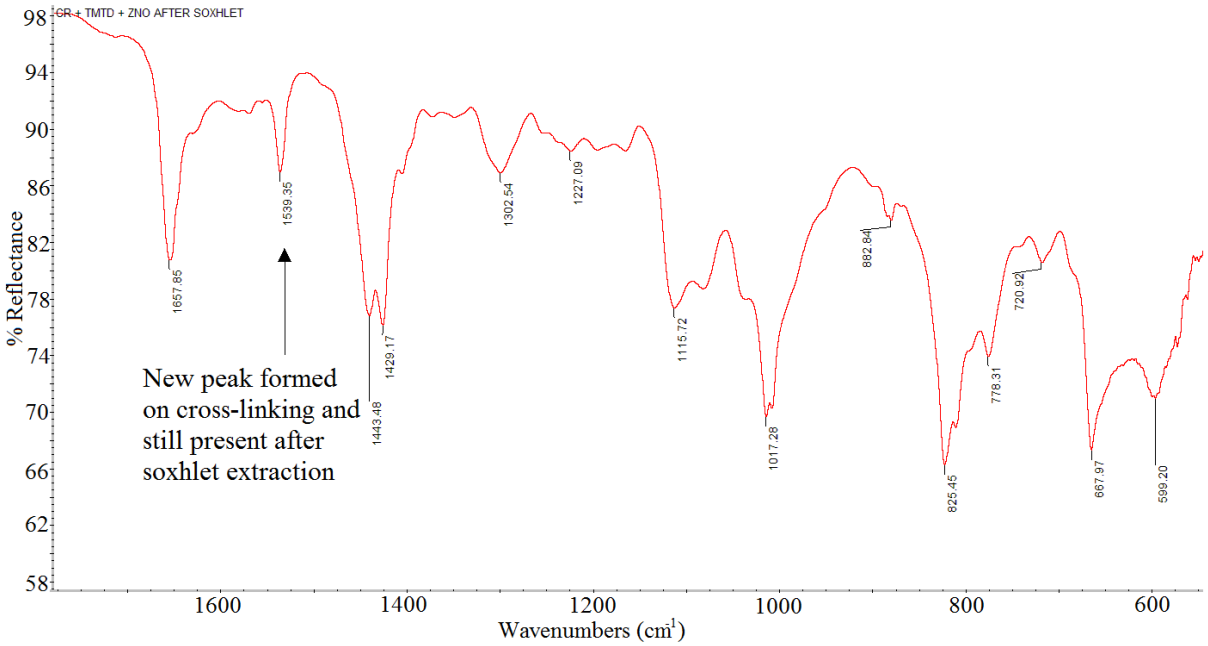


Figure 3.27. FTIR spectrum of polychloroprene cured with 3 phr TMTD and 5 phr ZnO after methanol soxhlet extraction showing a new peak at ~ 1540 cm^{-1}.

The FTIR spectra of ZDBC with ZnO cross-linking polychloroprene before and after curing show the removal of a 1496 cm^{-1} peak (Figure 3.28), this also occurred when ZDBC was used alone to cross-link polychloroprene. This peak is associated with the N-C=S structure in ZDBC; and its disappearance is indicative therefore that ZDBC reacts during the cross-linking process. In the ZDBC/ZnO system, the appearance of a new peak in the FTIR spectrum at 1580 cm^{-1} can be attributed to ZnO cross-linking. There is also a new peak at ~ 1540 cm^{-1} which is a similar peak to that obtained in the TMTD/ZnO system, suggesting that both systems cross-link polychloroprene in a similar manner. This is expected, as TMTD, once activated by ZnO has a similar structure to ZDBC. Consequently, the 1540 cm^{-1} peak in the FTIR spectrum of the ZDBC/ZnO system can be attributed to the C=S which also occurs in the TMTD/ZnO cross-linked system, due to their similar cross-linking mechanisms.

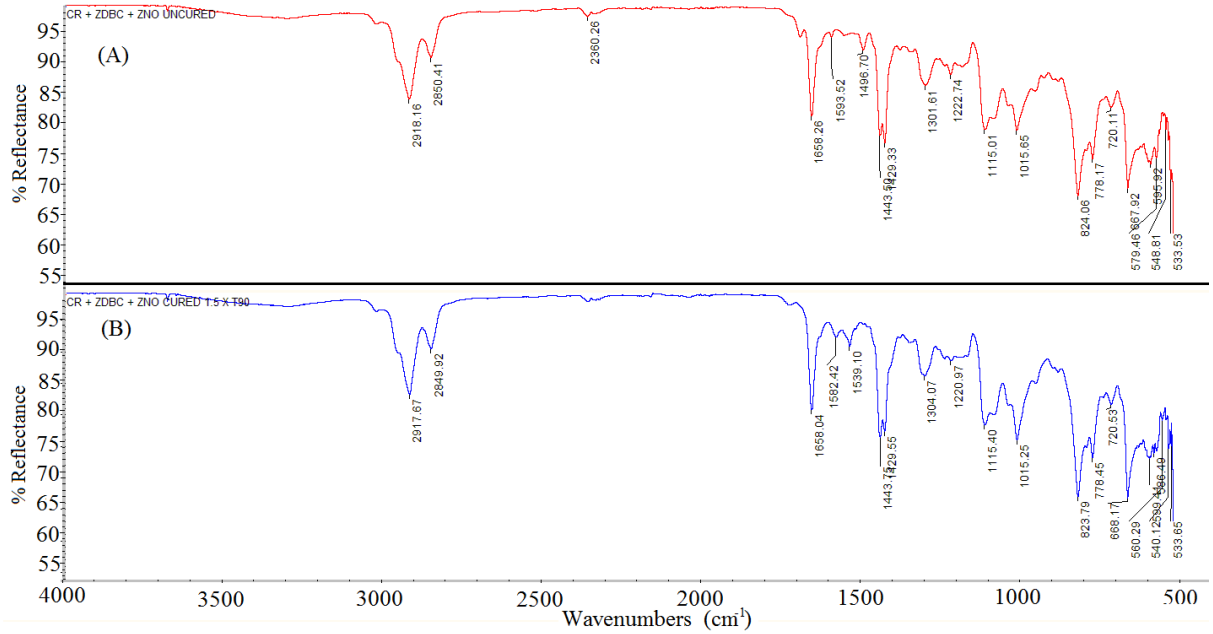


Figure 3.28. FTIR spectra of polychloroprene containing 2 phr ZDBC and 5 phr ZnO; (A) before curing and (B) after curing.

As seen with TMTD, the xanthogen polysulfide AS100 does not cross-link polychloroprene on its own, but does so in the presence of ZnO. This is because the disulfide and polysulfide bonds respectively of both accelerators are cleaved by Zn^{2+} from ZnO, which 'activates' the accelerators, allowing them to cross-link. Therefore, polychloroprene cured with AS100 and ZnO should produce similar peaks in the FTIR spectrum after curing to those produced when TMTD (with ZnO) are used to cure polychloroprene. This is indeed the case with new peaks formed at 1580 cm^{-1} and 1540 cm^{-1}. Therefore, these peaks can be given a similar assignment

to those in the ZDBC/ZnO and TMTD/ZnO systems. i.e. the 1580 cm^{-1} peak assigned to ZnO related cross-linking and the 1540 cm^{-1} assigned to a potential C=S bond.

Cross-linking polychloroprene with MMBI and ZnO only reveals a new peak at ~1580 cm^{-1}. This is the same peak that appears when ZnO alone is used to cross-link polychloroprene and therefore can be discounted as helping inform the cross-linking mechanism of MMBI and ZnO in polychloroprene. Additionally, as the tensile properties are much better with the MMBI and ZnO system used to cure polychloroprene than the ZnO or MMBI alone sample (higher UTS and 500 % modulus) as shown in Table 3.12 and Figure 3.24, indicating that a different mechanism is in effect to that happening when MMBI or ZnO are used alone. Unfortunately, it was beyond the scope of this project to investigate this further and in the wider context, did not aid in the elucidation of the ETU/ZnO cross-linking mechanism for polychloroprene.

The change in height of the 925 cm^{-1} peak over time has been plotted for the cross-linking reaction of polychloroprene with ETU and ZnO (Figure 3.29). It can be seen that the ETU/ZnO system promotes the rearrangement of the 1,2-isomer much quicker than ETU alone. This faster rearrangement should allow for faster cross-linking to occur. A comparison between the ETU/ZnO system and the ZnO only system shows that rearrangement of 90 % of the 1,2-isomer proceeds at a similar pace, however the final 10 % of the isomer takes approximately 8 minutes longer when ETU is present. This result is unexpected, as it was assumed that the 925 cm^{-1} peak would decrease at the speed of the fastest additive, i.e. rearrangement would occur at the same speed that occurs in the ZnO only system. Alternatively, rearrangement would occur faster as there would be more raw materials present to rearrange the 1,2-isomer (2 phr ETU and 5 phr ZnO, as opposed to only 5 phr ZnO). The results therefore, suggest that some ZnO and ETU must be taking part in another reaction inhibiting it from rearranging the 1,2-isomer, or that ETU is slowing the reaction down. If ZnO is taking part in another reaction which prevents it from promoting the rearrangement of the 1,2-isomer it may be that this reaction is one component of the overall cross-linking mechanism. This above result provides evidence that ZnO is playing a different role than when in polychloroprene alone, compared to when it is used in combination with ETU.

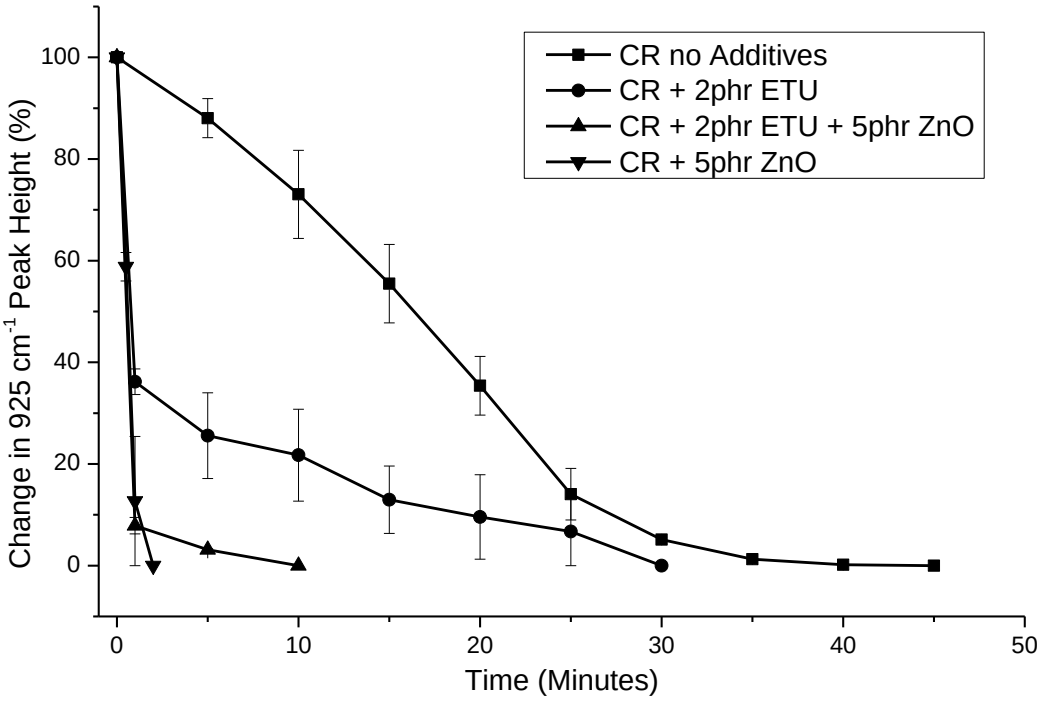


Figure 3.29. Change in height of the 925 cm^{-1} peak in polychloroprene as it cures at 160 °C with ETU and ZnO as additives, compared to ETU or ZnO as the only additive and to pure polychloroprene. Error bars are one standard deviation and are not visible after 30 minutes.

One of the by-products from the cross-linking reaction mechanism of polychloroprene with ETU and ZnO suggested by Pariser[31] is ethylene urea (EU). To ascertain the formation of EU, in the reaction, an ETU and ZnO cured polychloroprene sample was extracted in methanol using a soxhlet and the extracts examined by both gas-chromatography-mass-spectrometry (GC-MS) and thin layer chromatography (TLC). GC-MS revealed a mass ion of 86 g/mol at a retention time of 50.429 minutes corresponding to EU, while TLC carried out using ethyl acetate as the eluent compared to a sample of EU as a reference gave a similar retention factor of 0.05. FTIR analysis of the extract following removal of methanol *in vacuo* confirmed the presence of EU, although the extracts also contained ETU (Figure 3.30A). Confirmation was *via* the characteristic C=O stretch at 1670 cm^{-1} associated with EU. The same peak at 1670 cm^{-1} in the FTIR spectrum is seen when a 1:1 mixture of EU and ETU powder are mixed together and analysed (Figure 3.30B).

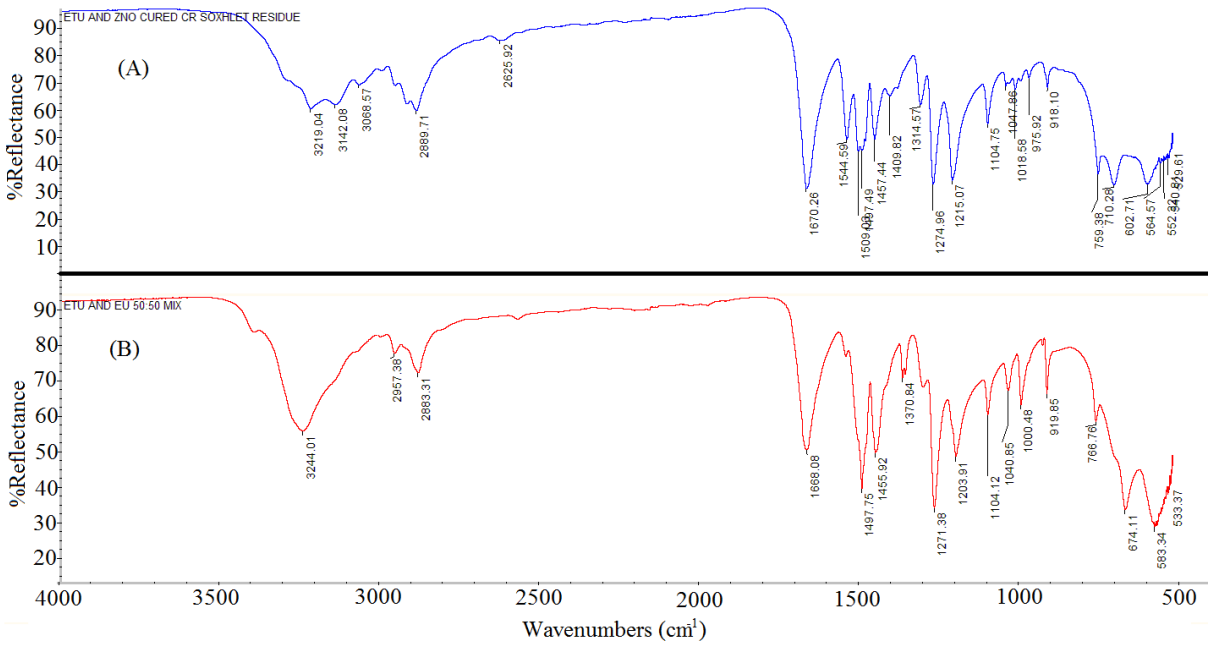


Figure 3.30. FTIR spectra showing (A) methanol soxhlet residue from polychloroprene cured with 2 phr ETU and 5 phr ZnO; and (B) a 50:50 mixture of ETU and EU.

A further experiment was performed to prove the formation of EU as by-product of the cross-linking reaction between ETU, ZnO and the polymer chain. The individual chemicals - ETU, ZnO and HCl (to replicate that formed in the rubber) were heated to 160 °C in the absence of any polymer, to assess the chemistry without cross-linking occurring. The reaction product formed was then mixed with methanol (to dissolve the ETU and any EU formed) and filtered to remove any undissolved material (such as any unreacted ZnO). GC-MS and TLC analysis both indicated the formation of EU. However, FTIR analysis performed on the residue (following methanol evaporation) did not appear to show the presence of the characteristic peak at 1670 cm^{-1} for EU (Figure 3.31) although it is possible that the reactions have caused a shift in the 1670 cm^{-1} peak to 1655 cm^{-1}. A similar experiment was run with ETU and ZnO only, i.e. without HCl, but no reaction took place. Unfortunately due to the conflicting results, it is not possible to state with absolute certainty whether EU forms within the rubber as a consequence of the cross-linking mechanism or by the reaction of the individual chemical separately. Therefore the discovery of EU after cross-linking polychloroprene with ETU and ZnO is not conclusive proof of Pariser's mechanism. Nevertheless, the fact that EU may form through a reaction of ETU with ZnO in the presence of HCl does not automatically rule out Pariser's mechanism either. Additionally, the differences seen in the FTIR spectra between the reaction mixture of chemicals examined trying to form EU and the residue from the

soxhlet extracted polychloroprene rubber (which did show EU formation) indicates they contain different reaction products. The soxhlet extraction residue appears to only contain ETU and EU and these results suggest that the EU found after soxhlet extraction may be due to the cross-linking reaction. Therefore, the mechanism Pariser postulated still stands.

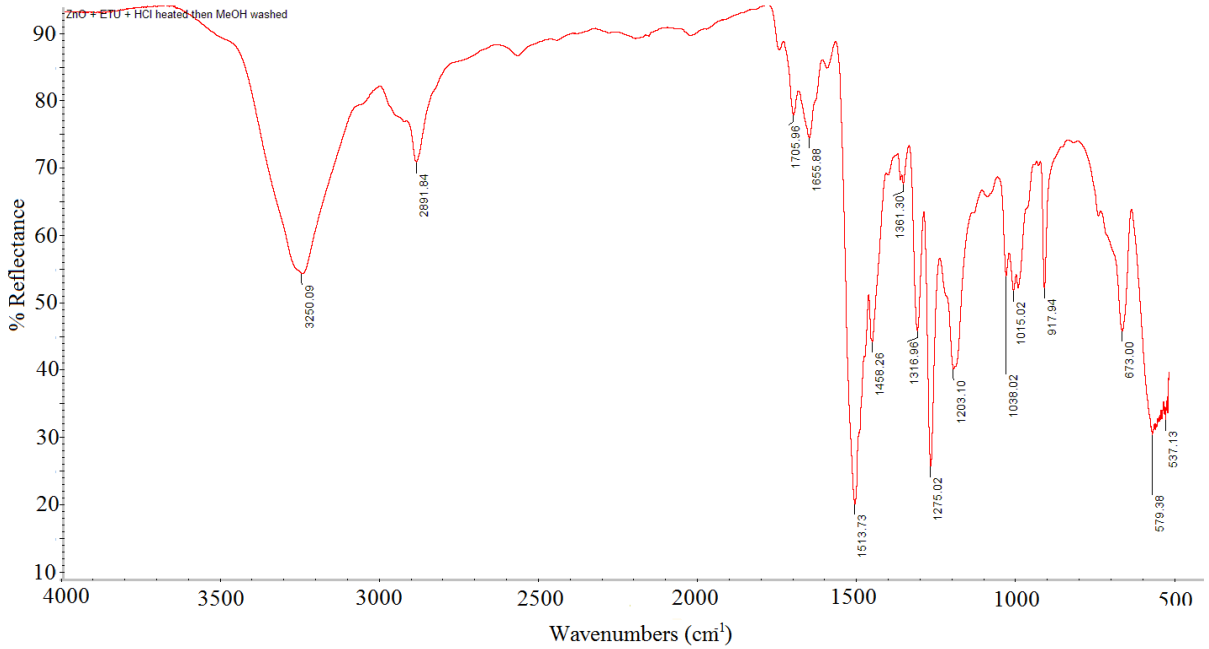


Figure 3.31. FTIR of mixture of ETU, ZnO and HCl heated to 160 °C then washed with methanol.

From the different mechanisms that have been proposed in the literature, it is possible that several different types of bridge may be formed between polychloroprene polymer chains, namely C-C, C-S-C, C-O-C and C-N-C. To ascertain if the bridge formed on cross-linking is a C-S-C bond, Raman spectroscopy was performed on polychloroprene cross-linked with ETU and ZnO. It was hoped that this would aid the knowledge about what the cross-link bridge actually is in polychloroprene, (i.e. it is known that the cross-link bridge in natural rubber is a sulfur bridge). This method of examination would allow the peaks associated with these bonds to be more easily seen than through FTIR. Unfortunately the only differences between the spectra of the cured and uncured samples were disappearance of peaks at 922 cm^{-1} and 506 cm^{-1} which are both associated with ETU (Figure 3.32). This does not disprove any mechanism, as the level of cross-links formed would be small, however, it also does not aid in the elucidation of the mechanism.

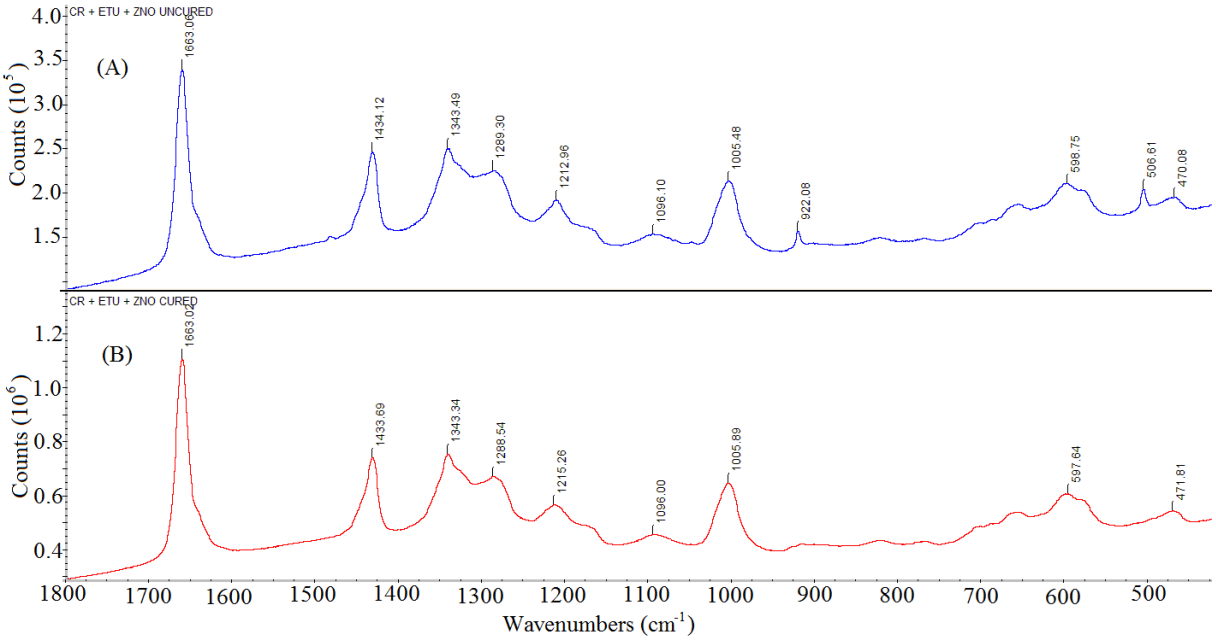


Figure 3.32. Raman spectra of polychloroprene containing 2 phr ETU and 5 phr ZnO, (A) before and (B) after curing.

3.3.2. Polychloroprene and Zinc Oxide Cross-Linked with Ethylene Thiourea or Model Compounds

Having examined ZnO and ETU individually and jointly in polychloroprene, and tested traditional rubber accelerators on their own and with ZnO, model compounds were subsequently assessed with ZnO in polychloroprene. This was done both spectroscopically and through mechanical property determination. In looking at how the various model compounds cross-link polychloroprene in conjunction with ZnO, it was envisioned that the mechanism that occurs using the ETU/ZnO system could be better understood. More specifically, a better understanding of the role both nitrogen and sulfur atoms play in cross-linking was anticipated. Therefore amine-containing model compounds were initially tested followed by sulfur-containing compounds both with ZnO in polychloroprene. This was different to previous model compound studies herein, where they were studied in polychloroprene on their own. In this section the model compounds were tested in conjunction with ZnO in polychloroprene.

The amine-containing model compounds selected comprised a linear primary amine (butylamine), linear primary diamine [1,4-diamino butane (DAB)], cyclic secondary amine (piperidine), cyclic secondary diamine (piperazine) and linear secondary amine

(dibutylamine). Also tested were model compounds with a structure similar to ETU, such as dibutyl thiourea (DBTU) and ethylene urea (EU). The structures of the model compounds are shown in Table 3.5. By testing these model compounds in polychloroprene with ZnO, it was hoped evidence could be gleaned which would help understand the role the nitrogen atoms in ETU play in the cross-linking mechanism of polychloroprene when ZnO is present.

The rheological properties of polychloroprene cured with amine-containing model compounds and ZnO were examined and the results shown in Table 3.13. Most formulations showed an improvement in cross-linking, compared to results of polychloroprene cured with the model compounds alone (cure rates shown in Figure 3.33 and MH shown in Figure 3.34). The sample cured with DAB and ZnO gave a cure rate and MH that was almost identical to that of polychloroprene cross-linked with DAB alone. Additionally, butylamine and piperazine cross-linked samples showed a small improvement in the cure characteristics when compared to the samples without ZnO. This can be attributed to the way in which they cross-link; the addition of ZnO will not alter the mechanism through which this occurs. Amines are able to react with the polymer chain *via* their nitrogen atoms, and excess amine can mop-up any HCl formed. These results suggest that amines are better at reacting with the HCl than ZnO; which would be expected from the relative basicity of an amine to ZnO.

Table 3.13. Rheological properties of amine-containing model compounds in polychloroprene. Each formulation contains 5 phr ZnO, and the various model compounds are present at 2 phr.

	ETU	**ZnO**	**DBTU**	**EU**	**butyl-amine**	**DAB**	**pipera-zine**	**piperi-dine**	**dibutyl-amine**
MH (lb.in)	15.29	5.17	12.98	3.16	10.08	12.71	17.39	6.32	4.44
TS1 (mm:ss)	01:03	02:40	00:46	04:53	02:07	01:23	00:37	01:58	04:33
T90 (mm:ss)	07:25	08:39	03:16	11:44	10:23	10:56	07:44	08:55	12:16
Cure (lb.in/min)	4.96	1.5	12.3	0.36	1.64	1.84	6.02	1.12	0.37

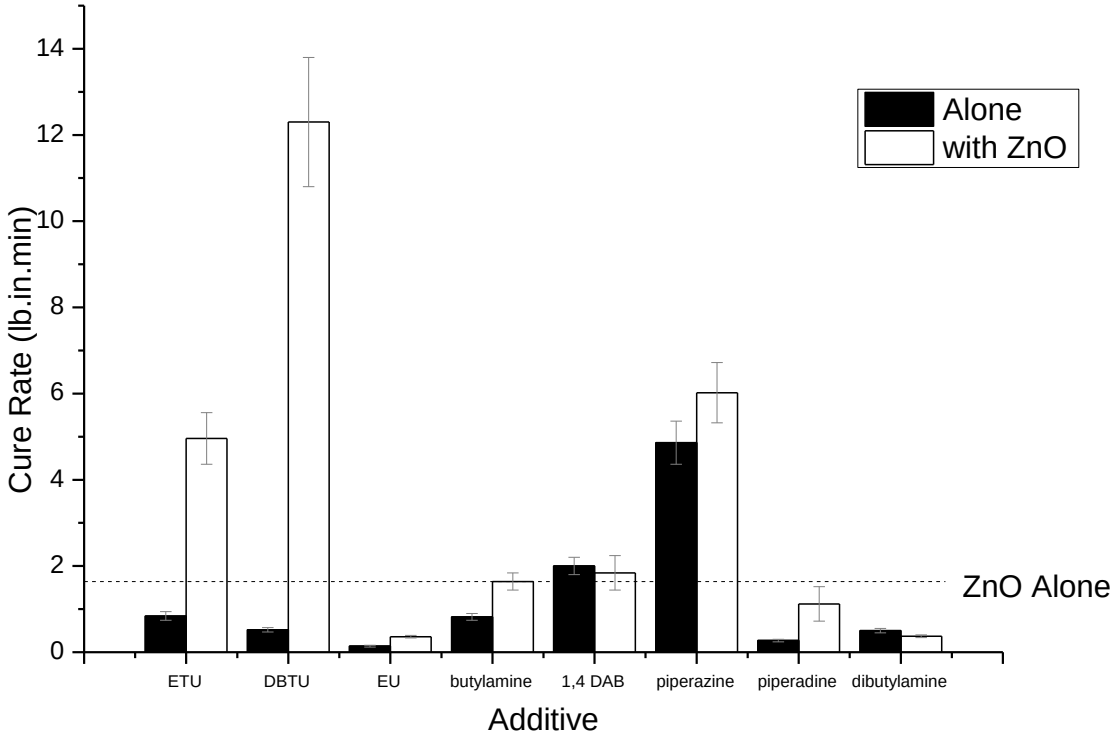


Figure 3.33. Cure rates of polychloroprene cured with 2 phr amine-containing model compounds compared with and without 5 phr ZnO. Error bars show one standard deviation from three data sets.

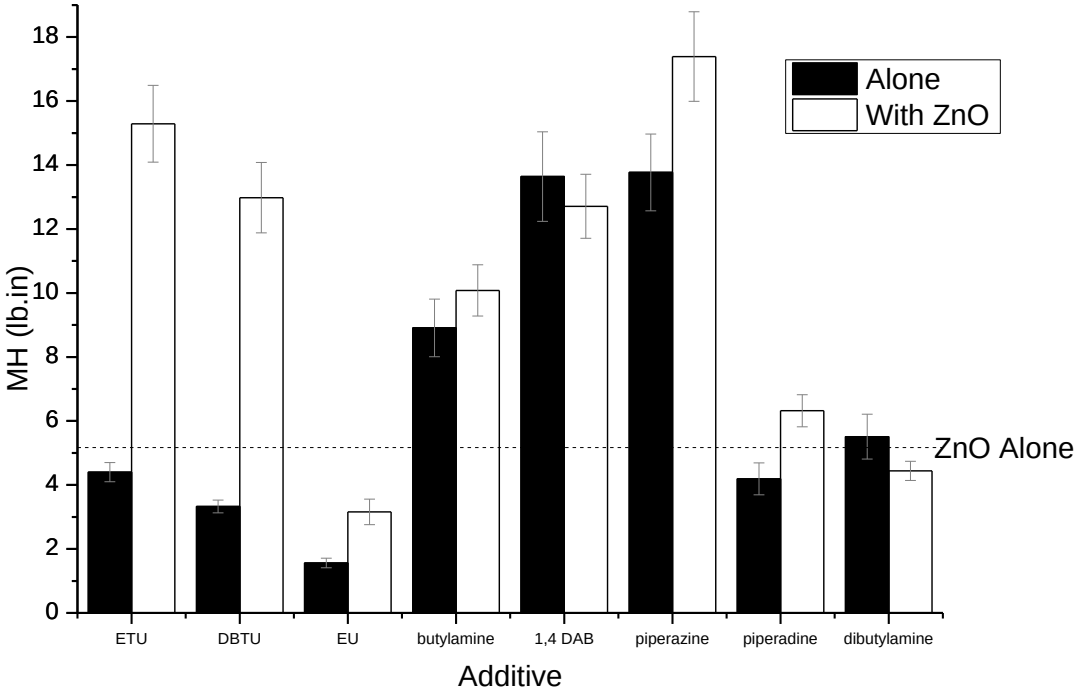


Figure 3.34. Maximum torque of polychloroprene cured with 2 phr amine-containing model compounds with and without 5 phr ZnO. Error bars show one standard deviation from three data sets.

The sample cured with dibutylamine and ZnO, showed less effective cross-linking compared to the sample cured without ZnO. This can be seen through the lower cure and MH values, indicating that cross-linking did not happen as fast or to the same extent. Although the lower scorch and T90 are a move towards more acceptable results, the values would still be considered to be poor cross-linking i.e. worse than cross-linking polychloroprene with ZnO on its own. Similarly, piperidine and EU (Figures 3.33 and 3.34) when used to cross-link polychloroprene with ZnO, give rheological results similar or worse than when ZnO alone is used. Nevertheless, they are both better at cross-linking polychloroprene when used in combination with ZnO than on their own. This potentially indicates that ZnO is undergoing a reaction or complexation with the amino groups of the amine compounds rendering them less able to cross-link. This appears to happen more predominantly with the secondary amine-containing formulations. Although thioureas contain an amino group, the presence of the adjacent sulfur means that the nitrogen is in a different chemical environment compared to primary amines which will affect the reactivity of the nitrogen. The DBTU-containing formulation performs much better with ZnO (much like the ETU-containing formulation). Consequently, a different cross-linking mechanism must be going on in thiourea-containing formulations compared to the formulations containing other secondary amines in the presence of ZnO. This indicates the importance of the role of sulfur in ETU, as reinforced by the poor results obtained with EU with ZnO. It is possible that this may be due to the sulfur in a thiourea being less electronegative than the oxygen in a urea compound; additionally the sulfur still has the reactivity from a lone pair. As carbons do not contain a lone pair, in secondary amines the only reactive site would be the nitrogen atoms.

Spectra of polychloroprene examined using FTIR after curing with the amine-containing model compounds with ZnO that did not cross-link very well on their own (namely dibutylamine, EU and piperidine) give new peaks only in the 1580 cm^{-1} region (associated with ZnO cross-linking). This is illustrated in Figure 3.35 where the FTIR spectrum of dibutylamine and ZnO cross-linking polychloroprene has been selected as an exemplar.

The new peak at ~1580 cm^{-1} associated with ZnO cross-linking indicates that any cross-linking occurring in these samples is *via* that of the 'ZnO alone' mechanism. However, as the mechanical properties show poorer cross-linking than ZnO alone, (i.e. lower MH and cure rate) there must be another reaction taking place. This reaction is either between the ZnO and the model compound or with the model compound and the cross-linking sites, which compete with the cross-linking reactions. Both of these unwanted side reactions would attend fewer

cross-links compared to when ZnO cross-links polychloroprene alone. Unfortunately, no direct evidence for either of these reactions can be gleaned from the FTIR spectra of any of the tested samples. Nonetheless, the likelihood of reactions between the model compounds and ZnO must be remembered when considering how ETU cross-links as ETU may also react with ZnO as part of that cross-linking mechanism.

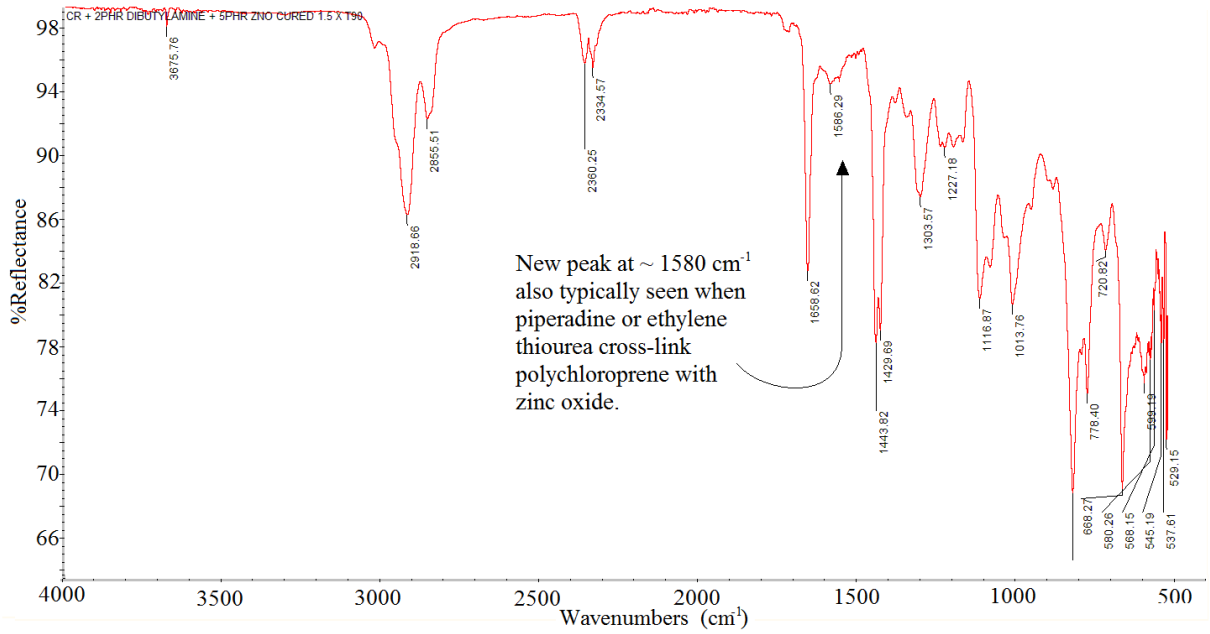


Figure 3.35. FTIR spectrum of dibutylamine and ZnO after cross-linking polychloroprene, showing a peak at ~1580 cm^{-1}, which is also typical of cross-linking with ethylene urea or piperidine in conjunction with ZnO.

Both piperazine and DBTU, when mixed into polychloroprene in conjunction with ZnO produce a peak at ~1558 cm^{-1} in their FTIR spectrum before curing has occurred. This peak is not present in any of the raw materials. After curing, this peak shifts to 1575 cm^{-1} in the DBTU-containing sample and to 1593 cm^{-1} in the piperazine-containing sample. In piperazine only-cured polychloroprene (i.e. no ZnO), the peak at ~1558 cm^{-1} was also seen before curing, but it remained after curing had occurred, and was reduced greatly after soxhlet extraction with methanol. This suggests the formation of a salt, potentially piperazine hydrochloride, and may also imply that in the presence of ZnO a different salt is formed, such as piperazine dihydrochloride or a zinc amine complex, and hence the shift in peak position. A similar process may be occurring when DBTU and ZnO in combination cross-link polychloroprene, DBTU does not cross-link polychloroprene well on its own whereas with ZnO it cross-links to a much greater extent. However, why DBTU would be able to cross-link in this manner and ETU cannot is unclear. It is possible that DBTU alone forms a salt in the

uncured rubber, causing the peak at 1558 cm^{-1}, but when cross-linking with ZnO no salt is formed.

The polychloroprene sample containing DAB and ZnO was examined by FTIR spectroscopy before and after cross-linking. A peak at ~ 1560 cm^{-1} can be seen in the sample before it is cross-linked, and this peak was also seen when DAB was used on its own to cross-link polychloroprene. The 1560 cm^{-1} peak disappears and new peak appears at ~ 1580 cm^{-1} after cross-linking (Figure 3.36). The latter peak has been identified before (Section 3.1.1) and is associated with the cross-linking of polychloroprene with ZnO alone. This suggests that cross-linking is occurring through ZnO pathway rather than *via* the DAB pathway. Both pathways cannot occur simultaneously, as they both involve a reaction with the chlorine atom. Results from mechanical properties concur with this analysis, as the rheological results of DAB are worse when cross-linking polychloroprene in conjunction with ZnO, compared to when DAB cross-links polychloroprene alone.

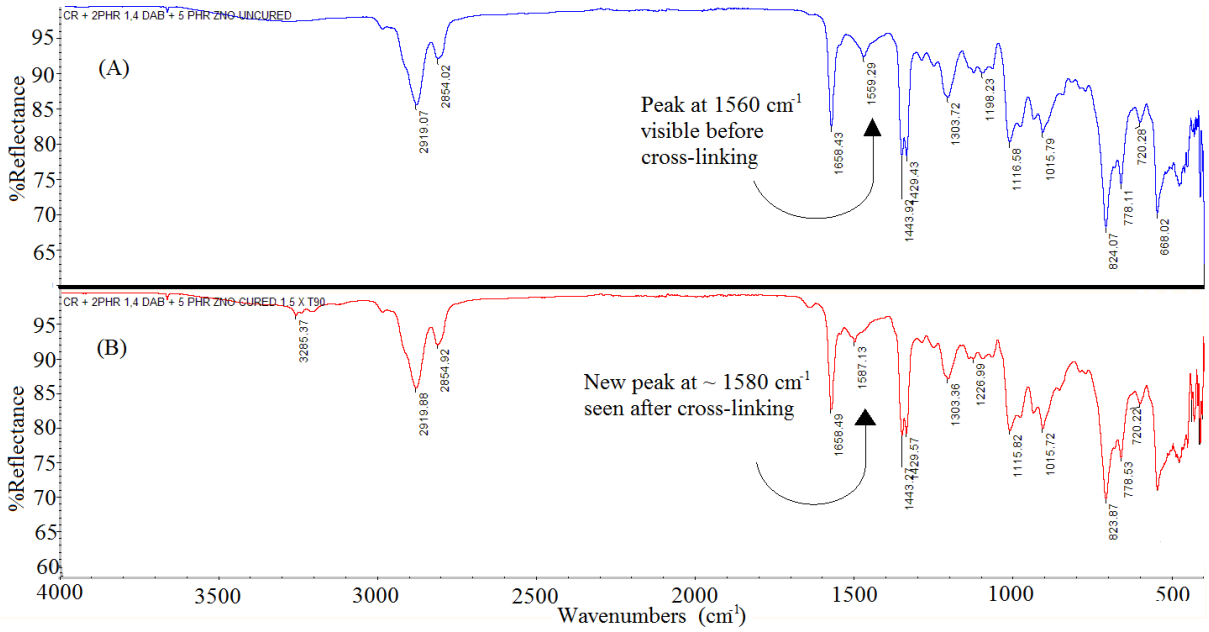


Figure 3.36. FTIR spectra of polychloroprene with 2 phr 1,4-diaminobutane and 5 phr ZnO; (A) before cross-linking, and (B) after cross-linking.

Similar to the amine-containing model compound studies carried out, different sulfur-containing model compounds were also tested in conjunction with ZnO; two linear dithiols [1,6-hexanedithiol (HDT) and 1,8-octanedithiol (ODT)] and linear mono-thiol (hexanethiol). These model compound studies were carried out to provide insight into the role of sulfur in the polychloroprene cross-linking mechanism involving ETU and ZnO together.

The mechanical properties of the vulcanisate cured with the mono-thiol and ZnO gave rise to very poor rheological results (Table 3.14) as demonstrated by a low cure rate and low MH. Similarly, tensile properties were low with UTS reaching only 1.5 MPa in this system. The results, although slightly superior to the mono-thiol alone as a cross-linker (which can be attributed to ZnO cross-linking), indicate that as a cross-linker alone the mono-thiol is unable to cross-link polychloroprene even in the presence of ZnO. They also suggest that the mono-thiol prevents ZnO from cross-linking. This may be due to the mono-thiol reacting with the active site on the polymer chain generated by ZnO. Thus, the mono-thiol effectively blocks off potential cross-linking sites and since the mono-thiol only contains functionality at one end of the chain, it is unable to form full cross-links.

Table 3.14. Mechanical results of polychloroprene cross-linked with sulfur-containing model compounds at 2 phr with 5 phr ZnO.

		ZnO	**hexanethiol**	**HDT**	**ODT**
100 % Mod (MPa)		0.48	0.32	0.54	0.65
300 % Mod (MPa)		0.6	0.32	0.87	1.03
500 % Mod (MPa)		0.82	0.36	1.33	1.87
UTS (MPa)		4.5	1.5	9.9	9.2
Elongation at break (%)		DNB*	DNB*	928	857
15 min MDR test at 160°C	**MH (lb.in)**	5.17	2.75	8.15	10.81
	TS1 (mm:ss)	02:40	03:10	04:08	02:37
	T90 (mm:ss)	08:39	06:30	13:23	13:08
	Cure lb.in/min	1.5	0.6	0.88	1.04

* Sample did not break before tensometer reached full extension (see Appendix A).

The mechanical properties for polychloroprene cross-linked with dithiols (Table 3.14) indicate that they are able to cross-link polychloroprene in conjunction with ZnO to a greater extent than would be possible by using just ZnO alone. Additionally, as none of the thiol-containing systems were able to cross-link alone any mechanical properties greater than those of ZnO-cured polychloroprene must be due to a synergistic cross-linking mechanism. A greater extent of cross-linking can be seen through the higher UTS, 500 % modulus and MH values compared to the properties of ZnO alone cured polychloroprene (Figure 3.37). Thus,

the dithiol is aiding in cross-linking, and as the mono-thiol is unable to cross-link polychloroprene even in the presence of ZnO, this suggests that the dithiols are 'slotting in' as a cross-link bridge between the two polymer chains. This slotting in would be *via* the thiol functionality at the end of the alkyl chain. If it were the presence of a thiol alone that aided cross-linking of polychloroprene, the mono-thiol would also be able to act as a cross-linker, as occurs with the mono-amine, butylamine, which is able to cross-link with its single amine functionality. The increase in MH and cure rate when the chain length between the dithiols is increased supports this theory further. Admittedly, there are only two data points and more work would need to be undertaken to confirm this. Nevertheless, as 'slotting in' can only occur when cross-linking is done in unison with ZnO, the ZnO must be reacting with (activating) the polymer chain to generate an active cross-linking site to allow cross-linking to happen. This activation of the polymer chain allows the sulfur of the dithiol to cross-link and could be occurring when ETU cross-links with ZnO. Such evidence suggests that ETU could cross-link polychloroprene through the sulfur when used as a cross-linker in conjunction with ZnO.

The only differences between the FTIR spectra of polychloroprene compounded with ZnO and the mono-thiol, when uncured and cured is the peak at 1580 cm^{-1} associated with ZnO cross-linking (Figure 3.38). This complements the mechanical property results which indicate that no further cross-linking occurs as a result of mono-thiol addition. If the mono-thiol were to react with the polymer chain through sulfur, it would leave an alkyl chain tethered to the polymer backbone which is unable to form a complete cross-link. Consequently, mono-thiols deactivate potential cross-link sites (without completing a cross-link) and in the cross-linking reaction generate vulcanisates with poorer mechanical properties compared to polychloroprene cross-linked with ZnO alone. This is illustrated in Figure 3.37, and thus adds credibility to the theory of the dithiols 'slotting in' as a bridge between the two polymer chains *via* the functional end groups of the alkyl chain.

Examination of the FTIR spectra for polychloroprene cured with ODT and ZnO reveals a new peak at 1537 cm^{-1} after cross-linking, and this peak remains after the rubber has been purified *via* a soxhlet extraction in methanol (Figure 3.39). The peak at ~1580 cm^{-1} that generally appears after ZnO has been used to cross-link polychloroprene alone or in conjunction with other additives is not present. This is the first instance where ZnO has been employed as part of the cross-linking system and the 1580 cm^{-1} peak has not been present in the FTIR spectrum of the cross-linked rubber even when ETU is used. The absence of the 1580 cm^{-1} peak

indicates that a different cross-linking mechanism to the ZnO cross-linking mechanism is occurring due to the presence of the dithiol. Also, as previously discussed, as the dithiol cannot cross-link on its own therefore the ZnO must be mediating this different cross-linking mechanism in some manner.

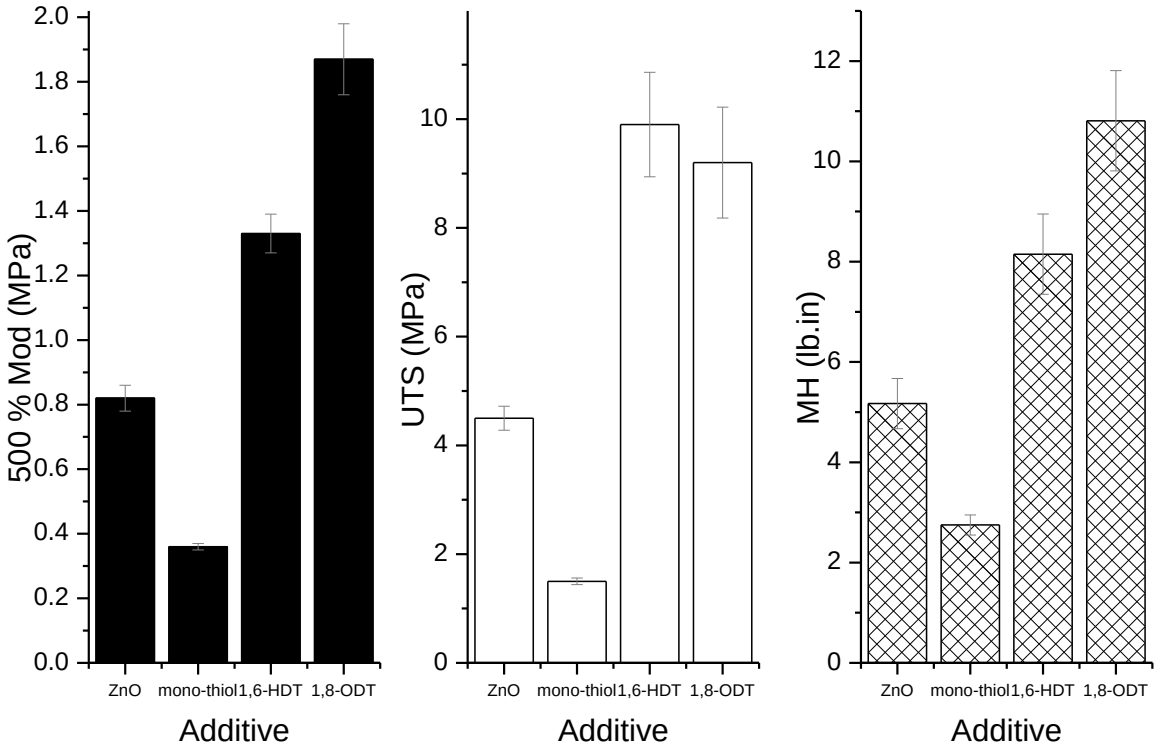


Figure 3.37. Mechanical properties of polychloroprene cross-linked with 5 phr ZnO alone and with 2 phr of mono-thiol or 2 phr of different length dithiols. Error bars show one standard deviation from three data sets.

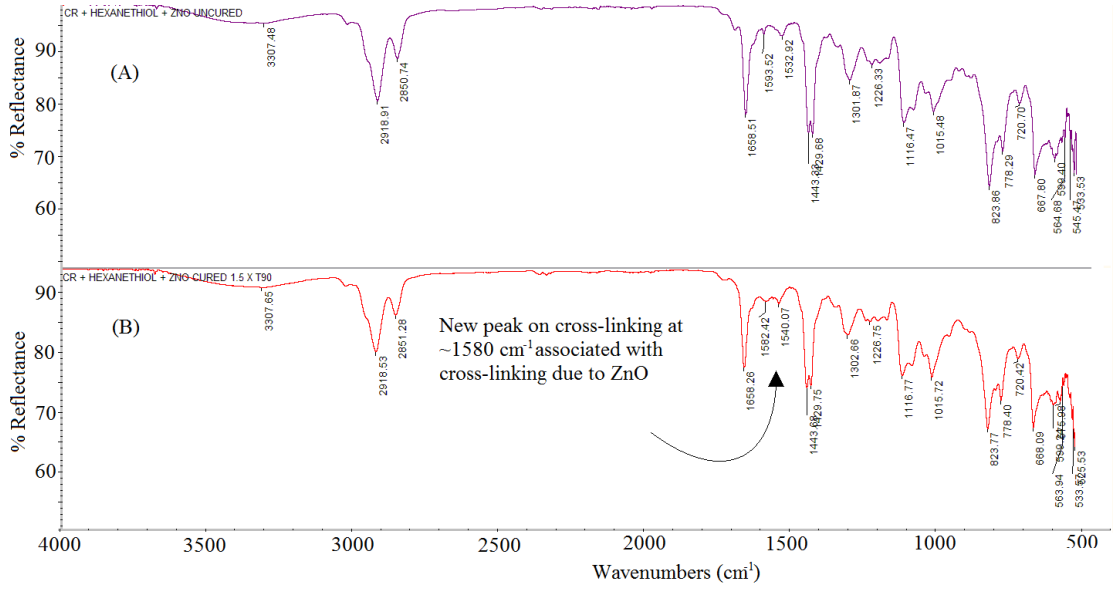


Figure 3.38. FTIR spectra of polychloroprene containing 2 phr hexanethiol and 5 phr ZnO; (A) before curing, and (B) after curing.

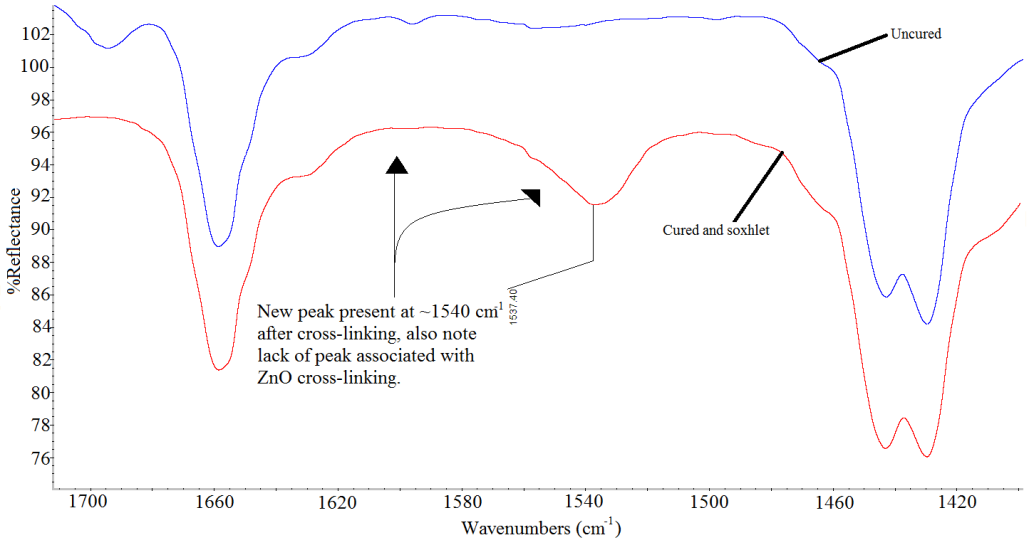
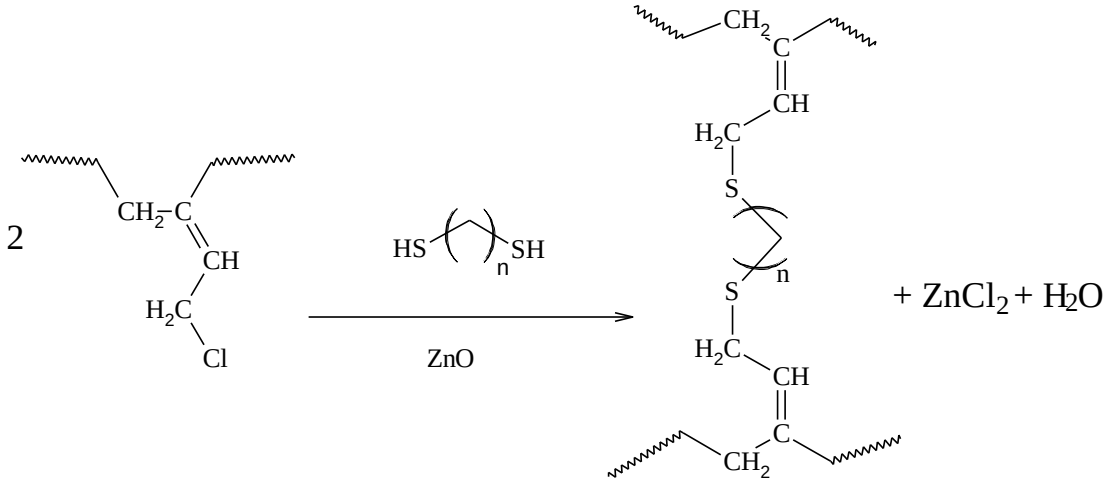


Figure 3.39. FTIR spectra in the range 1400-1700 cm^{-1} of polychloroprene compounded with 5 phr ZnO and 2 phr 1,8-octanedithiol, before and after curing (with soxhlet extraction). The traces have been translated along the reflectance axis for clarity.

ZnO must be activating the polymer chain first by creating an active cross-linking site which then enables the dithiol to form a cross-link. The mechanical properties of the vulcanisate indicate greater cross-link density is obtained with the dithiol in conjunction with ZnO than when either is used in polychloroprene separately. As the 1580 cm^{-1} peak usually seen in samples cured with ZnO is not present when polychloroprene is cross-linked with both dithiol and ZnO, the reaction of the dithiol with the active site created by the ZnO must be more favourable than the cross-linking mechanism of ZnO alone. A simplified reaction scheme is shown in Scheme 3.3 illustrating the importance of the sulfur atom in cross-linking.



Scheme 3.3. Simplified proposed reaction scheme for cross-linking polychloroprene with a dithiol and zinc oxide. The length of alkyl chain between the sulfur atoms in the cross-link will be dependent on the alkyl length of the dithiol used.

3.3.3. Oligochloroprene and Zinc Oxide Cross-Linked with Ethylene Thiourea or Model Compounds

Up to now ETU and ZnO have been studied in polychloroprene rubber gum stock; herein their inclusion in oligochloroprene (molecular weight ~3000 g/mol) is discussed. Several model compounds previously studied (Section 3.3.2) were examined. This included the amine-containing molecules, piperazine, 1,4-diaminobutane (DAB) and dibutyl thiourea (DBTU) and the sulfur-containing compound, 1,8-octanedithiol (ODT). All were examined in the cross-linking of oligochloroprene in conjunction with ZnO. Initially, the FTIR spectra of the various compounded formulations were studied before and after curing. Due to the scale of reaction carried out with the oligomers, activated ZnO was used allowing a smaller quantity to be employed. Activated ZnO also has a smaller particle size and can be mixed with the oligomers more easily.

By cross-linking low molecular weight oligochloroprene with various additives it was hoped that a greater insight into the FTIR peaks formed during the cross-linking reaction could be observed compared to the reaction in higher molecular weight rubber. This would be because the oligochloroprene should be less complicated than the polychloroprene rubber having shorter chains and not containing talc and anti-tackifiers, therefore observation of the change in peaks in the FTIR spectrum should be simplified. Unfortunately, this was not the case. The FTIR spectra of oligochloroprene after cross-linking were very similar to their rubber counterparts. Figure 3.40 shows the similarity between oligochloroprene and polychloroprene rubber both cross-linked with ETU and ZnO. The main difference is the ~1580 cm^{-1} peak associated with ZnO cross-linking which does not appear in the cross-linked oligochloroprene spectrum. This lack of peak is not due to activated ZnO being used, as testing performed in polychloroprene rubber using activated ZnO at the same level used in the oligomers still produced the 1580 cm^{-1} peak.

When oligochloroprene was heated to 160 °C with ETU and ZnO to simulate cross-linking, a white solid formed within 10 minutes. FTIR examination on the isolated solid showed many bands in common with the oligomer, due to difficulty in removing excess oligomer from the solid. However, by using an FTIR software package (Omnic) it was possible to subtract the oligomer spectrum to afford a more representative spectrum of the solid (Figure 3.41A).

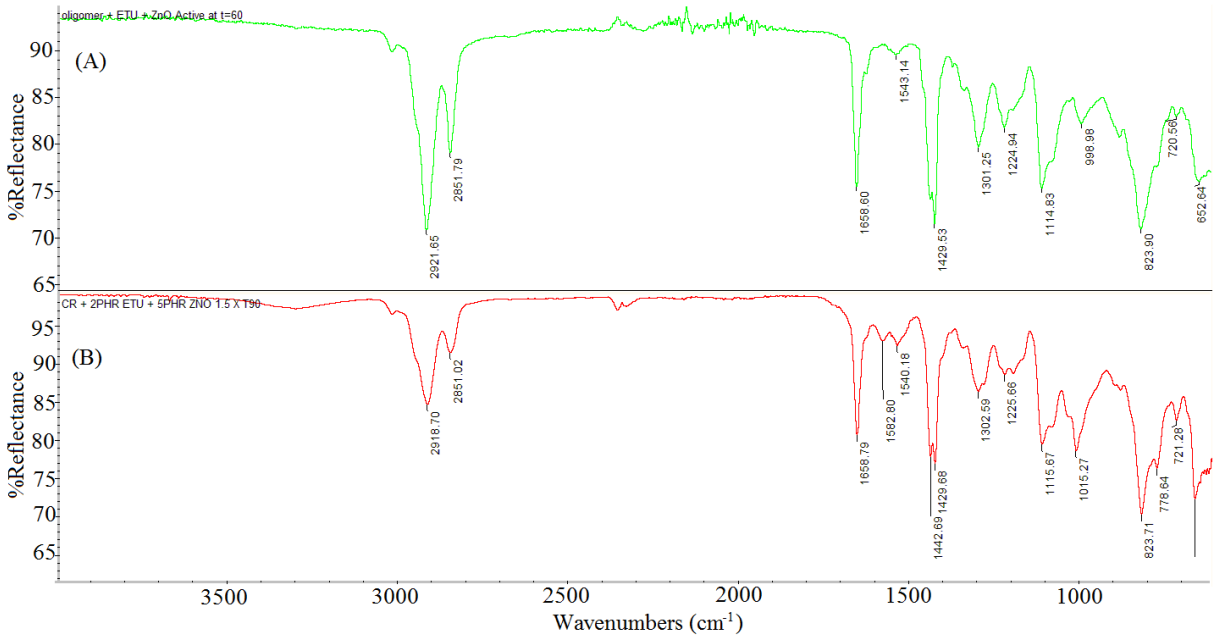


Figure 3.40. Comparison of FTIR spectra, (A): oligochloroprene cross-linked with 2 phr ETU and 1 phr ZnO active; (B): polychloroprene rubber cross-linked with 2 phr ETU and 5 phr ZnO.

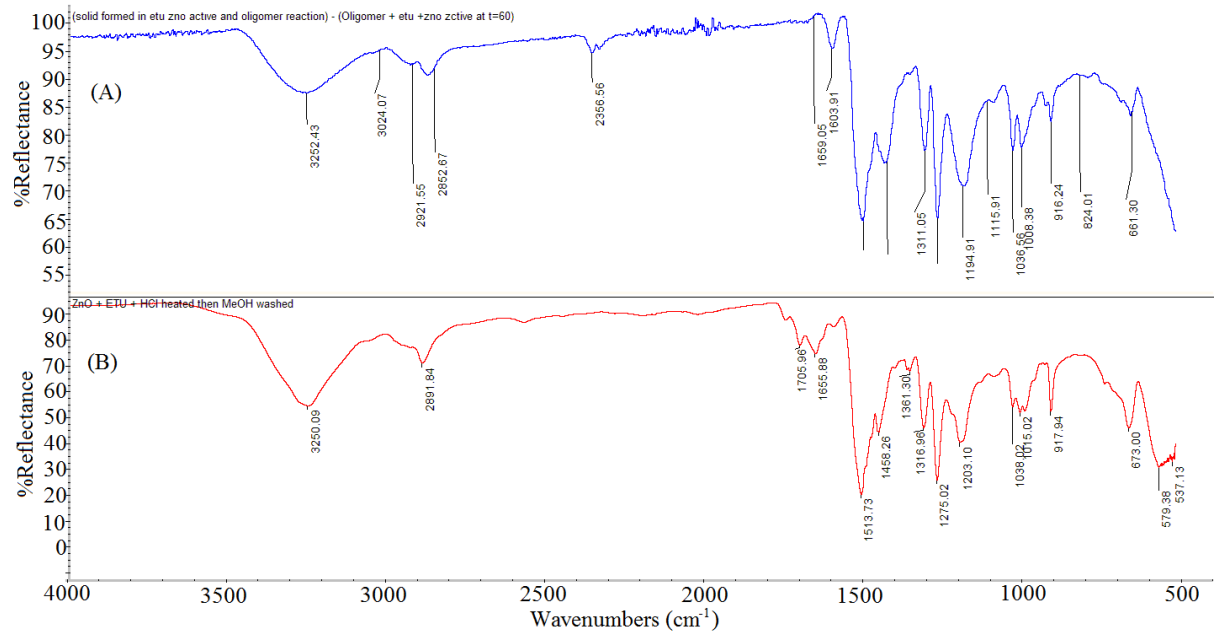


Figure 3.41. FTIR spectra of; (A) solid formed in oligochloroprene when heated with ETU and ZnO with the oligomer background subtracted, and; (B) solid formed when ETU, ZnO and HCl are heated, then washed with methanol.

Initially, it was suspected that this solid was a salt formed by a reaction between ETU and HCl (evolved during the cross-linking reaction). However, the FTIR spectrum of a sample of ETU and HCl heated and mixed together in a separate experiment was very different to that of the solid from the oligomer reaction. Likewise, when ZnO and ETU were mixed at elevated temperatures, the FTIR spectrum of the resultant compound was dissimilar to that of the solid obtained from oligochloroprene cured with ETU and ZnO. In another experiment ETU, ZnO and HCl were then heated together at 160 °C for one hour and then left to cool. Once cooled, the product was washed with methanol to remove any unreacted ETU, and then dried. The resultant powder was then examined by FTIR spectroscopy and proved to be very similar to the solid created in the oligomer reaction (Figure 3.41B). As a final reaction, ZnO and HCl were reacted together and shown to form zinc chloride, suggesting a reaction between ETU and zinc chloride could be occurring during the cross-linking process. This hypothesis was put to the test by combining ETU and zinc chloride. The FTIR spectrum of the resultant solid was found to be similar to that of solid formed in the reaction of oligomer with ETU and ZnO. These results suggest that in the oligomer curing reaction with ETU and ZnO there is formation of a solid through a reaction between ETU and zinc chloride, consequently proving the formation of zinc chloride during the cross-linking process.

Unfortunately GPC and NMR experiments run on the cross-linked oligochloroprene provided little additional information. It had been hoped that using these techniques, only possible because oligomers are more soluble than rubber, would give a greater insight into the bonds formed during cross-linking, through NMR and the level of cross-linking achieved, *via* GPC. However, the study using oligomers has enabled the reaction products of cross-linking to be examined which would not have been possible to achieve in the rubber gum stock.

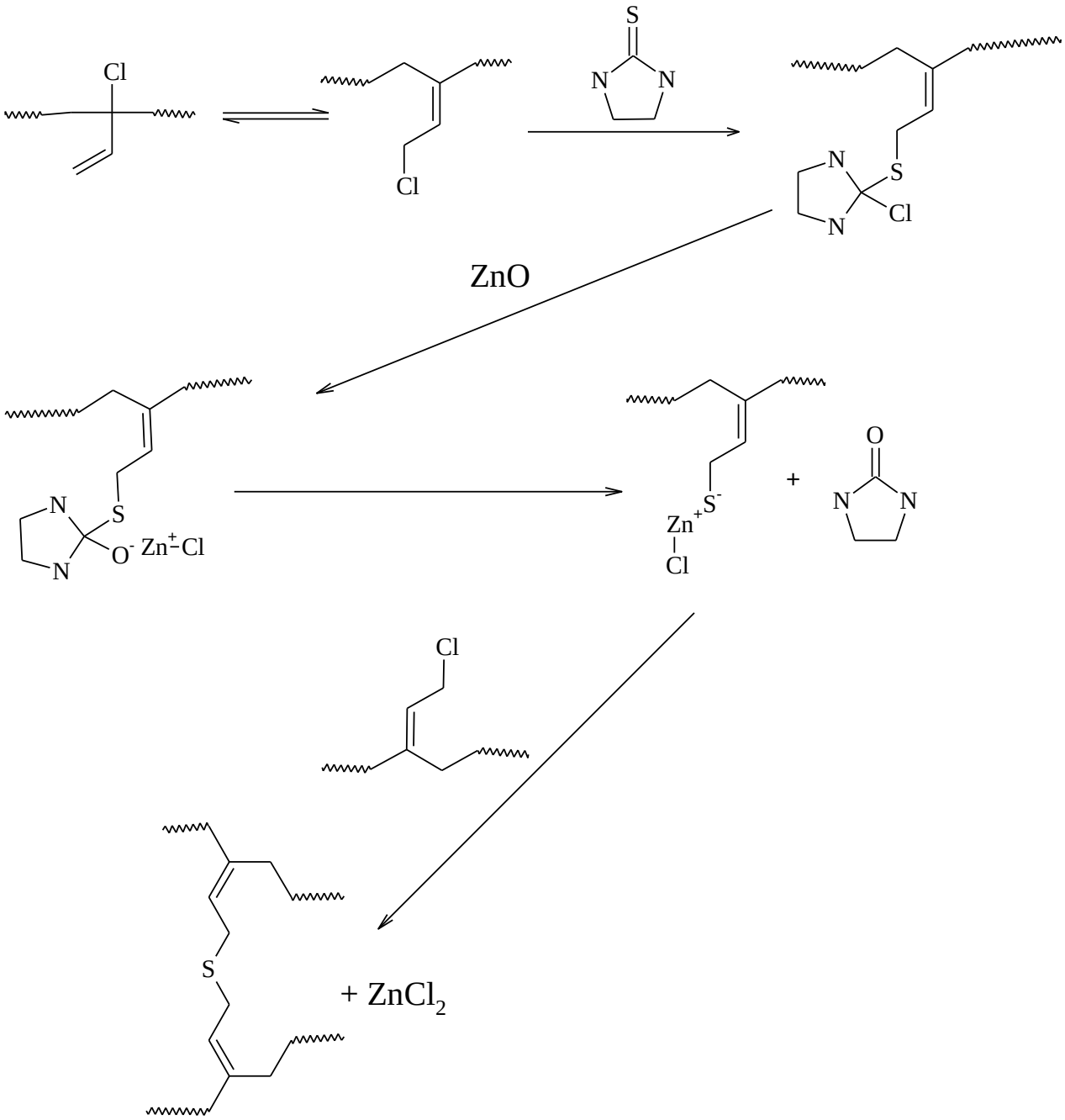
3.3.4. Comparison of the Results of Polychloroprene Containing Zinc Oxide and Other Additives with Existing Cross-linking Theories

The most prevalent cross-linking theory for polychloroprene with ETU and ZnO is that reported by Pariser (Scheme 3.4).[31] In his mechanism, zinc chloride and ethylene urea (EU) are formed as a by-product of the reaction. It has been seen that both of these products are formed during cross-linking of polychloroprene with ETU and ZnO, although definitive proof that they are produced by the cross-linking reaction has not been achieved. Similarly, it has been shown through model compound studies using dithiols and studies with traditional

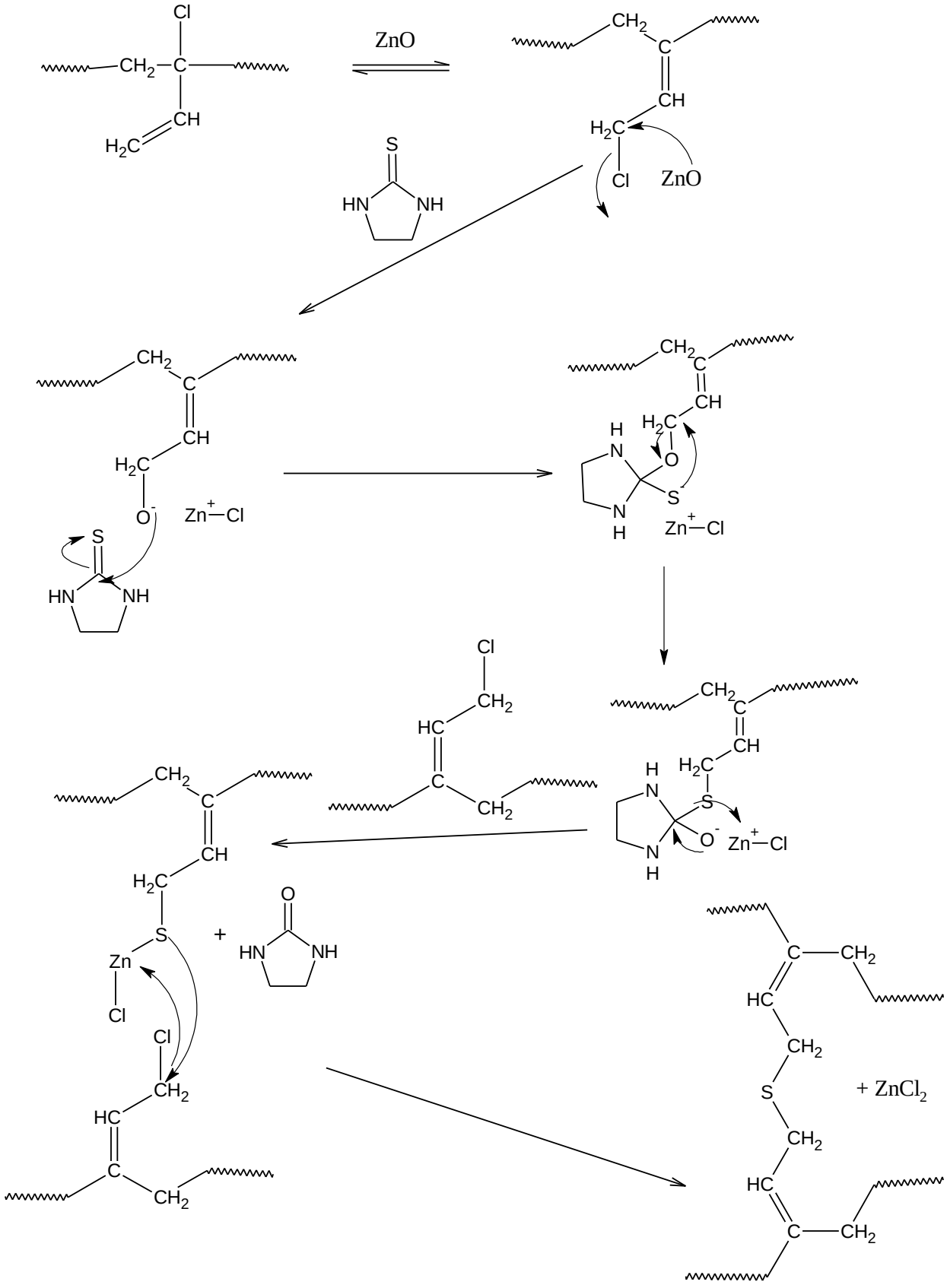
accelerators including thiurams that the sulfur atom of ETU is important when used in conjunction with ZnO. It was shown that the sulfur atom was able to cross-link polychloroprene, but only in the presence of ZnO. Consequently, results from this project suggest that ZnO reacts first with the polymer chain in the cross-linking mechanism to activate the polymer chain, thus allowing cross-linking to occur with the sulfur atom of ETU. Therefore, a possible new mechanism for cross-linking polychloroprene with ETU and ZnO is shown in Scheme 3.5. In this proposed new mechanism, ZnO first creates an active site on the polymer chain through substitution of chlorine for oxygen. This then enables ETU to cross-link through its sulfur. It is also possible for thiuram-based accelerators to cross-link polychloroprene in this manner once they have been activated. After this initial stage, the remainder of the mechanism follows the proposed route of that proposed by Pariser.

Evidence gathered herein also suggests that this is not the only mechanism occurring during the cross-linking reaction, and that the mechanisms by which both ETU and ZnO cross-link polychloroprene separately are also occurring. This makes conclusive proof of each separate mechanism difficult to achieve. It has also been seen that some traditional accelerators (e.g. thiurams) require activation before they are able to cross-link polychloroprene, e.g. through the use of ZnO. It may be possible to use a diamine and a thiuram in combination to cross-link better than either separately (Table 3.15).

The results shown in Table 3.15 suggest that 1,4-diaminobutane (DAB) can activate tetramethyl thiuramdisulfide (TMTD) to an extent that cross-linking is improved compared to either of the raw materials alone. This can be seen through the higher cure rate and UTS and lower scorch time. Applying this knowledge, a diamine (as an activator) with a thiuram may produce a new accelerator, which can cross-link polychloroprene in the same way as ETU. This work is the basis for studies into safer new accelerators and is discussed in greater detail is Chapter 4.



Scheme 3.4. Cross-linking mechanism for polychloroprene with zinc oxide and ethylene thiourea working in unison as first proposed by Pariser.[31]



Scheme 3.5. New cross-linking mechanism for polychloroprene with ETU and ZnO, based on the results of the findings herein.

Table 3.15. Comparison of rheological properties of polychloroprene cured with tetramethyl thiuramdisulfide (TMTD) and 1,4-diaminobutane (DAB), separately and in conjunction.

		TMTD (3 phr)	DAB (0.75 phr)	TMTD (3 phr) + DAB (0.75 phr)
100 % modulus		0.24	0.66	0.61
300 % modulus		0.2	1.01	1.02
500 % modulus		0.18	1.50	1.73
UTS (MPa)		0.3	8.1	12
Elongation at break (%)		DNB*	727	894
15 minute MDR test at 160 °C	**MH (lb.in)**	2.19	9.98	9.44
	TS1 (mm:ss)	13:09	02:25	00:58
	T90 (mm:ss)	13:54	12:14	07:12
	Cure rate (lb.in/min)	0.2	0.99	2.26

*Sample did not break (see Appendix A).

3.4. Chapter Conclusions

The mechanisms by which ETU and ZnO cross-link polychloroprene, individually, and in combination with each other, have been investigated. Results herein suggest that ZnO alone cross-links polychloroprene *via* a cationic mechanism, most likely that proposed by Vukov.[11] Evidence for this includes the appearance of the 1580 cm^{-1} peak in the FTIR spectra on curing, nominally ascribed to a carbon-carbon double bond. Evidence is also provided that mechanisms, such as the formation of an ether linkage and the mechanism proposed by Mallon *et al*,[10] do not occur.

When cross-linking occurs with ETU alone there is evidence for the bis-alkylation mechanism proposed by Kovacic.[24] This includes the acidic environment detected when ETU cross-links oligochloroprene signifying the generation of HCl. Also, a new peak in the FTIR spectrum is formed at 1550 cm^{-1} which does not disappear on soxhlet extraction, indicating a new type of chemical bond is being created during curing. Furthermore, there is indirect evidence that the cross-link bridge is formed through the nitrogen atoms as sulfur-containing compounds used as model compounds and thiuram-based accelerators were unable to react with the polymer chain on their own. There is also evidence that other amine-containing compounds cross-link

in a similar manner. Butylamine is able to cross-link polychloroprene rubber and could do so because of the functionality of the nitrogen. Additionally, linear diamines of different lengths all produced similar physical properties regardless of alkyl length, indicating that they all had cross-links between two polymer chains through each nitrogen atom.

Finally, the cross-linking reaction when both ETU and ZnO are present in polychloroprene was examined. It has been shown that the mechanism employed by each of the raw materials separately is occurring. Likewise, there is evidence that at least a third mechanism is in operation. This third mechanism included the formation of EU and zinc chloride, as seen in the mechanism proposed by Pariser[31]. However, Pariser's mechanism shows the sulfur atom of ETU reacting with the polymer chain first. Our evidence shows this not to be the case. Compounds containing a thiol group can react with the polymer chain in the presence of ZnO, but only once ZnO has generated an active site. Therefore, the results herein indicate that a new mechanism is in effect. This mechanism is similar to that of the Pariser mechanism, but ZnO reacts first with the polymer chain before ETU. A diagram showing the three mechanisms in effect when ETU and ZnO are present in polychloroprene is shown in Figure 3.42.

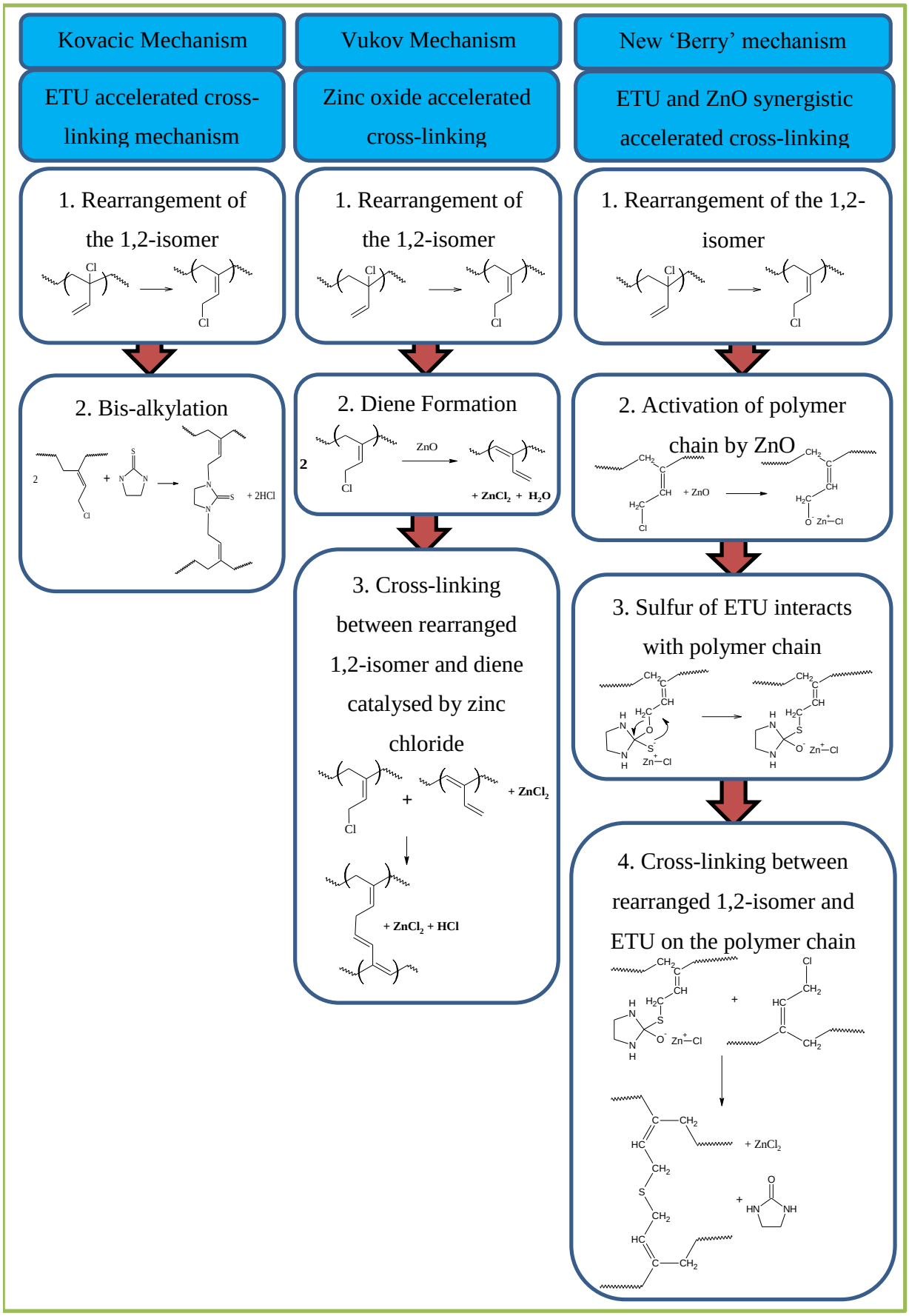


Figure 3.42. Cross-linking mechanisms in effect when ETU and ZnO are present in polychloroprene.

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CHAPTER 4

INVESTIGATION OF NEW ACCELERATORS TO CROSS-LINK POLYCHLOROPRENE

4. Investigation of New Accelerators to Cross-link Polychloroprene

This chapter shows the steps taken in the discovery of a new safer accelerator for polychloroprene. Through the knowledge gleaned of the mechanism of 'ETU curing polychloroprene' in Chapter 3 and examination of existing widely used rubber accelerators, this is achieved. The mechanism by which existing accelerators cross-link polychloroprene is examined and, from this, a list of candidate possible accelerators is drawn up. After the synthesis of the candidate molecules, these accelerators have been studied in polychloroprene on their own and those most able to cross-link examined in combination with an activator.

As described in Chapter 3, ETU (in combination with ZnO) is the most effective accelerator for polychloroprene. Results show the important aspects of ETU in cross-linking are the secondary amine groups and the C=S group. It is also noted that one role ZnO plays when cross-linking polychloroprene with ETU is as an activator to enable the sulfur atom of ETU to cross-link. From the results seen with traditional rubber accelerators discussed in Chapter 3 (Tables 3.3, 3.4, 3.11 and 3.12) thiuram- and dithiocarbamate- based accelerators (which both contain amine groups and C=S groups) were able to cross-link polychloroprene. This was shown to occur to a greater extent in the presence of an activator, such as ZnO. Studying the relationship between traditional accelerators and activators, and examining other potential cross-linkers helps to inform which constituent parts the new accelerator should contain. As previously mentioned it is worth noting that use of imperial units are widely accepted in rubber technology and as such are used throughout for mechanical property characterisation. Additionally, all additives are measured by weight as is standard practice in rubber technology rather than stoichiometrically.

4.1. Studies with Existing Accelerators

Chapter 3 shows that thiuram- and dithiocarbamate-based accelerators are able to cross-link polychloroprene (results reproduced in condensed form in Table 4.1). They were both seen to be significantly better as curing agents in the presence of ZnO; the thiuram would not cross-link polychloroprene at all without ZnO. The effect of ZnO within the formulation was to either activate the polychloroprene chain to allow cross-linking to occur or to activate the accelerator to enable it to cross-link. This occurs in sulfur cross-linking of natural rubber when the activated sulfurating agent is formed by a reaction of ZnO with an accelerator. The dithiocarbamate used in Table 4.1 contained a zinc ion and was able to cross-link to a similar

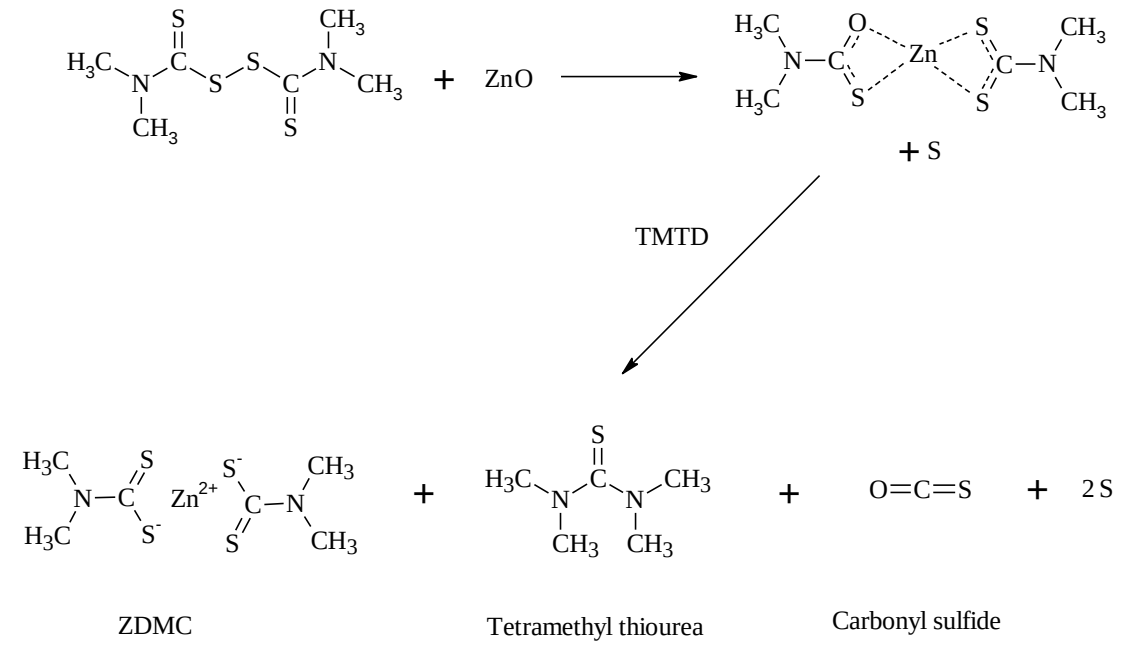
extent with and without ZnO. When cross-linking polychloroprene ZnO appears to react with the thiuram-based accelerator in a similar manner to when a thiuram-based accelerator and ZnO are used in traditional rubber formulations. More specifically the thiuram (TMTD in this case) is effectively split by the zinc cation (Zn^{2+}) and forms zinc dimethyldithiocarbamate (ZDMC), as shown in Scheme 4.1. It has also been shown in Chapter 3 that ZnO is present to facilitate the rearrangement of the 1,2-isomer in polychloroprene allowing for quicker and stronger cross-linking to occur. Thus ZnO is needed for two purposes; firstly, to rearrange the 1,2-isomer to allow cross-linking to occur and secondly, to activate the thiuram-based accelerator to make it able to act as a cross-link agent.

Table 4.1. Rheological properties of polychloroprene cross-linked with different additives.

Formulation	**Accelerator type**	**15 minute MDR test at 160 ºC**			
		MH (lb.in)	**TS1 (mm:ss)**	**T90 (mm:ss)**	**Cure (lb.in/min)**
ETU (3 phr)	Thiourea	4.03	02:01	10:02	0.8
TMTD (3 phr)	Thiuram	2.19	13:09	13:54	0.2
ZDBC (3 phr)	Dithiocarbamate	4.22	01:04	08:11	3.94
ETU (3 phr) + ZnO (5 phr)	Thiourea	14.66	00:56	05:41	5.41
TMTD (3 phr) + ZnO (5 phr)	Thiuram	7.6	00:55	06:01	6.6
ZDBC (3 phr) + ZnO (5 phr)	Dithiocarbamate	5.01	00:53	05:39	4.12

The cure characteristics, featured in Table 4.1 and illustrated more clearly in Figure 4.1; show that ETU can cross-link polychloroprene alone, but is much improved by the addition of ZnO (with the cure rate increasing six-fold). On the other hand there is only a small increase in cure rate with the addition of ZnO to ZDBC. Finally, TMTD cannot cross-link polychloroprene without ZnO, but can cross-link extremely well in the presence of ZnO. These results prove the importance of ZnO as an activator, or more precisely the zinc cation, formed when ETU or TMTD cross-link with ZnO and already present in ZDBC.

It is evident that the new accelerator would benefit from having a dithiocarbamate group present, as compounds containing this group achieve a high extent of cross-linking of polychloroprene, once the chain has been activated. Additionally, the dithiocarbamate group can react with other functional groups, such as an amine, to create a salt. As previously noted this occurs when thiuram-based accelerators react with ZnO to create zinc dithiocarbamates. This would enable the new accelerator to have dual cross-linking functionality.



Scheme 4.1. Reaction between TMTD and ZnO when curing occurs, showing the formation of a dithiocarbamate – zinc dimethyldithiocarbamate (ZDMC).[1]

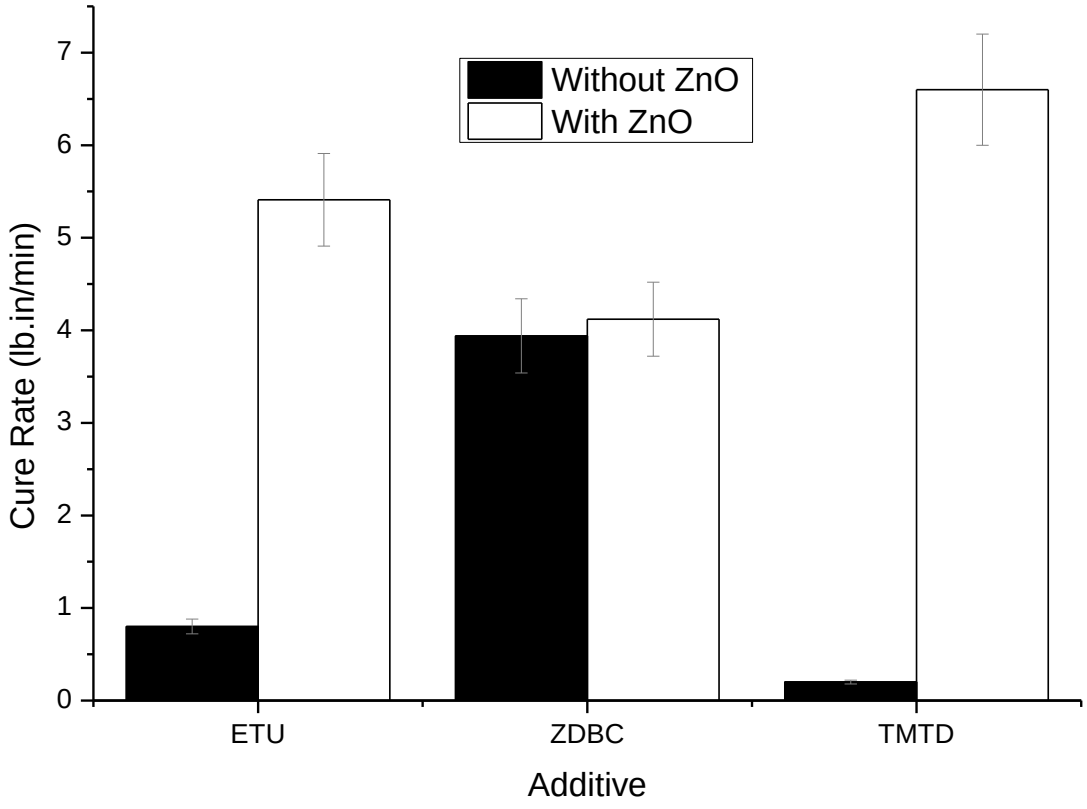


Figure 4.1. Cure rates of polychloroprene cross-linked with various additives, with and without zinc oxide. N.B. Error bars show one standard deviation from three data sets.

An ancillary aim for this project was the reduction of zinc in the final formulation, both zinc dithiocarbamates and thiurams in combination with ZnO would thus not be suitable replacements for an ETU-based cross-linking system. Therefore, a chemical that can activate the chain in place of ZnO is required as part of the new accelerator. It is shown in Chapter 3 (Table 3.7) that diamines are able to react with the polychloroprene chain and that the length of the diamine is unimportant. Diamines are also able to remove any excess HCl formed during cross-linking. Consequently, diamines could complex with another chemical forming a single product, removing the necessity for the final accelerator to consist of several different additives 'mixed' together. Table 4.2 shows the improved cross-linking of polychloroprene with a thiuram accelerator in conjunction with a diamine. In this instance, TBzTD is used in place of the previously used TMTD, as it is a safer thiuram-based accelerator. The results for ultimate tensile strength are higher than those for a diamine alone, indicating that a higher extent of cross-linking is occurring (Figure 4.2).

Table 4.2. Selected mechanical properties of polychloroprene cross-linked with different diamines at 1.5 phr, with and without TBzTD at 3 phr.

Diamine with TBzTD	$H_2N-(CH_2)_3-NH_2$	$H_2N-(CH_2)_4-NH_2$	$H_2N-(CH_2)_6-NH_2$	$H_2N-(CH_2)_7-NH_2$	$H_2N-(CH_2)_{12}-NH_2$
500 % Mod (MPa)	3.22	2.31	1.55	1.53	2.20
UTS (MPa)	14.6	12.6	14.3	12.1	14.4
Elongation at break (%)	729	745	DNB*	DNB*	982
MH (lb.in)	12.86	12.37	7.58	6.68	8.82
TS1 (mm:ss)	00:24	00:30	02:18	02:15	01:23
Diamine alone	$H_2N-(CH_2)_3-NH_2$	$H_2N-(CH_2)_4-NH_2$	$H_2N-(CH_2)_6-NH_2$	$H_2N-(CH_2)_7-NH_2$	$H_2N-(CH_2)_{12}-NH_2$
500 % Mod (MPa)	2.99	3.56	4.82	3.69	2.10
UTS (MPa)	6.5	7	8.4	6.7	7.8
Elongation at break (%)	560	559	552	571	685
MH (lb.in)	13.98	14.03	14.2	13.28	11.91
TS1 (mm:ss)	01:34	01:32	01:35	01:40	02:04

*The samples tested did not break (see Appendix A).

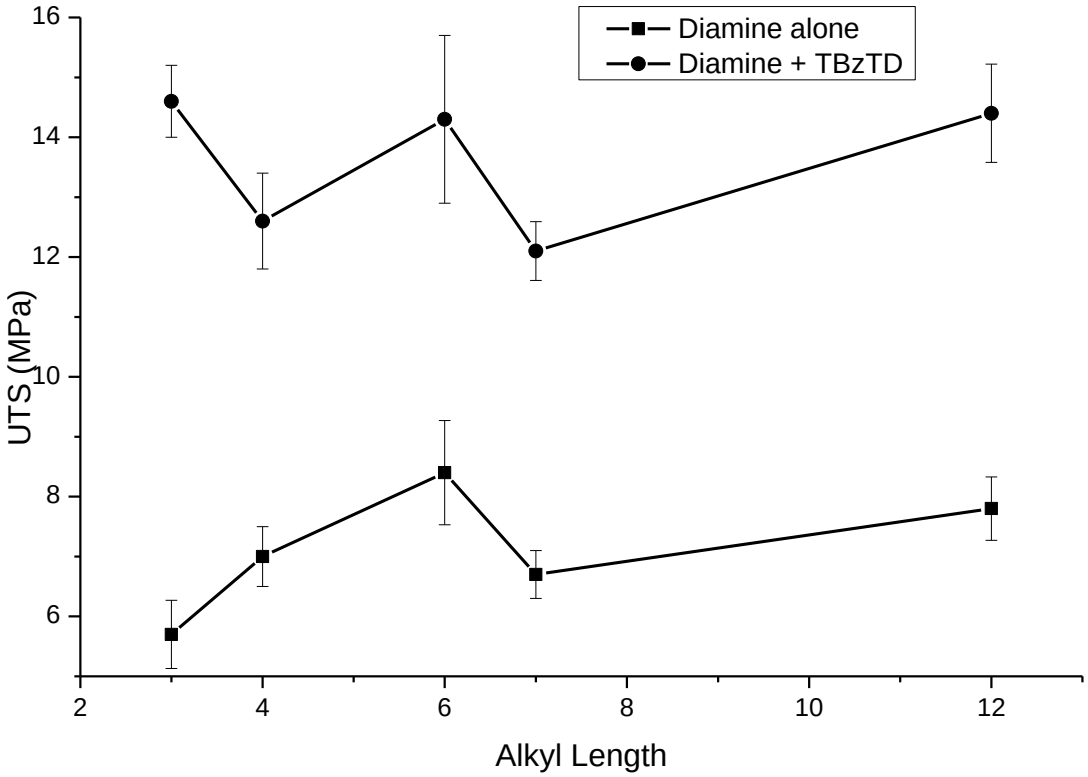


Figure 4.2. Ultimate tensile strength of polychloroprene cured with diamines alone and in combination with tetrabenzyl thiuramdisulfide (TBzTD). Error bars show one standard deviation from three data sets.

A result of note is the increase in extension at break when polychloroprene is cross-linked with TBzTD in combination a diamine. Some of the samples did not break during tensile testing. An increase in the extension at break could be due to fewer cross-links being formed, producing a network with more flexibility and less rigidity. However, as the UTS are higher with TBzTD in combination with a diamine, results also suggest that those cross-links formed are stronger. The cross-links themselves are also likely to be different with the TBzTD system containing sulfur cross-links, whereas the diamine only system will have carbon-carbon cross-links. Lower scorch times were also observed for the shorter length diamine chains in conjunction with TBzTD, in part due to the high concentration of amine, as the formulations are made by weight and not stoichiometrically. Such lower scorch times could also be due to the longer chain diamines being less able to activate the thiuram accelerator, this is possibly due to steric hindrance; although no research into this has been conducted, and this could form the basis of future work. The ability of other additives such as 3-amino-1-propanol and piperazine, (the latter of which has been used as an analogue of ETU in some cross-linking studies),[2] to cross-link polychloroprene renders them possible suitable additions to the

dithiocarbamate group. They should also be able to form the salt that would be required to form a multi-functional accelerator.

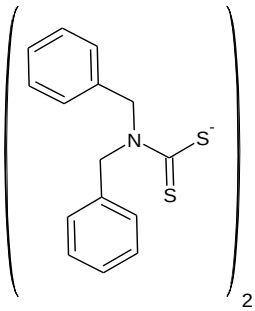
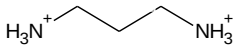
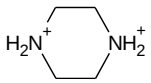
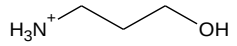
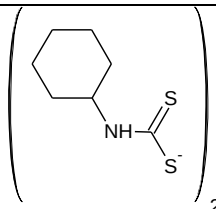
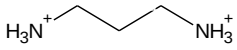
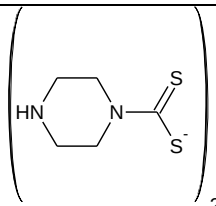
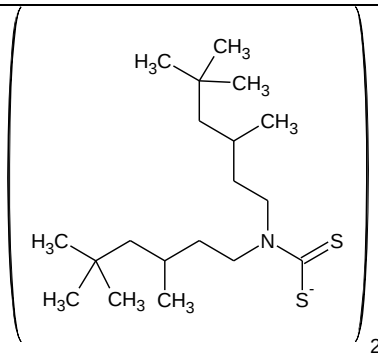
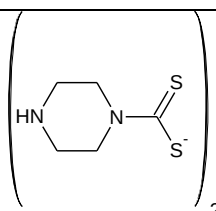
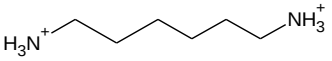
4.2. Proposition of New Accelerators

This section provides a list of accelerators synthesised and the reasoning behind each of the candidate accelerators selected. Assessments were carried out with polychloroprene rubber initially, as a screening test. All of the potential candidate accelerators were screened by researchers at the University of Milano Bicocca, Italy, using computational analytical techniques; quantitative structure-property relationship (QSPR) and quantitative structure-activity relationships (QSAR) to predict their toxicity levels. These techniques enables structures which are potentially hazardous (for various reasons such as toxicity, carcinogenicity, irritant etc.) to be identified without doing any physical testing of the compound. All of the compounds tested were found to be safer than ETU using this software. Any candidate accelerator which was found to pass the tests set down would still have to undergo experimental toxicity studies if it were to go to commercialisation as these computational techniques are only suitable for material used in small quantities and are just used as a guide to inform potential candidates. All of the proposed accelerators contain two elements; a cross-linker part and an activator part, reacted together to form a complex or salt (Table 4.3).

As previously shown in Chapter 3, the important aspects of ETU are the R-N-R group and the C=S, therefore the synthesised new accelerators contain these species. It has also been shown in Section 4.1 that an activator will aid in cross-linking, and that diamines can act as activators, of both accelerators and the polymer chain. Table 4.3 shows that the first three proposed new accelerators (PNA1-PNA3) all contain a dibenzyldithiocarbamate group as the cross-linker, with each having a different activator. This enables the ability of different types of molecules to perform as an activator to be evaluated. The next three accelerators assessed (PNA4-PNA6), all have 1,3-diaminopropane as the activator element and differing cross-linkers. This will allow a judgement to be made on the group behind the dithiocarbamate moiety of the cross-linker component of the accelerators. The final PNA assessed contains a previously tested cross-linker and a longer chained diamine, enabling the length of diamine to be evaluated. Initially, the accelerators were compared to each other with the most promising being taken forward and compared to ETU (Section 4.3). All physical testing was done on

pure polychloroprene gum stock with 0.6 phr stearic acid as a processing aid, additives at quoted levels and no other additives used except where stated.

Table 4.3. List of proposed new accelerators (PNAs) synthesised for this project, showing the two separate aspects of each accelerator.

Abbreviation	Section Discussed	Cross-linker	Activator
PNA1	4.2.1		
PNA2	4.2.1		
PNA3*	4.2.1		
PNA4	4.2.2		
PNA5	4.2.2		
PNA6	4.2.2		
PNA7	4.2.3		

*Note PNA3 is a complex between only one cross-linker and activator.

4.2.1. Candidates Accelerators Based upon Dibenzyldithiocarbamate

The first set of proposed new accelerators (PNAs) synthesised were based upon the dibenzyldithiocarbamate group, as a cross-linking agent, common to both TBzTD and zinc dibenzyldithiocarbamate (ZBEC). The dibenzyldithiocarbamate was used in place of the dimethyldithiocarbamate (seen in TMTD) as it is considered to be safer. This group is in salt form with different amine containing species, which are present as activators in the cross-linking process. The first compound that the dibenzyldithiocarbamate was complexed with is 1,3-diaminopropane (Figure 4.3) in a ratio of 2:1.

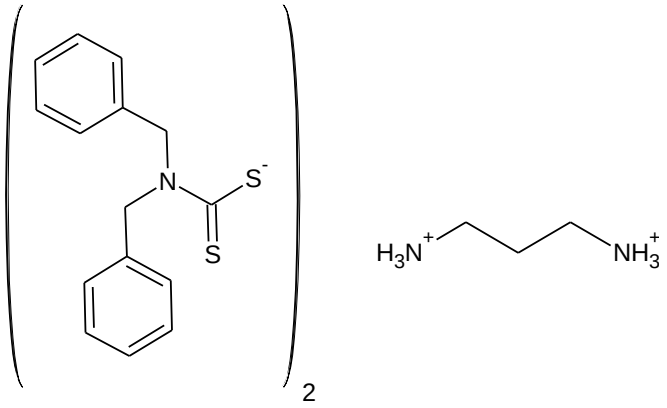


Figure 4.3. Structure of the complex of dibenzyldithiocarbamate and 1,3-diaminopropane, (PNA1).

The complex shown in Figure 4.3 is referred to as proposed new accelerator 1 (or PNA1). It is composed of a section of molecule present in both ZDBC and TBzTD, which has been shown to be good at cross-linking polychloroprene, and is in conjunction with a linear diamine. It was envisaged that when curing occurs, the linear diamine would separate and activate the polymer chain. Results in Chapter 3 have shown that linear diamines cross-link polychloroprene with no other additives present. However, they do have some health issues, so by binding the diamine within this complex it is hoped that these health issues can be overcome.

The spectrum of PNA1 from FTIR analysis (Figure 4.4) shows a peak at 2955 cm^{-1} associated with =C-H stretching, due to the two benzyl groups.[3, 4] Additionally a peak at 1556 cm^{-1} is present from $N^{+}H_3$ bending, and the band around 1492 cm^{-1} can be attributed to N-C=S stretching.

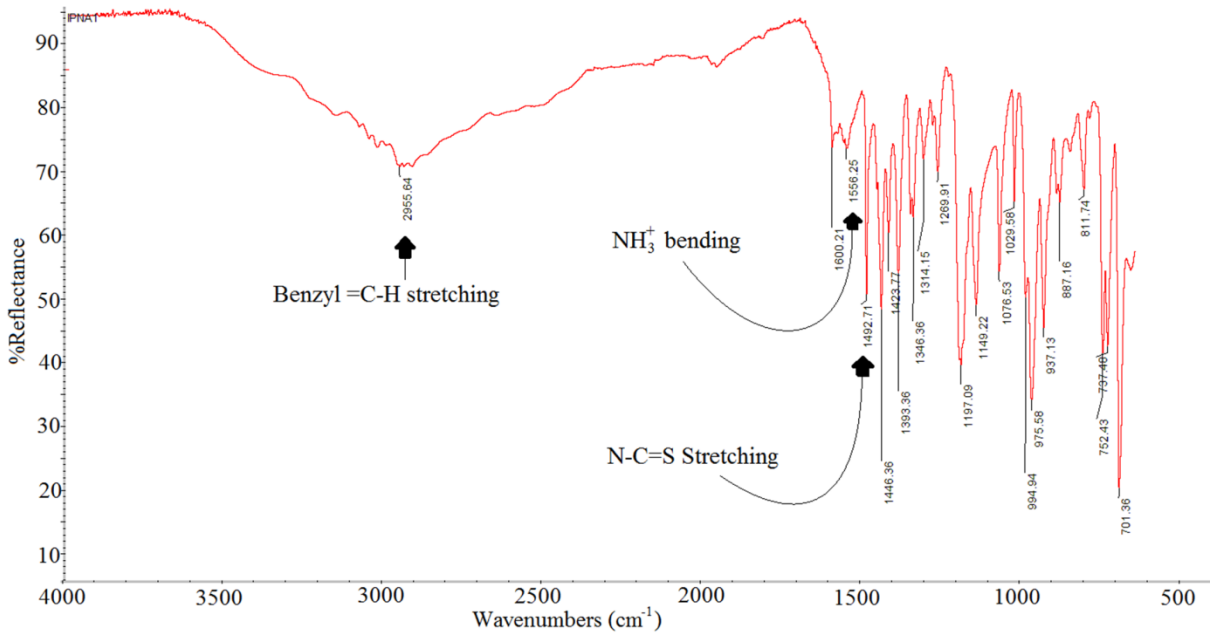


Figure 4.4. FTIR spectrum of new accelerator PNA1.

The next proposed accelerator also uses the dibenzyldithiocarbamate, as in PNA1, but in this case it is coupled with piperazine (Figure 4.5). As with PNA1, the second proposed new accelerator is a salt (PNA2). It was predicted that PNA2 would be able to utilise the cross-linking abilities of the dibenzyldithiocarbamate group, with the activating abilities of piperazine. Compared to PNA1 it was anticipated that the cyclic amine would rearrange the 1,2-isomer quicker, enabling faster cross-linking to occur.

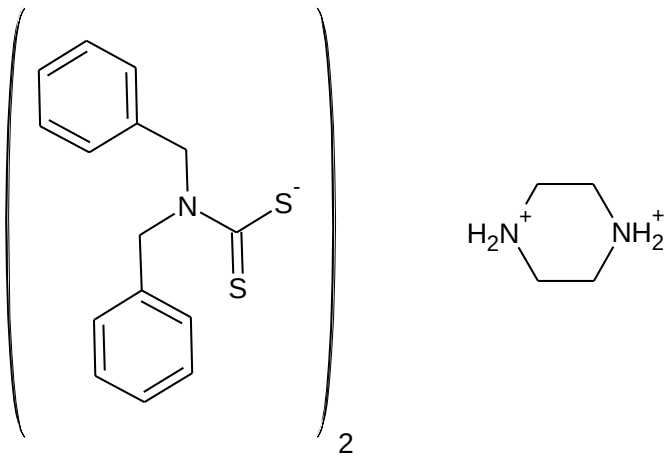


Figure 4.5. Structure of the complex of dibenzyldithiocarbamate and piperazine, (PNA2).

FTIR analysis of PNA2 (Figure 4.6) shows a peak at 2917 cm^{-1} associated with =C-H stretching in the spectrum, due to the two benzyl groups.[3, 4] Furthermore a peak at 2441 cm^{-1}

from N^+H_2 bending can be seen, and the band around 1492 cm^{-1} can be attributed to N-C=S stretching.

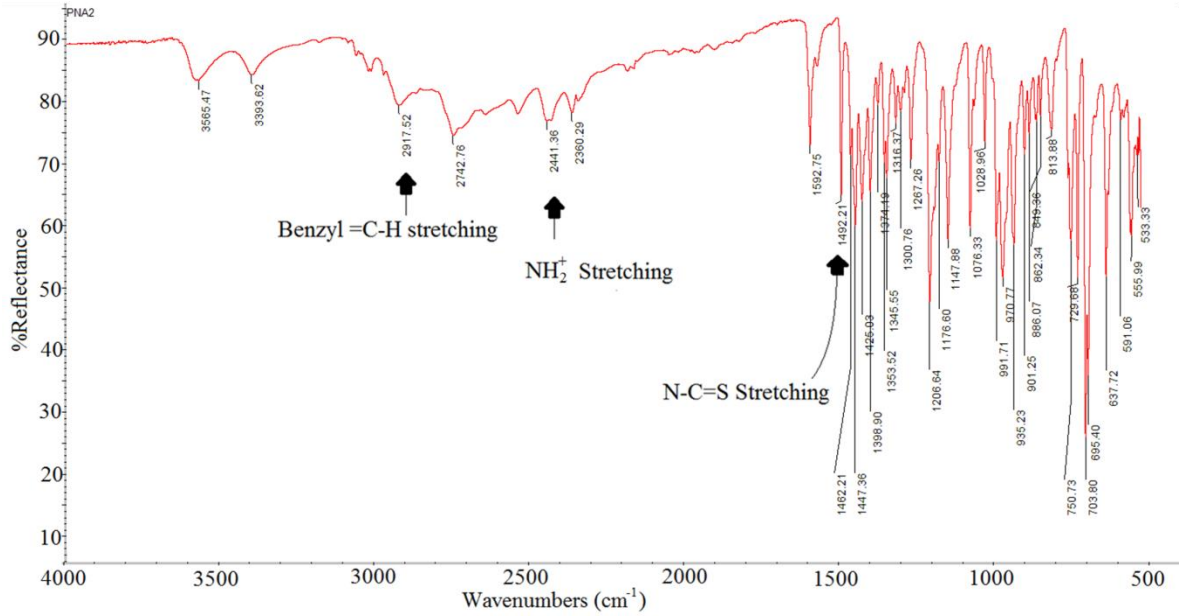


Figure 4.6. FTIR spectrum of new accelerator PNA2.

The final proposed new accelerator based on dibenzyldithiocarbamate, comprised a species containing an amine group and an alcohol group (Figure 4.7) rather than a diamine. As with the two previous proposed new accelerators the complex between dibenzyldithiocarbamate and 6-amino-hexan-1-ol (PNA3) had the dibenzyldithiocarbamate present for its cross-linking abilities. However, instead of a diamine PNA3 is coupled with a species with bi-functionality, namely an amine and an alcohol. It was hoped that by having two different groups on the activator part of this potential new accelerator it may alter cross-linking abilities owing to the dissimilar reactivity of the different functionalities. Due to the presence of only a single amine group on the activator section, the ratio between cross-linker and activator sections was 1:1, opposed to the 2:1 ratio used in the other PNAs.

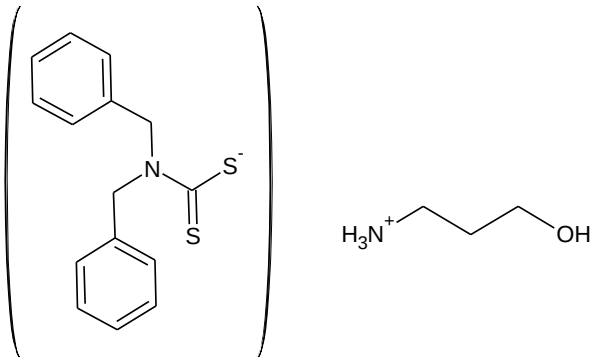


Figure 4.7. Structure of the complex between dibenzyldithiocarbamate and 6-amino-hexan-1-ol, (PNA3).

PNA3 was analysed by FTIR (Figure 4.8), the spectrum shows a peak at 2929 cm^{-1} associated with =C-H stretching, assigned to the two benzyl groups.[3, 4] Additionally a peak at 1544 cm^{-1} from $N^{+}H_3$ bending can be seen, and the band around 1493 cm^{-1} is attributed to N-C=S stretching. Furthermore, there is a peak at 3256 cm^{-1} from OH stretching.

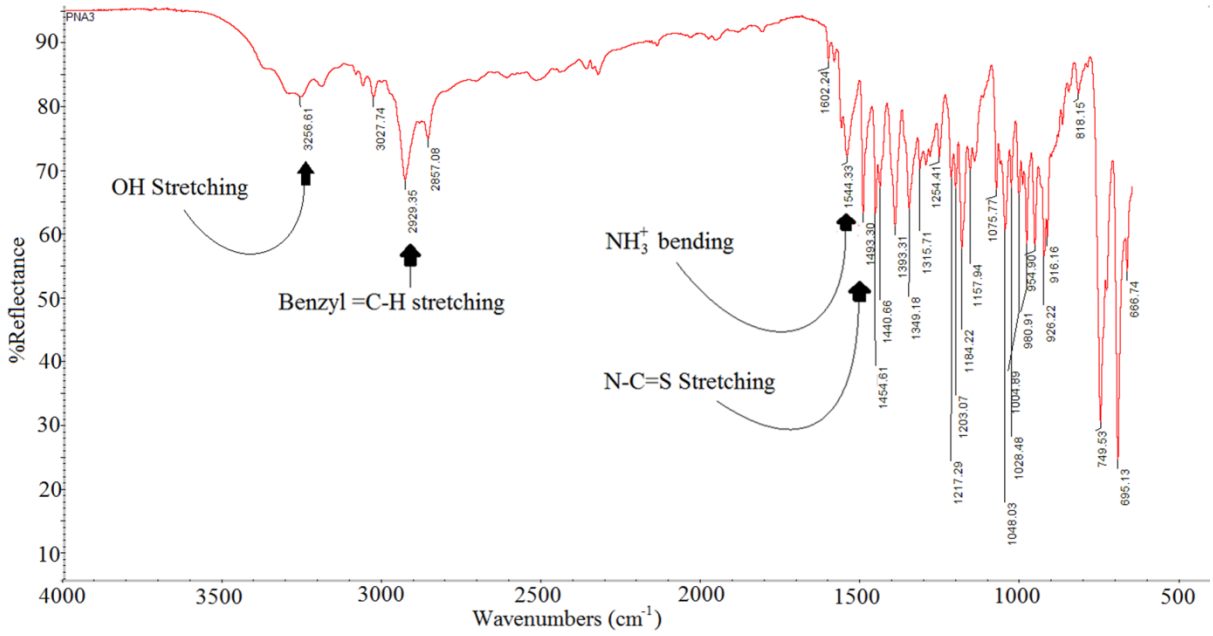


Figure 4.8. FTIR spectrum of new accelerator PNA3.

Rheological and tensile tests were performed on polychloroprene to screen the various PNAs (Table 4.4); this allowed those with the best results to undergo further testing. Also, at this initial stage, the data acquired helped to inform the next step in the design of the new accelerator. Results in Table 4.4 show that all of the PNAs cross-linked polychloroprene, proving the concept of a salt comprising a cross-linker and an activator. In these accelerators dibenzyldithiocarbamate acts as the cross-linker and is complexed with various amine-containing activators. The PNA1 system, which contains a linear diamine activator, cross-links with the highest UTS, shortest scorch and highest cure (Figure 4.9). This is an unexpected result as previous results with just piperazine or 1,3-diaminopropane show that the piperazine has the lower scorch time and higher cure. The binding within the complex therefore strongly affects the cross-linking activity of the individual components. The other activator component of the PNAs tested was in PNA3, 6-amino-hexan-1-ol, a linear alkyl chain with an amine group at one end and an alcohol group at the other. PNA3 has improved cross-linking of polychloroprene in the rheological tests (compared to PNA2), with a lower scorch time and higher cure; however the tensile properties were not as high (lower UTS etc.).

When compared to PNA1, PNA3 cross-linked more poorly in every aspect, both rheological and tensile properties were inferior, having a lower cure, MH and UTS. In summary, when combined with dibenzyldithiocarbamate a linear activator appears to perform better than a cyclic one. It also appears that a diamine is more effective than a mono-functional amine and alcohol. The results suggest that the primary amine can activate the chain faster than an alcohol, and that when cross-linking occurs the amine produces stronger cross-links.

Table 4.4. Rheology and tensile properties of polychloroprene containing 2.5 phr of various proposed new accelerators.

		PNA1	PNA2	PNA3
100 % Mod (MPa)		0.65	0.52	0.47
300 % Mod (MPa)		1.10	0.71	0.59
500 % Mod (MPa)		2.23	1.03	0.81
UTS (MPa)		9.5	7.6	4.9
Elongation at break (%)		878	907	DNB*
15 min MDR at 160 ºC	**MH (lb.in)**	6.93	6.31	4.58
	TS1 (mm:ss)	00:42	02:11	01:54
	T90 (mm:ss)	08:59	12:39	11:34
	Cure (lb.in/min)	3.05	0.76	0.85

* Did not break – Sample did not break within the extension of the test (see Appendix A).

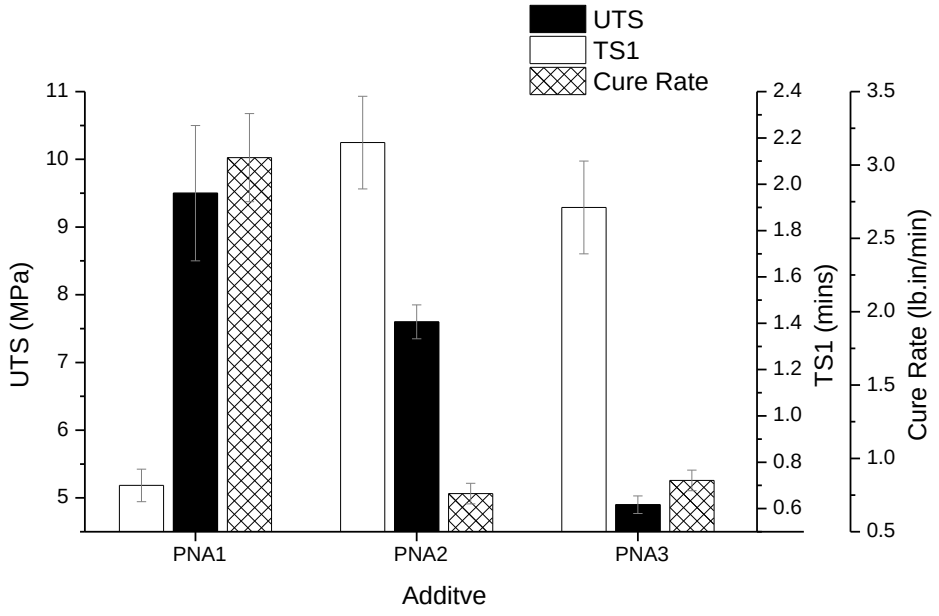


Figure 4.9. Mechanical properties of polychloroprene cross-linked with 2.5 phr of various proposed new accelerators. Error bars show one standard deviation from three data sets.

4.2.2. Candidate Accelerators with 1,3-Diaminopropane as Activator

Having shown that using a linear diamine as the activator of the PNA produced very good results, next studied was the 'cross-linking agent' component. Several different cross-linking molecules were trialled in conjunction with 1,3-diaminopropane. The first of these new cross-linkers was cyclohexyl-dithiocarbamic acid, combined as a salt with 1,3-diaminopropane (Figure 4.10), referred to as PNA4.

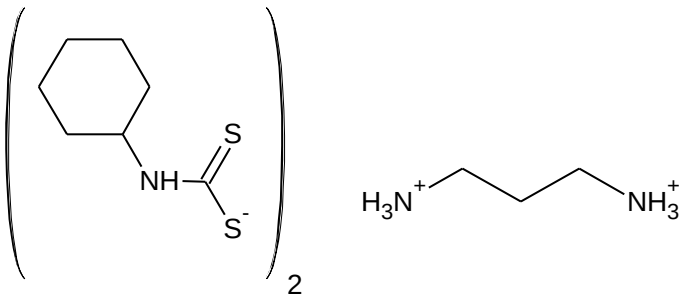


Figure 4.10. Structure of complex formed between cyclohexyl-dithiocarbamic acid with 1,3-diaminopropane (PNA4).

Compared to the cross-linking segment of PNA1, the cross-linking segment of PNA4 still has the dithiocarbamate group, but the remainder of the molecule has been decreased in complexity and size. This was achieved through the removal of one of the benzyl groups and the substitution of the other benzyl group with a cyclohexyl group. It was hoped that by having a smaller, more flexible molecule, there would be less steric hindrance which would make this molecule more reactive. Additionally, the change from a tertiary to a secondary amine within this cross-linker would aid in its reactivity.

Analysis of PNA4 by FTIR spectroscopy (Figure 4.11) shows a peak at 2927 cm^{-1} associated with -C-H stretching, due to the cyclohexyl group, in its spectrum.[3, 4] Additionally a peak at 2542 cm^{-1} is from $N^{+}H_3$ bending, and the band around 1492 cm^{-1} can be attributed to N-C=S stretching.

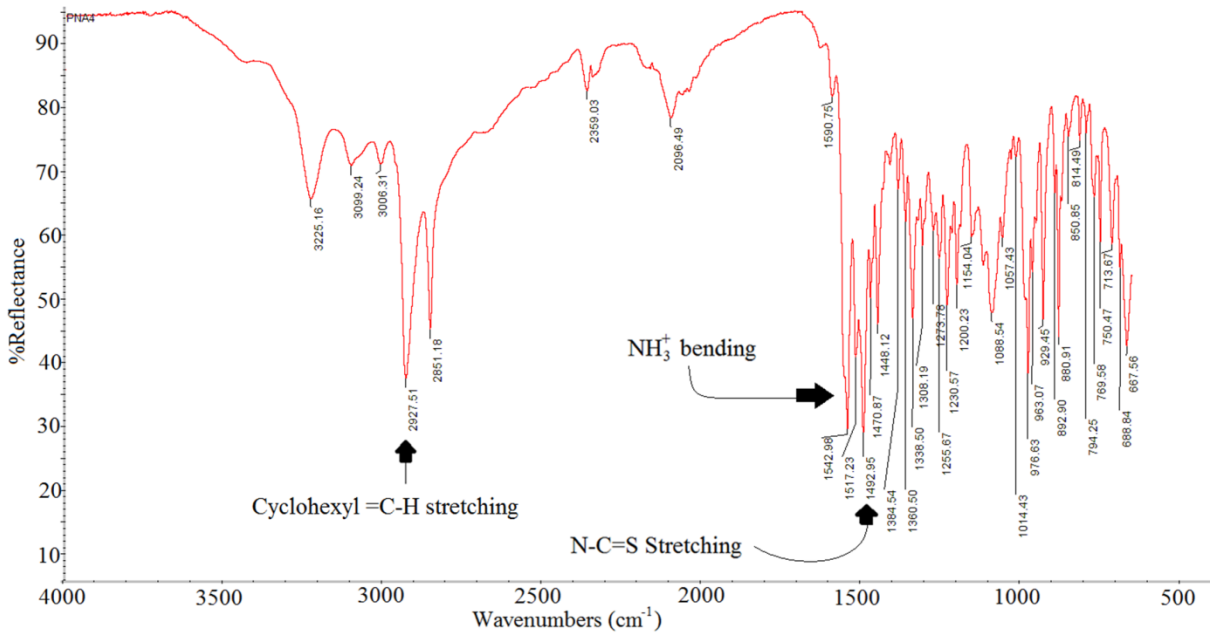


Figure 4.11. FTIR spectrum of new accelerator PNA4.

PNA5 (Figure 4.12) further simplified PNA4 by making the cross-linking section of the accelerator smaller again, in the hope of even less steric hindrance. However, it has also reduced the flexibility of the molecule and reverts the secondary amine within the cross-linker to a tertiary amine (as seen in PNA1-PNA3). This was achieved by having piperazine-1-carbodithionic acid as the cross-linking section. It was hoped that PNA5 would be able to utilise the piperazine based group on the cross-linking unit as well as using the diamine in activating the polymer chain. If true it would enable this molecule to cross-link very quickly. The spectrum of PNA5 achieved by FTIR analysis (Figure 4.13) shows a peak at 3182 cm^{-1} from $N^{+}H_3$ bending, and the band around 1451 cm^{-1} can be attributed to N-C=S stretching.[3, 4]

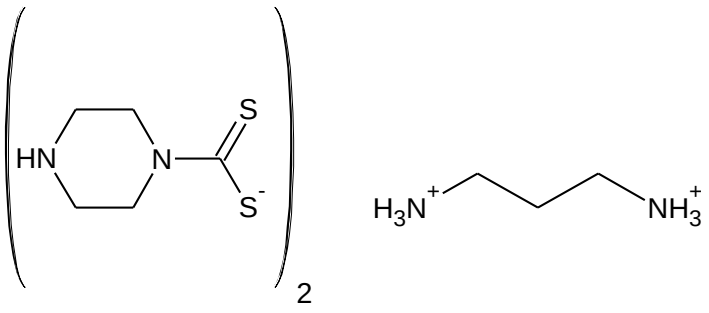


Figure 4.12. Structure of salt complex of piperazine-1-carbodithioic acid and 1,3-diaminopropane salt (PNA5).

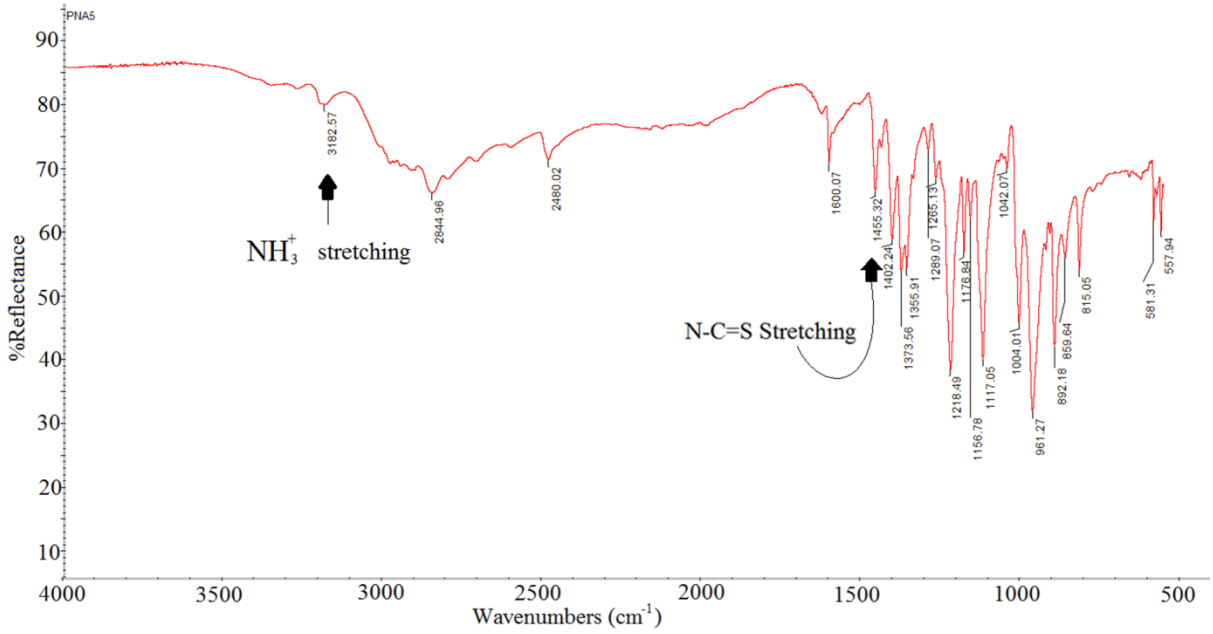


Figure 4.13. FTIR spectrum of new accelerator PNA5.

The other proposed new accelerator using 1,3-diaminopropane, had a larger cross-linker section (Figure 4.14), compared to previous accelerators. It was therefore expected that this molecule would perform worse than the PNA4 and PNA5 due to steric hindrance. There would also be less active centres in the same volume when used, as in rubber formulations materials are measured by weight and not by moles.

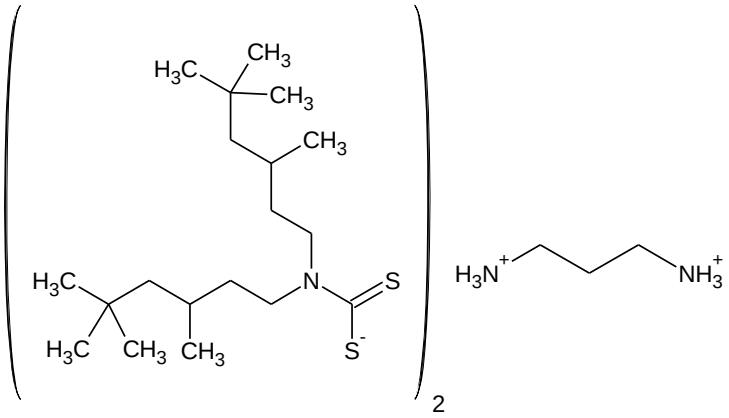


Figure 4.14. Structure of salt complex formed by bis-(3,5,5-trimethyl-hexyl)-dithiocarbamic acid and 1,3-diaminopropane (PNA6).

The cross-linking section of PNA6, as with the other PNAs, contains a dithiocarbamate group, and similar to PNA5 is connected to a tertiary amine, however PNA6 has two identical alkyl groups attached to the tertiary amine. This molecule, unlike the other PNAs tested does not contain a cyclic group, so any difference between these structures can be compared. PNA6 is

similar to PNA1, with the two benzyl groups replaced by alkyl chains. Analysis of PNA6 by FTIR (Figure 4.15) showed a peak at 2951 cm^{-1} associated with CH_3 stretching in its spectrum.[3, 4] Additionally the band around 1464 cm^{-1} can be attributed to N-C=S stretching.

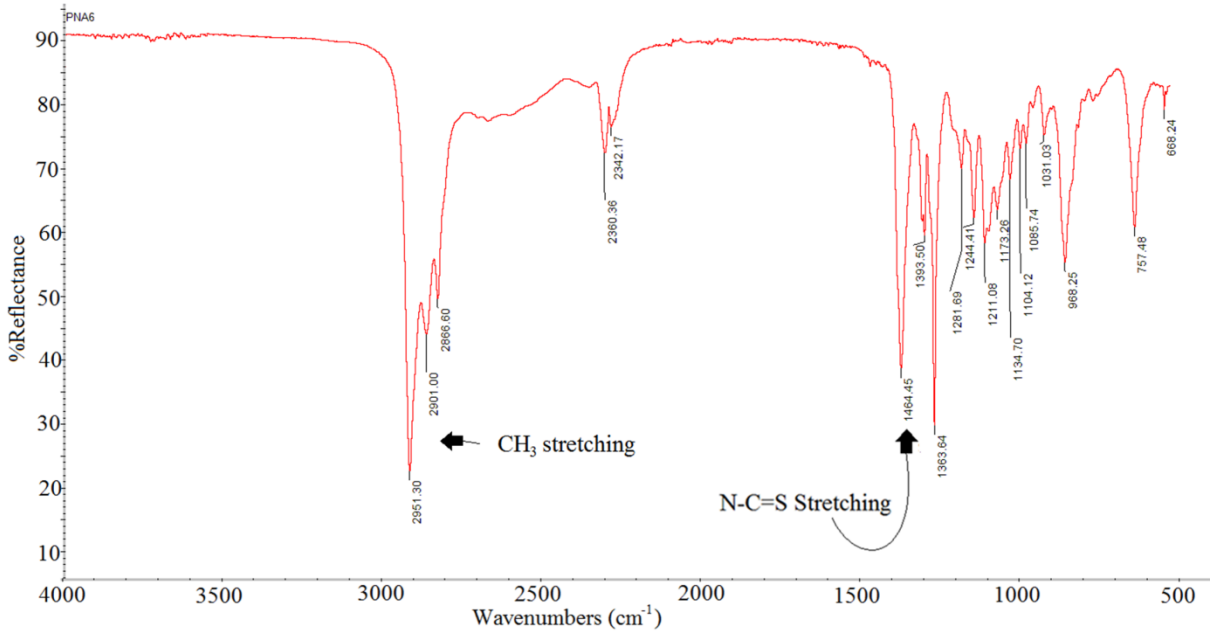


Figure 4.15. FTIR spectrum of new accelerator PNA6.

As with the previously tested PNAs, the molecules containing 1,3-diaminopropane have been examined *via* rheology and tensile testing (Table 4.5). Again, this is to allow them to be screened and give an indication for future molecules to be synthesised. The rheological results show that PNA4 cross-links faster than any of the other synthesised PNAs, including those based upon dibenzyldithiocarbamate (such as PNA1) (Figure 4.16). Table 4.5 also shows that all PNAs based upon 1,3-diaminopropane cross-link to some extent, proving that the dithiocarbamate group is useful as a cross-linking agent. The slightly unexpected result is that of PNA5 having a slower cure than PNA4, as PNA5 contains a piperazine-like structure within the cross-linking segment of the molecule and was therefore expected to cross-link very quickly. However, PNA4 cross-links much faster, attributed to the presence of a linear secondary amine present behind the dithio group. This is compared to PNA5 where a tertiary amine is adjacent to the dithio group. These results indicate that the flexibility of the cross-linker is important in cross-linking, with flexibility aiding in the speed of reactions as the more flexible PNA4 was able to cross-link faster. Additionally, the secondary amine is more reactive than the tertiary amine and its placement within the cross-linker is important. PNA5 contained a secondary amine in addition to a tertiary amine, but the secondary amine is part of a cyclic structure as opposed to near the dithio group. Section 4.2.1 showed that linear amines

were better at being an activator as part of a PNA than cyclic amines. Similarly in Chapter 3, Table 3.4 showed that dibutylamine, a linear secondary amine, had a higher cure rate than piperidine, a cyclic secondary amine.

Table 4.5. Mechanical properties of polychloroprene cross-linked with 2.5 phr of various PNAs.

		PNA4	PNA5	PNA6
100 % Mod (MPa)		0.8	0.71	0.48
300 % Mod (MPa)		1.69	1.17	0.55
500 % Mod (MPa)		4.14	1.84	0.68
UTS (MPa)		12.9	9.1	4.4
Elongation at break (%)		715	719	DNB*
15 min MDR at 160 ºC	**MH (lb.in)**	10.74	11.16	4.48
	TS1 (mm:ss)	00:29	00:55	07:19
	T90 (mm:ss)	03:35	07:24	13:36
	Cure (lb.in/m)	9.35	2.76	0.42

* Did not break – sample did not break at full extension when being tested (see Appendix A).

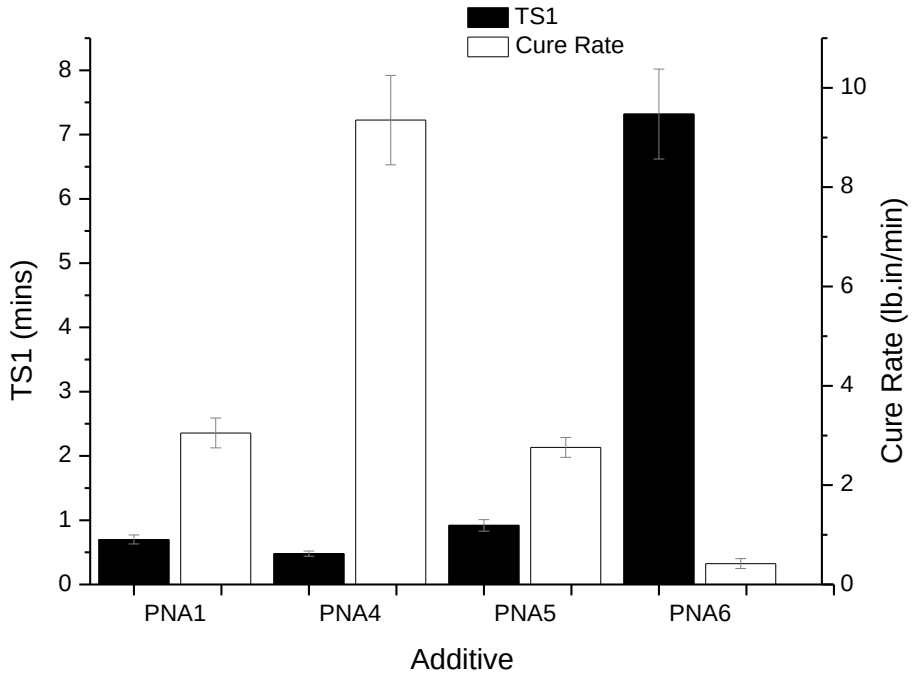


Figure 4.16. Rheological properties of polychloroprene cross-linked with 2.5 phr of various PNAs. Error bars show one standard deviation from three data sets.

The results suggest that the size of the cross-linking segment made a difference to cross-linking ability; PNA6 afforded a much higher scorch time and lower cure than PNA1. Here the only differences between the molecules are the groups attached to the tertiary amines in the cross-linking segment. The size of the PNA6 molecule has large inactive segments which cause much steric hindrance.

4.2.3. Candidate Accelerator with Longer Chain Linear Diamines

The final proposed new accelerator to be explored was similar to PNA5 but with a longer chain diamine as an activator. This was done to evaluate the chain length of the activator. Additionally, 1,6-diaminohexane used in PNA7 (Figure 4.17) is slightly safer to handle. Although once bound up within the complex the relative safety of the activator pre-complex appears to be largely irrelevant, the manufacture of the proposed new accelerator will be easier and safer with less hazardous constituent parts. The spectrum of PNA7 when analysed by FTIR (Figure 4.18) shows a peak at 3334 cm^{-1} from $N^{+}H_3$ bending, and the band around 1452 cm^{-1} can be attributed to N-C=S stretching.[3, 4]

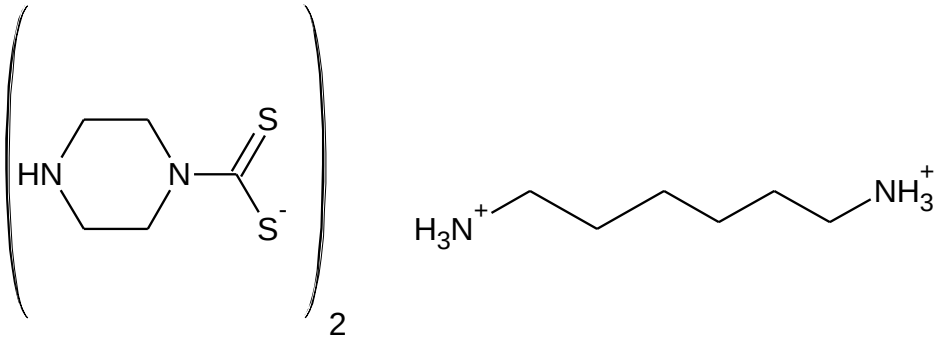


Figure 4.17. Structure of salt complex of piperazine-1-carbodithioic acid and 1,6-diaminohexane salt (PNA7).

As with PNA5, PNA7 contained piperazine-1-carbodithioic acid, but in combination with 1,6-diaminohexane. Table 4.6 demonstrates that the use of a longer chained linear diamine produces a longer scorch time and T90 and a lower cure. These results are indicative of a product that is slower to cross-link. This would seem to suggest that the use of a shorter chain diamine as the activator section produces an accelerator that can better cross-link polychloroprene. However as only two diamine lengths have been compared, these results are not conclusive and future work would be required to prove this.

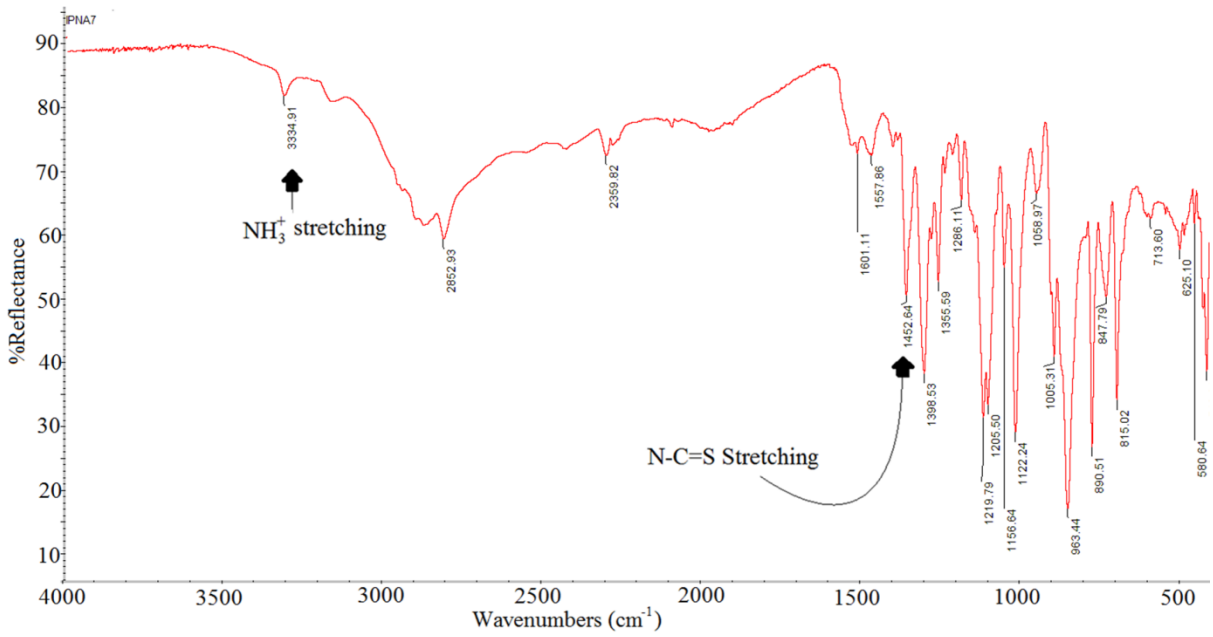


Figure 4.18. FTIR spectrum of new accelerator PNA7.

Table 4.6. Comparison of mechanical properties of polychloroprene cross-linked with 2.5 phr of either PNA5 or PNA7, whose difference is the length of linear diamine, with PNA5 containing 1,3-diaminopropane and PNA7 containing 1,6-diaminohexane.

		PNA5	PNA7
100 % Mod (MPa)		0.71	0.8
300 % Mod (MPa)		1.17	1.49
500 % Mod (MPa)		1.84	3.40
UTS (MPa)		9.1	8.0
Elongation at break (%)		719	617
15 min MDR at 160 ºC	**MH (lb.in)**	11.16	12.08
	TS1 (mm:ss)	00:55	01:17
	T90 (mm:ss)	07:24	11:10
	Cure (lb.in/min)	2.76	1.68

From the results gathered so far the molecules which have performed the most effective are PNA1, PNA4, PNA5 and PNA7. All of these molecules have a linear diamine as the activator section of the accelerator. These four molecules were to be taken forward to carry out more tests; however, due to difficulties with the manufacture of PNA1, the tests reported in the following section were conducted with the other three PNAs mentioned above and PNA2 in

place of PNA1. PNA3 was omitted as the bi-functionality of the activator segment, was not as good as a diamine in cross-linking, and PNA6 overlooked due to the poor cross-linking results attributed to the large cross-linker segment causing steric hindrance.

4.3. Cross-Linking Properties of the Best Performing Candidate Accelerators in Combination with Other Additives

Having narrowed the number of PNAs down to four (by studying them on their own in polychloroprene gum stock), they were next observed in conjunction with different additives. The first additive they were studied with was ZnO; this was to test compatibility with this commonly used additive. It also allowed a comparison with ETU and ZnO in the gum stock. The second additive examined in conjunction with the PNAs was secondary accelerator TBzTD; again for compatibility. After these tests were completed, a single, most effective, PNA could then be taken forward as the replacement for ETU for further tests and optimisation (Chapter 5). The new accelerators were tested in polychloroprene as described in Section 4.2 but with 5 phr ZnO now present, the mechanical properties are shown in comparison to ETU with ZnO in polychloroprene (Table 4.7).

Table 4.7. Physical properties of polychloroprene with 5 phr ZnO cured with 2.5 phr of a PNA or ETU.

		ETU	PNA2	PNA4	PNA5	PNA7
100 % Mod (MPa)		1.06	0.49	0.86	0.91	0.91
300 % Mod (MPa)		1.73	0.69	1.68	1.62	1.68
500 % Mod (MPa)		4.08	1.01	4.58	3.58	3.59
UTS (MPa)		10.0	8.3	8.2	5.6	7.3
Elongation at break (%)		600	DNB*	581	565	619
15 min MDR test at 160 °C	**MH (lb.in)**	15.01	6.29	14.58	14.69	12.95
	TS1 (mm:ss)	00:57	02:22	00:29	01:16	01:20
	T90 (mm:ss)	06:56	11:04	04:59	09:52	10:44
	Cure (lb.in/min)	5.26	0.71	9.93	2.62	2.11

*Sample did not break (see Appendix A).

Table 4.7 and Figure 4.19 show that all of the PNAs, when used in combination with ZnO, produce slightly lower UTS results than when the PNAs were used to cross-link polychloroprene alone, with the exception of PNA2. The results for the PNA2-containing samples do not break in either case (with or without ZnO), therefore the UTS quoted is the strength when the instrument has reached its full extension. This is compared to the results of the other PNAs, where the UTS quoted is when the sample breaks. Although the results (excluding PNA2) seem to indicate worse cross-linking, as there is a lower UTS, this is not the case. This can be seen when the 500 % moduli are compared - they all (excluding PNA2) have higher values (Figure 4.20), showing that in combination with ZnO more cross-links are formed producing stiffer rubbers. These results indicate that there is no unwanted interaction between the PNAs and ZnO.

The results also indicate that 5 phr ZnO is too much in this cure system. Literature states that there is an increase in UTS with an increase in cross-links up to a point, after which there will be a decrease in UTS.[5] The literature also states that the modulus at a given extension will continue to increase with an increase in cross-links.[5] This is what has been observed here. The exact level of ZnO needed in a cure system is dependent upon the requirements of the final properties. These assessments were performed as initial screening tests of the PNAs with ZnO; a more complete study of the level of ZnO required within a full commercial system is examined in Chapter 5.

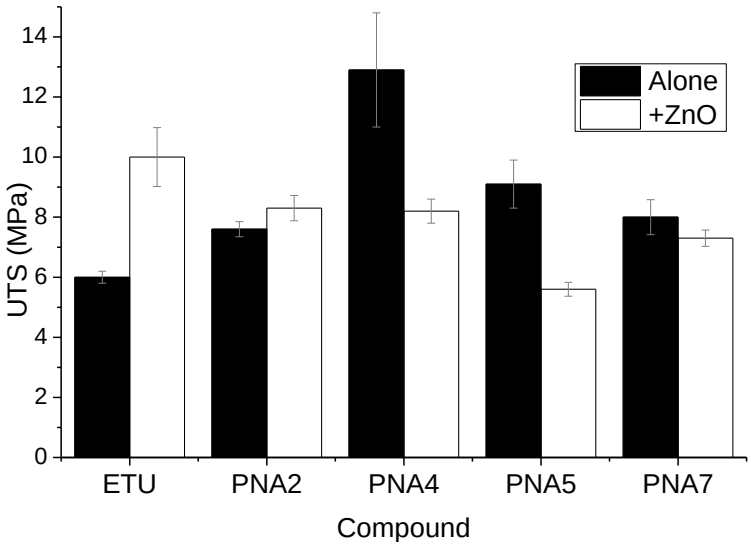


Figure 4.19. Comparison of ultimate tensile strength of polychloroprene cross-linked with various additives (at 2.5 phr), alone and in combination with 5 phr zinc oxide. Note the result from PNA2 is at the full extension of the machine rather than at breaking point, as with other samples. N.B. Error bars show one standard deviation from three data sets.

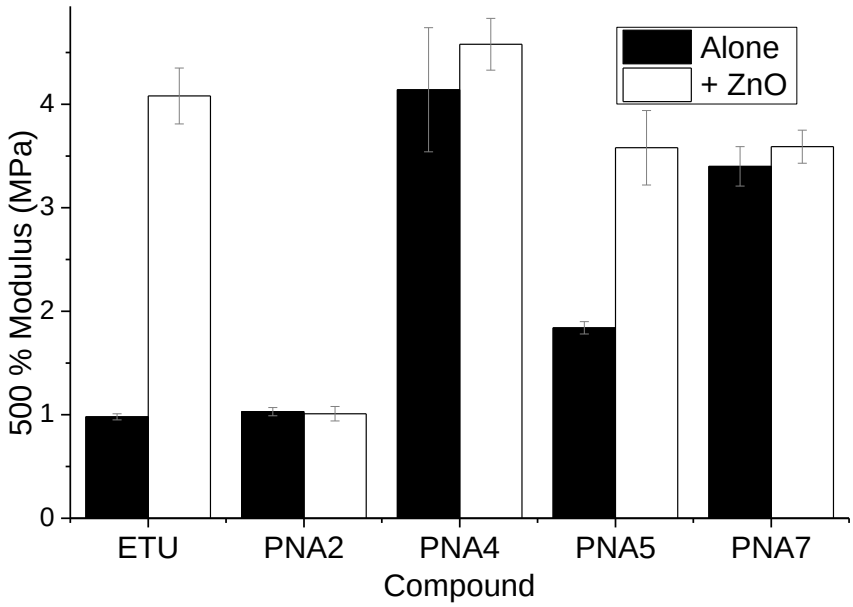


Figure 4.20. Comparison of the 500 % modulus of polychloroprene cross-linked with various additives (at 2.5 phr), both alone and in combination with 5 phr zinc oxide. Error bars show one standard deviation from three data sets.

Examination of the rheological properties shows that PNA5 and PNA7 have similar results (Figure 4.21). This is unsurprising as the only difference between them is the length of the diamine in each accelerator. Previous results (Section 3.2.2) have shown that the length of diamine does not make any difference to physical or mechanical properties. PNA5 (shorter amine), however, does give slightly more favourable properties, with higher MH and cure and lower T90. Consequently, the properties of the rubber cross-linked by PNA5 are closer to those of polychloroprene cross-linked with ETU and ZnO (compared to the PNA7 system). Polychloroprene rubber cross-linked with PNA2 showed rheological properties furthest away from ETU/ZnO cross-linked polychloroprene rubber. The MH and cure were much lower than the other samples and considerably inferior to the ETU and ZnO cured polychloroprene sample. PNA4 appears to produce the closest to the desired results, with an MH similar to that of the ETU and ZnO formulation, together with the lowest T90 and the highest cure rate of all samples tested, including the ETU and ZnO formulation. This would seem to indicate that PNA4 was the most effective additive of the proposed new accelerators. However, the scorch time is less than 30 seconds, which is about half that of the ETU/ZnO sample, and the same as when PNA4 cross-linked polychloroprene alone. A scorch time this low could cause problems with moulding samples as the rubber could begin to cure before the mould was fully filled. Furthermore when put into a filled master batch an increase in filler level could cause a

further decrease in scorch time.[6] This would produce poorly vulcanised samples which would not be sought in an industrial setting.

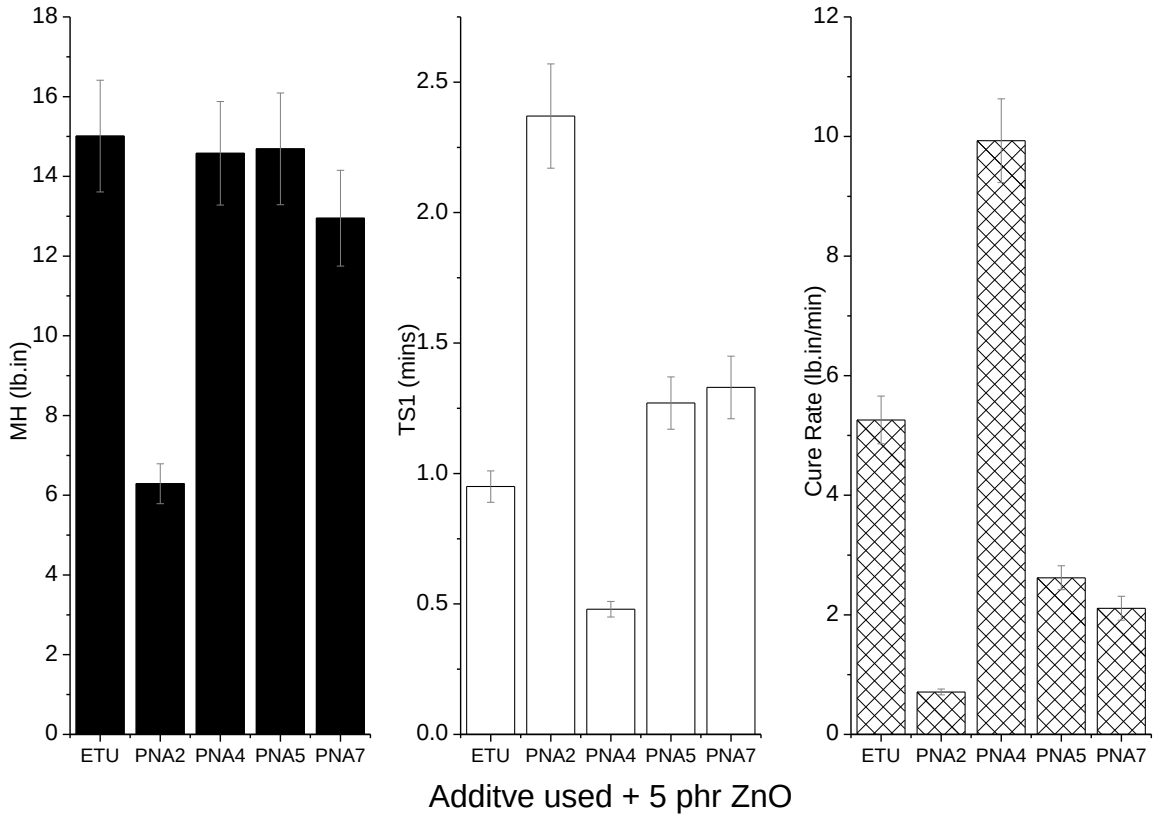


Figure 4.21. Rheological properties of polychloroprene with 5 phr zinc oxide, cross-linked with various other additives. Error bars show one standard deviation from three data sets.

The results of polychloroprene cross-linked with the proposed new accelerators in conjunction with ZnO appear to suggest that PNA5 is the most suitable replacement for ETU. This is due to the low scorch time of PNA4, which excludes this compound from being an acceptable additive. Additionally, PNA5 has similar tensile properties to the ETU/ZnO system, and rheological properties that are also not too dissimilar.

The selected PNAs were next studied in conjunction with TBzTD. As with all thiuram-based accelerators, TBzTD is known to not cure polychloroprene on its own but does so in the presence of an activator. As there is an activator present in the PNAs any improvement in the cures, (compared to the PNA alone in polychloroprene) must be due to a reaction between the activator and TBzTD. Therefore these results will be an indication of the performance of the activator. The mechanical results for the tests in polychloroprene are shown in Table 4.8.

Table 4.8. Rheological and tensile properties of polychloroprene with 2 phr TBzTD cross-linked with 2.5 phr of a proposed new accelerator.

		PNA2	PNA4	PNA5	PNA7
100 % Mod (MPa)		0.51	0.83	0.95	0.64
300 % Mod (MPa)		0.68	1.76	2.03	1.08
500 % Mod (MPa)		0.95	4.35	5.94	1.92
UTS (MPa)		6.8	10.1	6.8	10.3
Elongation at break (%)		DNB*	652	514	808
15 min MDR test at 160 ºC	**MH (lb.in)**	5.09	11.60	14.32	8.92
	TS1 (mm:ss)	03:34	00:29	00:28	01:51
	T90 (mm:ss)	12:57	04:14	05:20	11:39
	Cure (lb.in/min)	0.46	9.73	11.45	1.02

*Sample did not break (see Appendix A).

As when the PNAs were used in combination with ZnO, the most pertinent tensile property here is the 500 % modulus results rather than the UTS (Figure 4.22). This again is because of excess cross-link formation causing a reduction in the UTS, but an increase in modulus at a given extension. With PNA2 and PNA4 (in combination with TBzTD) the results at 500 % extension are very similar to those when the PNA is used alone. Thus, the addition of a secondary accelerator did not aid in the cross-linking process. These results are unsurprising and can be attributed to the fact that TBzTD is inactive in these compounds, as TBzTD must be activated to work. However, PNA5 produces a much higher 500 % modulus and PNA7 produces a much lower 500 % modulus, when compared to those polychloroprene samples cross-linked with only their respective PNAs. This big difference is due to the different diamine content, the 1,3-diaminopropane of PNA5 being much better at activating TBzTD. This can be seen in Table 4.2, where different length amines were tested with TBzTD, and 1,3-diaminopropane produced much higher 500% modulus compared to the 1,6-diaminohexane (which PNA7 contains). As PNA5 produces better results with TBzTD, than without this indicates that TBzTD is still being activated and cross-links in tandem with the PNA present in each sample Thus, the reactivity of the activator in PNA5 is such that it can activate the accelerator section of the PNA and activate TBzTD.

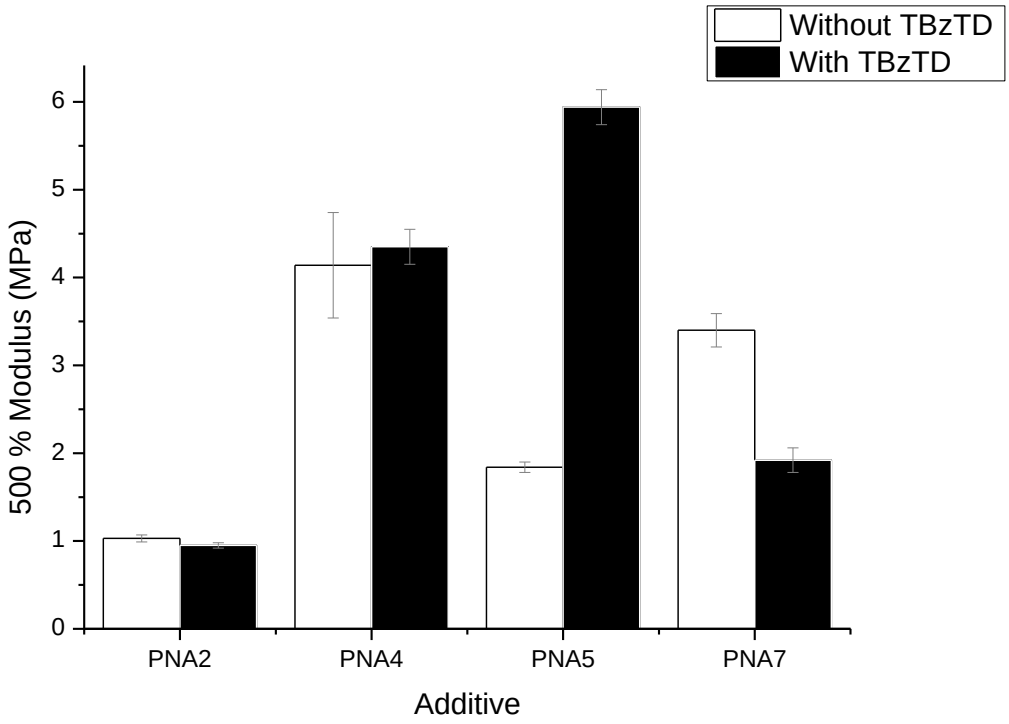


Figure 4.22. 500 % modulus results for various PNAs in polychloroprene, tested with and without TBzTD. Error bars show one standard deviation from three data sets.

The rheological results show that both PNA2 and PNA7 produce an increase in the scorch and T90 and a decrease in cure rate with the addition of TBzTD (compared to those samples tested without TBzTD) (Figure 4.23). Together with their tensile results discussed earlier in this section, this indicates that neither of these accelerators cross-link well in combination with TBzTD. The most likely explanation for this is the activator part of the PNAs. This can be seen with PNA5, having shown improved properties when in combination with TBzTD, but PNA7, whose only difference to PNA5 is the diamine of the activator, having the aforementioned decline in properties.

TBzTD has been shown to enhance cross-linking with PNA5. This can be seen through a lower scorch and T90 and a much higher cure rate compared to the polychloroprene sample cross-linked with only PNA5. Consequently, it can be surmised that the activator aspect of the PNAs makes a large difference to the performance of the PNA. Cross-linking polychloroprene with PNA4 and TBzTD produced rheological results that were very similar to those with PNA4 alone, typified by the very low scorch time and T90 and high cure rate. These results were also very similar to those of PNA5; both of these PNAs have the same

diamine as the activator, again adding credence to the importance of the activator. The results herein indicate that 1,3-diaminopropane (as the activator) gives the greatest and fastest cure. There is also the possibility that 1,3-diaminopropane activates the TBzTD allowing it to cross-link polychloroprene before the cross-linker component of the PNA does. This would indicate that the cross-linker part of the PNA curing polychloroprene was a secondary reaction and TBzTD cross-linking was the primary reaction. However, direct evidence of this would be difficult to ascertain as both TBzTD and the accelerator aspect of the PNA produce similar results.

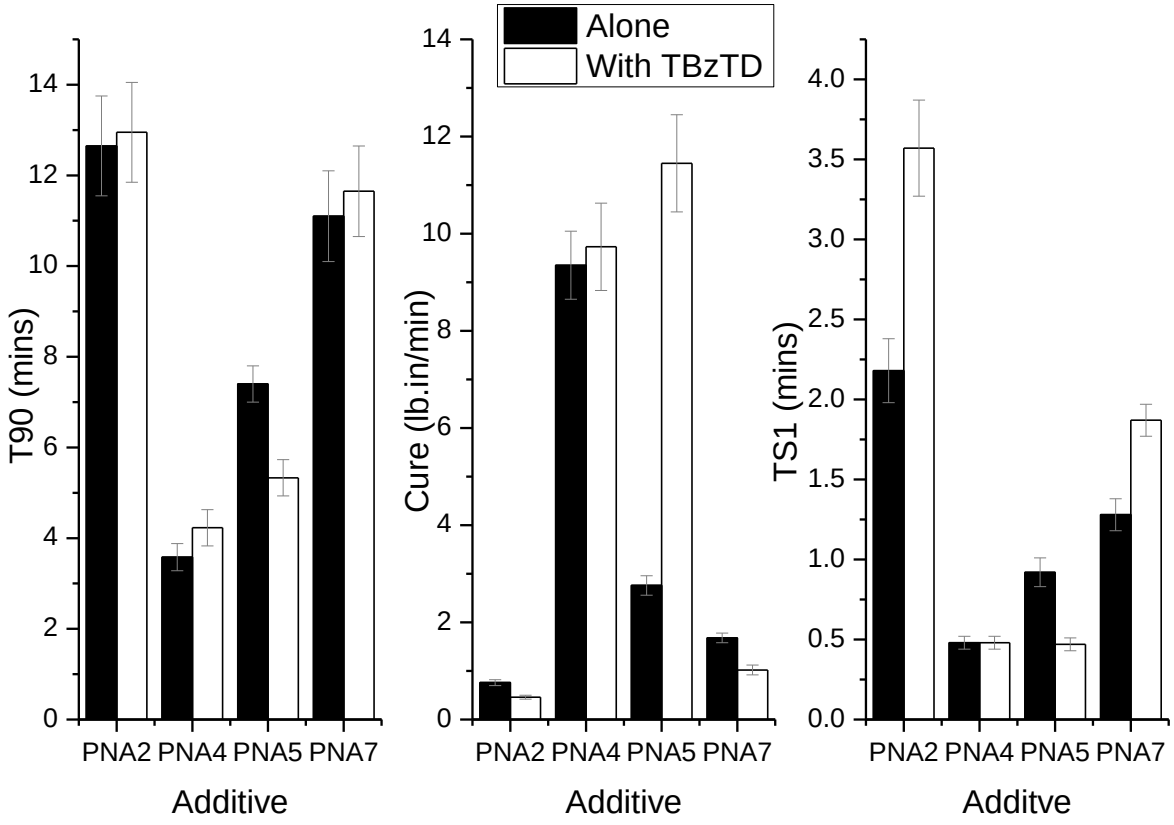


Figure 4.23. Rheological properties of polychloroprene cured with various PNAs with and without TBzTD. Error bars show one standard deviation from three data sets.

4.4. Chapter Conclusions

The results in Section 4.3 where the PNAs are examined with TBzTD or ZnO give indications of the best candidate to be taken forward to the next stage. In all three tests conducted with PNA4 in polychloroprene (on its own, with ZnO and with TBzTD), the scorch time was about 30 seconds. As these were all tested in unfilled rubber, this time is too low as it would present potential problems with premature curing when samples were being moulded in a filled

master batch i.e. curing before the mould has filled. For this reason, PNA4 has been discounted as a potential replacement for ETU. With PNA2, a poor cure was observed in all cases with a cure rate always below 1 lb.in/min. A low MH and high elongation at break were also seen in all of the results for PNA2, indicating a low amount of cross-links. Therefore PNA2 has been ruled out of any further tests. PNA5 and PNA7 give similar results to each other when tested on their own or in conjunction with ZnO. PNA5 produces a slightly higher cure rate and lower T90 in both cases. When they were both tested in conjunction with TBzTD, PNA5 cured much faster and at a much higher rate than PNA7. Consequently, PNA5 has been taken forward for testing and optimisation in a master batch. The main reason for this is the controllability of the formulations with PNA5 in, as the addition of ZnO increased the scorch and T90 times, whilst TBzTD reduced both of properties – compared to the polychloroprene that contained only PNA5. Thus, by using a combination of these two additives it should be possible to produce a master batch formulation that has similar properties to those of an ETU-containing formulation.

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CHAPTER 5

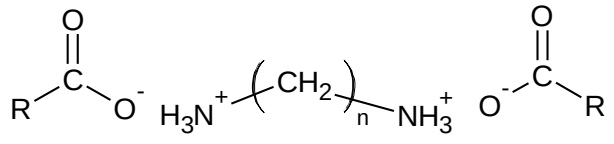
OPTIMISING A NEW POLYCHLOROPRENE ACCELERATOR FOR COMMERCIALISATION

5. Optimising a New Polychloroprene Accelerator for Commercialisation

A new accelerator, PNA5, has shown potential as a replacement for ETU in pure polychloroprene gum stock (Chapter 4). This has been observed when in combination with other additives. Therefore, this chapter details the optimisation of cross-linking additives in a polychloroprene master batch. The additives, whose levels were altered, included PNA5, magnesium oxide (MgO), zinc oxide (ZnO), tetrabenzyl thiuramdisulfide (TBzTD - as a secondary accelerator) as well as a multi-functional additive (MFA). Before the master batch was optimised the MFA was investigated. To do this, two diamines, and their ratio to stearic acid in the MFA were studied, and subsequently the champion MFA was investigated in gum stock. The MFA was present to reduce the levels of ZnO present in the final master batch. With the ultimate aim that a final filled master batch formulation comprising PNA5 could be found that matched the abilities of an ETU-containing master batch formulation. To this end, the level of amine present in PNA5 was also investigated with the hope that it could be made to more closely match the properties of ETU. As previously mentioned, it is worth noting that use of imperial units are widely accepted in rubber technology and as such are used throughout for mechanical property characterisation. Additionally, all additives are measured by weight rather than stoichiometrically as is standard practice in rubber technology.

5.1. Multi-functional Additive Studies

The use of an MFA to help cross-linking has been shown in several papers to reduce the need for ZnO when cross-linking polychloroprene.[1-3] This section discusses the use of an MFA, firstly by optimising the MFA to be used and then by testing it to show that a reduction in ZnO content in the final product would be possible. All of the MFAs used in this section are a complex between a linear diamine and stearic acid (Figure 5.1). Additionally, due to the presence of stearic acid in the MFA, all MFAs were tested with no other additives in pure rubber gum at levels quoted.



Fatty Acid Linear Diamine Fatty Acid

Figure 5.1. Multi-functional additive complex structure, comprising of two fatty acids and a linear diamine.

Initially, a stoichiometric ratio between the diamine and stearic acid of 1:2 was used. Two different diamines were tested as part of the MFA; these were 1,3-diaminopropane, (1,3-MFA) and 1,4-diaminobutane (1,4-MFA). Both of these MFAs were shown to cross-link polychloroprene without the need for other additives (Table 5.1); with 1,3-MFA affording slightly superior cross-linking properties than 1,4-MFA (higher cure and UTS) (Figure 5.2). This trend has been shown previously when the shorter chain diamines were used in conjunction with TBzTD (Table 4.2), where they produced more favourable results compared to the longer diamines. When these results are compared to the diamines cross-linking polychloroprene on their own, the diamines alone all produced similar results (Table 3.7).

Table 5.1. Mechanical properties of polychloroprene cross-linked with 1.5 phr of two different multi-functional additives.

	Tensile Tests cured 160 °C for 1.5 x T90				**15 minute MDR test at 160 °C**			
	100 % Mod (MPa)	**500 % Mod (MPa)**	**UTS (MPa)**	**Break (%)**	**MH (lb.in)**	**TS1 (mm:ss)**	**T90 (mm:ss)**	**Cure (lb.in/m)**
1,3-MFA	0.55	1.08	9.1	DNB*	8.0	02:44	09:29	1.16
1,4-MFA	0.49	0.79	6.7	DNB*	6.74	05:22	12:13	0.66

*Sample did not break before tensometer reached full extension (see Appendix A).

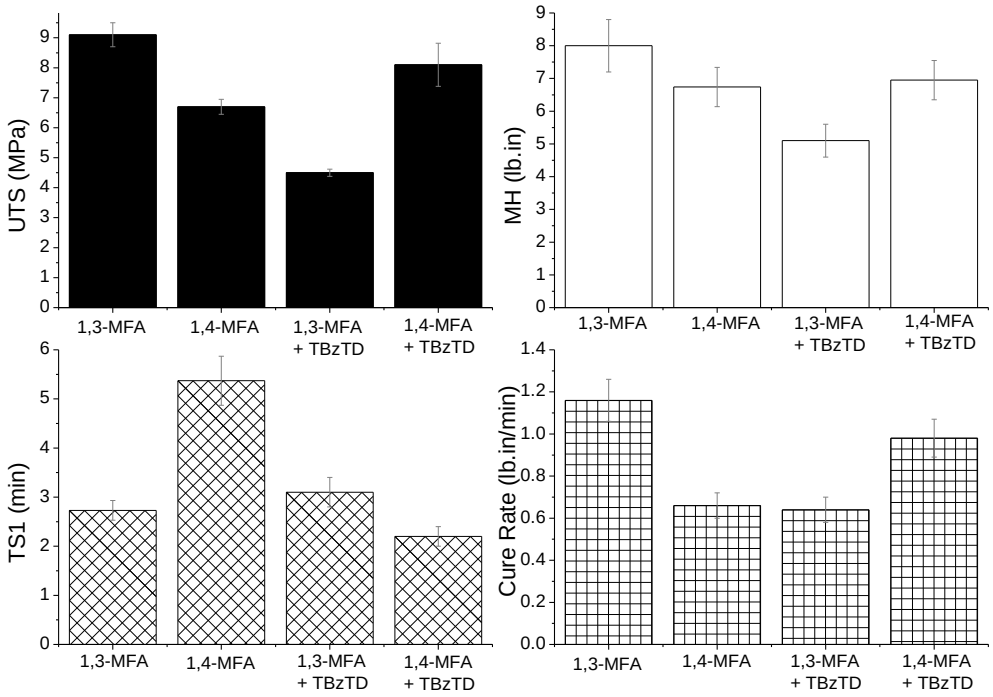


Figure 5.2. Mechanical properties of polychloroprene with 1.5 phr multi-functional additives, on their own and in conjunction with 2 phr TBzTD. Error bars show one standard deviation from three sets of data.

The designated role of the MFA, however, was not as an accelerator itself but as an activator, in addition to its role as a processing aid. To this end, the two MFAs were tested in conjunction with TBzTD (Table 5.2.).

Table 5.2. Mechanical properties of polychloroprene containing 2 phr TBzTD in addition to 1.5 phr of two different MFAs.

	Tensile Tests cured 160 °C for 1.5 x T90				**15 minute MDR test at 160 °C**			
	100 % Mod (MPa)	**500 % Mod (MPa)**	**UTS (MPa)**	**Break (%)**	**MH (lb.in)**	**TS1 (mm:ss)**	**T90 (mm:ss)**	**Cure (lb.in/m)**
1,3-MFA	0.50	0.73	4.5	DNB*	5.1	03:06	09:59	0.64
1,4-MFA	0.54	1.07	8.1	DNB*	6.95	02:12	10:05	0.98

*Sample did not break before tensometer reached full extension (see Appendix A).

Table 5.2 shows that TBzTD works more favourably with 1,4-MFA than 1,3-MFA, producing higher UTS and higher cure – both compared to 1,4-MFA alone and 1,3-MFA with TBzTD (Figure 5.2). Conversely, 1,3-MFA is less effective at cross-linking polychloroprene when in combination with TBzTD, than when alone (indicated by a lower MH, UTS and cure rate). The results also indicate that 1,3-MFA alone is a better cross-linker than any of the other formulations containing an MFA, producing a higher UTS, MH and cure than any of the other tested formulations.

The standard ratio of diamine to stearic acid in an MFA is 1:2, but to try and improve the cross-linking performance the level of diamine was increased to 1:1. Initially, the MFAs were trialled in polychloroprene in combination with TBzTD as a cross-linker, to see if the increase in diamine would improve their ability as an activator. Table 5.3 shows the mechanical properties of the 1:1 MFAs when tested with TBzTD. The results which contain the 1:1 MFAs are very similar to those of the 2:1 MFAs when in combination with TBzTD (Figure 5.3).

Table 5.3. Mechanical properties of polychloroprene cured with 2 phr TBzTD, and 1.5 phr MFA where the diamine to stearic acid ratio of 1:1.

	Tensile Tests cured 160 °C for 1.5 x T90				**15 minute MDR test at 160 °C**			
	100 % Mod (MPa)	**500 % Mod (MPa)**	**UTS (MPa)**	**Break (%)**	**MH (lb.in)**	**TS1 (mm:ss)**	**T90 (mm:ss)**	**Cure (lb.in/m)**
1,3-MFA (1:1)	0.53	0.78	5.0	DNB*	5.15	02:51	09:51	0.64
1,4-MFA (1:1)	0.48	0.87	7.2	DNB*	6.33	02:32	10:22	0.80

*Sample did not break before tensometer reached full extension (see Appendix A).

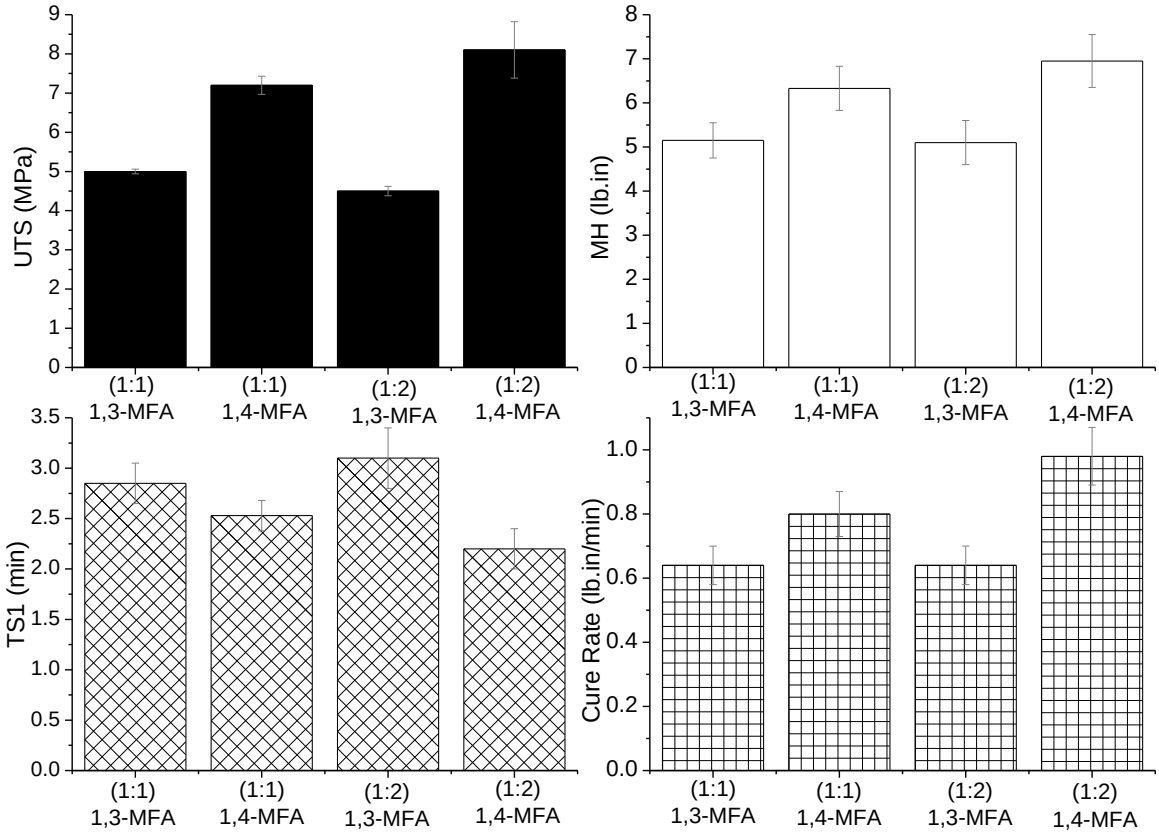


Figure 5.3. Mechanical properties of polychloroprene in combination with 2 phr TBzTD cross-linked with multi-functional additives containing diamine to stearic acid ratio of 1:1 or 1:2. Error bars show one standard deviation from three sets of data.

Figure 5.3 shows that 1,4-MFA is slightly more able to cross-link polychloroprene than 1,3-MFA when they are used in combination with TBzTD, seen through higher UTS and cure

rate. Additionally, the results for both 1,3-MFA and 1,4-MFA at ratios of 1:1 are almost identical to those at a ratio of 2:1, and as a 2:1 MFA would be safer and cheaper to manufacture than a 1:1 MFA, due to the lower level of diamine, no further work was completed in this area of study. Additionally, 1,4-MFA has been shown to be better at activating TBzTD than 1,3-MFA, therefore follow-on studies proceeded with 1,4-MFA, with a stearic acid to diamine ratio of 2:1.

To ascertain if the use of an MFA could reduce the level of ZnO required in a formulation, 1,4-MFA was tested in polychloroprene gum stock in both an ETU-containing and a PNA5-containing formulation (Table 5.4). These formulations had low levels of ZnO and are directly compared to formulations without the MFA but with higher levels of ZnO.

Table 5.4. A comparison between polychloroprene with standard formulations and those with low ZnO contents which contain an MFA, for both ETU and PNA5. The level of each of the additives is measured in phr.

Formulation		**5.1**	**5.2**	**5.3**	**5.4**
ETU		1	1	-	-
ZnO		5	1	5	1
MgO		4	4	4	4
1,4-MFA		-	1.5	-	1.5
PNA5		-	-	2.5	2.5
Stearic acid		1	-	1	-
100 % Mod (MPa)		1.22	1.10	1.15	1.04
300 % Mod (MPa)		2.02	1.91	1.97	1.60
500 % Mod (MPa)		5.59	4.68	4.85	3.34
UTS (MPa)		9.8	9.9	7.7	9.7
Elongation at break (%)		561	603	556	648
15 min MDR test at 160 ºC	**MH (lb.in)**	17.58	14.69	16.72	14.17
	TS1 (mm:ss)	01:16	01:19	01:10	00:46
	T90 (mm:ss)	09:47	11:26	10:33	05:46
	Cure (lb.in/min)	3.12	1.8	2.8	5.16

The tensile results in Table 5.4 and Figure 5.4 are similar for all four formulations. This signifies that not only can the addition of an MFA reduce the required level of ZnO, but also that PNA5 may be a suitable replacement for ETU. However, when the rheological results are examined in more detail they indicate that in the ETU formulation (formulation 5.2 which has low ZnO and an MFA), the T90 increased and the cure rate reduced. If this were to be commercialised for use in an ETU formulation, work would be required to more closely replicate the results of the high ZnO formulation. However, as the aim of this project is to replace ETU it is not of interest to do so. When PNA5 is used, the addition of the MFA increases the cure rate and nearly halves the T90. This is unsurprising as PNA5 is known to be activated by diamines and the MFA contains a diamine. Therefore, the MFA activates the PNA5 accelerator quicker due to the increased level of diamine present in the formulation. In short, these results suggest that the use of an MFA in a master batch formulation will reduce the level of ZnO needed.

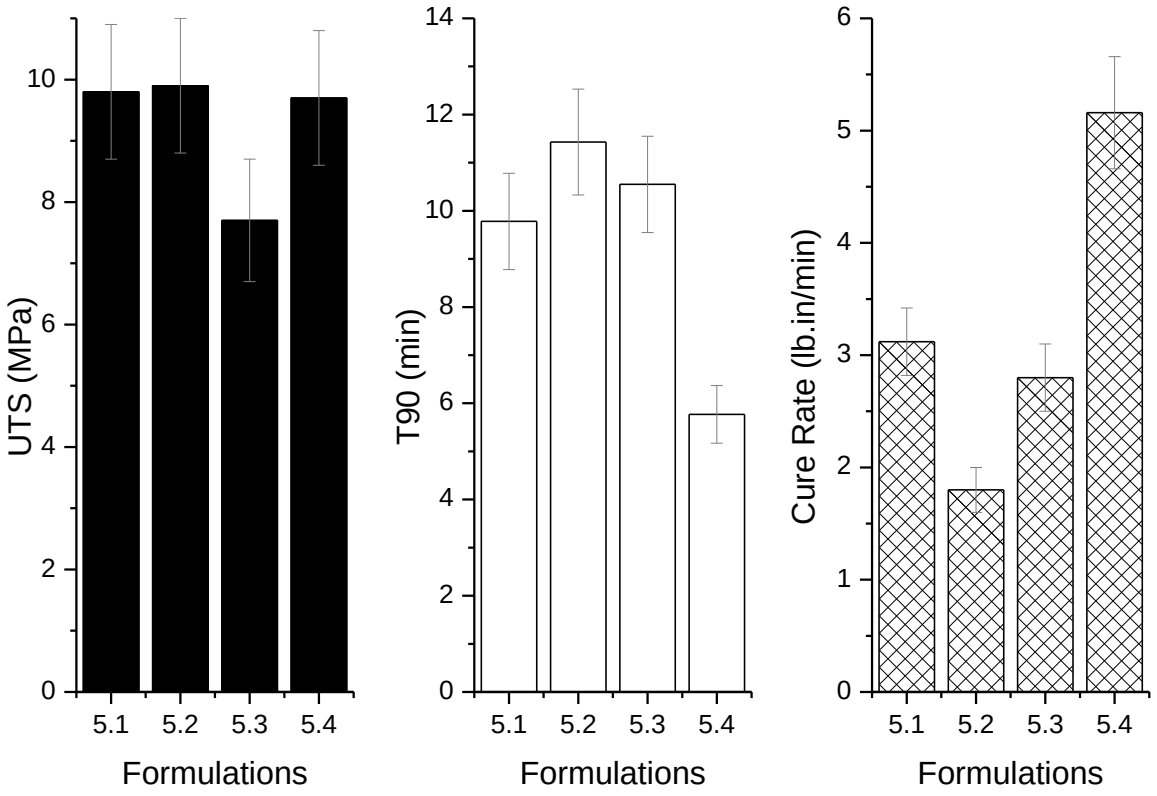


Figure 5.4. Mechanical properties of formulations comparing MFA and ZnO levels in either ETU-containing or PNA5-containing formulations (exact contents shown in Table 5.4). Error bars show one standard deviation from three sets of data.

5.2. Using Thiurams and Diamines for Model Studies

The new accelerator, PNA5, is based around a dithiocarbamate structure, and it has previously been shown in this study that TBzTD is activated by diamines (Section 4.1, Table 4.2). This is due to TBzTD being a thiuram-based accelerator. Consequently, to help optimise the cross-linking of PNA5, different levels of a diamine (1,4-diaminobutane) and TBzTD in polychloroprene gum stock were studied. Initially the level of TBzTD was kept constant (3 phr) and the level of diamine altered, before the diamine level was kept constant (0.75 phr) and the level of TBzTD varied.

5.2.1. Cross-linking Studies with Various Levels of 1,4-Diaminobutane

To begin with the level of TBzTD in polychloroprene gum stock was kept at 3 phr, with the level of 1,4-diaminobutane tested at various quantities between 0.25 and 1.5 phr. It has previously been shown that TBzTD does not cross-link on its own therefore there are no results for TBzTD alone. The results (Table 5.5) show that a maximum tensile strength is reached when the 1,4-diaminobutane is between 0.5 and 0.75 phr.

Table 5.5. Mechanical properties for polychloroprene gum stock with 3 phr TBzTD and various levels of 1,4-diaminobutane.

1,4-diaminobutane level (phr)		**0.25**	**0.35**	**0.5**	**0.75**	**1.0**	**1.5**
500 % Mod (MPa)		1.34	1.16	2.07	2.73	2.21	2.31
UTS (MPa)		12.6	11.9	14.4	14.3	14.1	12.6
Elongation at break (%)		DNB*	DNB*	892	747	804	745
15 min MDR test at 160 ºC	**MH (lb.in)**	8.58	8.51	10.66	11.63	11.87	12.37
	TS1 (mm:ss)	02:40	01:46	00:35	00:30	00:30	00:30
	T90 (mm:ss)	10:47	09:44	07:35	06:37	06:14	05:44
	Cure (lb.in/min)	1.48	1.46	5.92	8.64	9.66	9.66

*Sample did not break before full extension was reached (see Appendix A).

There are several trends seen in the rheological data due to an increase of diamine in the cross-linking formulation (with a constant level of TBzTD) (Figure 5.5). An increase in the cure rate and a decrease in scorch are observed, up to a level of 1 phr of diamine after which a plateau is seen. Additionally, an increase in MH and decrease in T90 are also observed, with the respective rate of increase and decrease reducing above 1 phr diamine, although a plateau is not quite reached. These results indicate that as the amount of diamine is increased more cross-linking is occurring and at a higher rate (up to a maximum level). These results are as expected, as the more diamine present, the faster the activation of TBzTD and so the quicker cross-linking can occur. Also, as more TBzTD will be activated quicker it will enable more cross-links to occur. These increases occur up to a certain level of diamine after which it is not possible for activation of TBzTD to occur faster or in greater quantity. This may be due to a saturation level of diamine being reached.

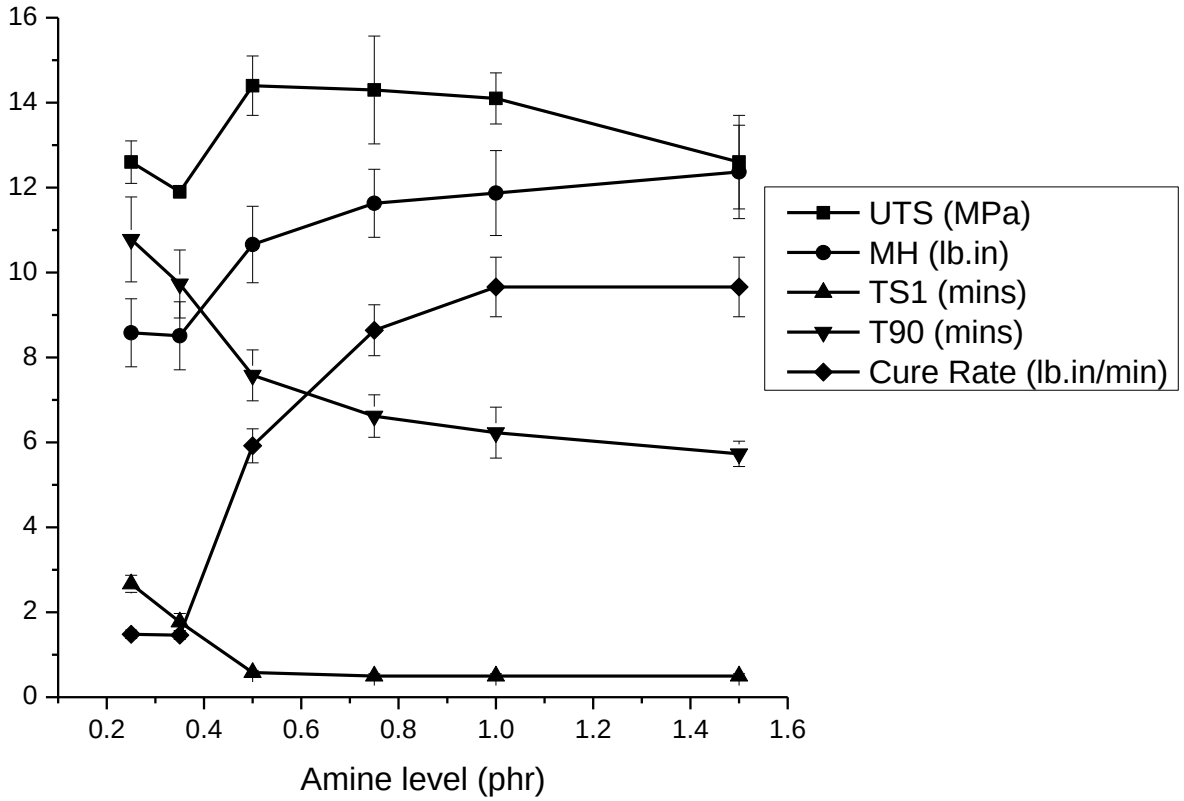


Figure 5.5. The effect of 1,4-diaminobutane level on the mechanical properties polychloroprene. 3 phr TBzTD was used in all cases. Error bars show one standard deviation from three sets of data.

In summary, for formulations containing 3 phr TBzTD, the maximum level of 1,4-diaminobutane required is 1 phr, as there is little improvement in physical properties above this level. It can also therefore be inferred that for a lower level of TBzTD, a lower

level of 1,4-diaminobutane would be needed. This hypothesis was examined with 2 phr TBzTD tested with various levels of 1,4-diaminobutane (from 0.35 to 1.5 phr) (Table 5.6). It is noteworthy that the strain at break for this set of formulations (with 2 phr TBzTD) was sufficiently low across the samples to be measured, unlike the corresponding formulations containing 3 phr TBzTD (Table 5.5). Furthermore, a reduction in the strain at break was observed as the level of diamine was increased (Figure 5.6).

Table 5.6. Mechanical properties of polychloroprene gum stock with 2 phr TBzTD and various levels of 1,4-diaminobutane.

1,4-diaminobutane level (phr)		**0.35**	**0.5**	**0.75**	**1.0**	**1.5**
500 % Mod (MPa)		1.77	1.99	2.33	1.99	1.73
UTS (MPa)		14.3	12.0	13.3	11.5	10.6
Elongation at break (%)		944	848	851	785	746
15 min MDR test at 160 ºC	**MH (lb.in)**	8.63	9.83	10.29	10.46	11.21
	TS1 (mm:ss)	00:47	00:34	00:33	00:33	00:33
	T90 (mm:ss)	08:19	07:10	07:14	06:28	05:38
	Cure (lb.in/min)	3.32	6.74	7.56	8.22	8.00

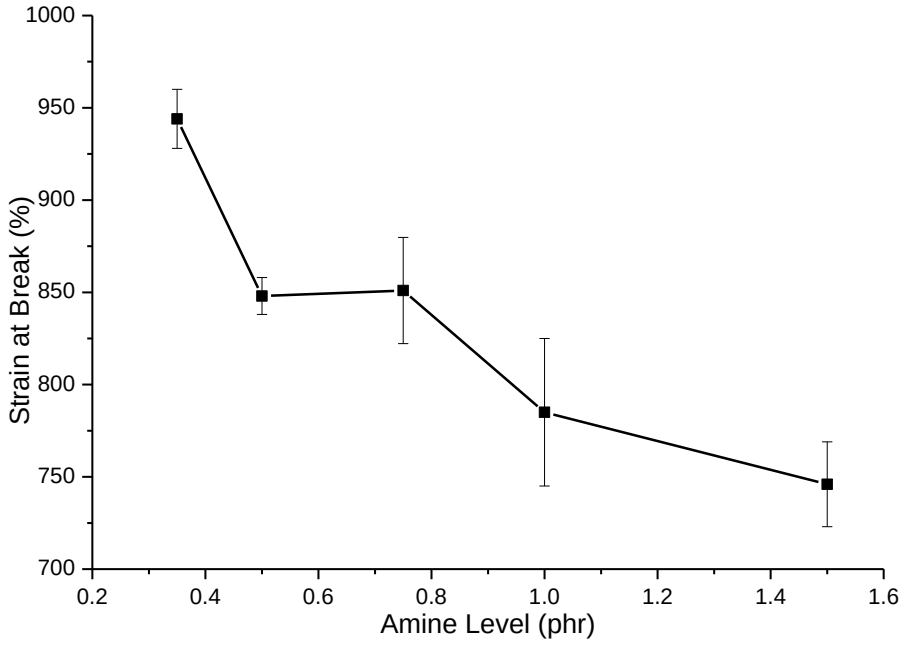


Figure 5.6. Change in extension at break when polychloroprene is cured with various levels of diamine and 2 phr TBzTD. Error bars show one standard deviation from three sets of data.

The cure rate shows a similar diamine level independence after a threshold has been observed, as with the 3 phr TBzTD samples (Figure 5.7). Correspondingly, the level at which this occurs is the same as with the 3 phr TBzTD samples, that is 1 phr diamine. When 2 phr TBzTD was used in conjunction with 1,4-diaminobutane (to cross-link polychloroprene) the MH increased at a steady rate above 0.5 phr diamine. The TS1 values were independent of the level of diamine, however, both the T90 and UTS reduce as the level of diamine increases. The largest change in these properties occurs below 0.75 phr, with the rate of change reducing after this point, although no plateau is reached.

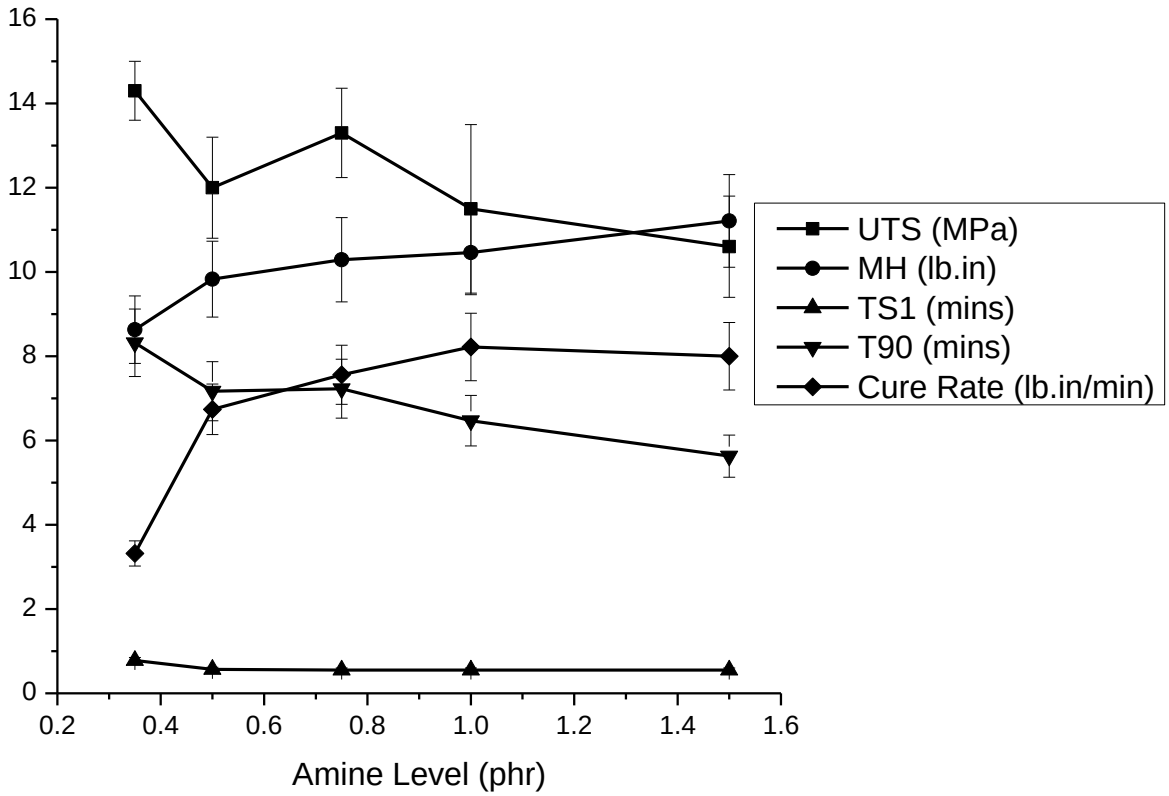


Figure 5.7. Effect of 1,4-diaminobutane level on the mechanical properties when polychloroprene is cured with 2 phr TBzTD. Error bars show one standard deviation from three data sets.

A levelling off of rheological characteristics was only observed with cure rate and TS1 when increasing the diamine level. It is possible that the small changes in the physical properties observed with 2 phr TBzTD above 0.75 phr were due to the diamine cross-linking as opposed to activating the thiuram-based accelerator. Thus, the theory that beyond a particular level of diamine there will be no improvement in the physical properties, and that this level of diamine

is dependent upon the amount of TBzTD present, may be true. However, this is only applicable when comparing the properties caused by TBzTD cross-linking and not those influenced by cross-linking due to the diamine. Unfortunately, this hypothesis would be difficult to test, as the diamine will always cross-link when used on its own, and with lower levels of TBzTD, less diamine will be needed for it to be in excess.

5.2.2. Effect of Tetrabenzyl Thiuramdisulfide Level of Mechanical Properties

After studying how a change in the level of diamine affected the physical properties of cross-linked polychloroprene, a change in the level of TBzTD was studied (0 to 3 phr) with a fixed quantity of 1,4-diaminobutane (0.75 phr). The results in Table 5.7 show the UTS to be similar in all of the formulations where TBzTD is present; they also show an increase in UTS from no TBzTD to the inclusion of 1 phr.

Table 5.7. Mechanical properties for polychloroprene gum stock with various levels of TBzTD and 0.75 phr of 1,4-diaminobutane.

TBzTD level (phr)		**0**	**1**	**2**	**3**
500 % Mod (MPa)		1.50	1.36	2.33	2.73
UTS (MPa)		8.1	13.3	13.3	14.3
Elongation at break (%)		719	946	851	747
15 min MDR test at 160 ºC	**MH (lb.in)**	9.97	8.02	10.29	11.63
	TS1 (mm:ss)	02:25	00:38	00:33	00:30
	T90 (mm:ss)	12:14	06:35	07:14	06:37
	Cure (lb.in/min)	0.99	5.56	7.56	8.64

Figure 5.8 shows an increase in the cure rate as the quantity of TBzTD was increased. The TS1 and T90 initially decrease with the addition of TBzTD from 0 to 1 phr, and become independent of the level of TBzTD content above 1 phr. It can also be seen that the MH decreased upon the initial addition of TBzTD, but then increased as the level of TBzTD increased. These results all indicate that with the addition of TBzTD to 1,4-diaminobutane in polychloroprene, cross-linking occurs to a greater extent and that it occurs faster, seen

through the higher UTS and lower TS1 and T90. It can also be seen that, once present, as the level of TBzTD increases the level of cross-linking concomitantly increases, shown by higher cure rates and MH and also indicated by an increase in the 500 % modulus (Table 5.7). The results of the extension at break also appear to indicate that this is occurring (Figure 5.9), where there is an increase with the lowest addition of TBzTD, but then upon higher additions, the extension at break decreases.

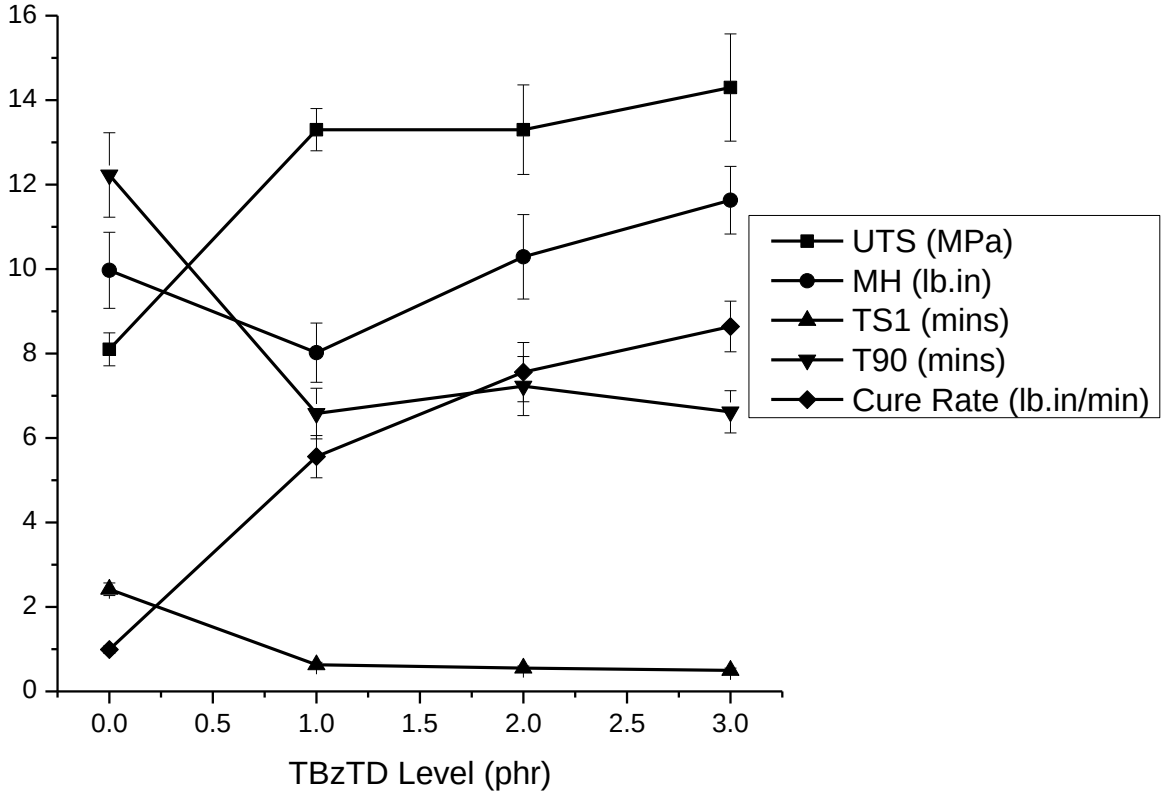


Figure 5.8. Effect of level of TBzTD on the mechanical properties when polychloroprene is cross-linked with 0.75 phr 1,4-diaminobutane. Error bars show one standard deviation from three data sets.

The results of the studies regarding levels of diamine and TBzTD have shown that only a low level (of both additives) is required to ensure good cross-linking. This, combined with TBzTD being used as a secondary accelerator and the extra diamine being present in the form of the MFA, confirms that only low amounts of each additive will be required in the commercial formulation.

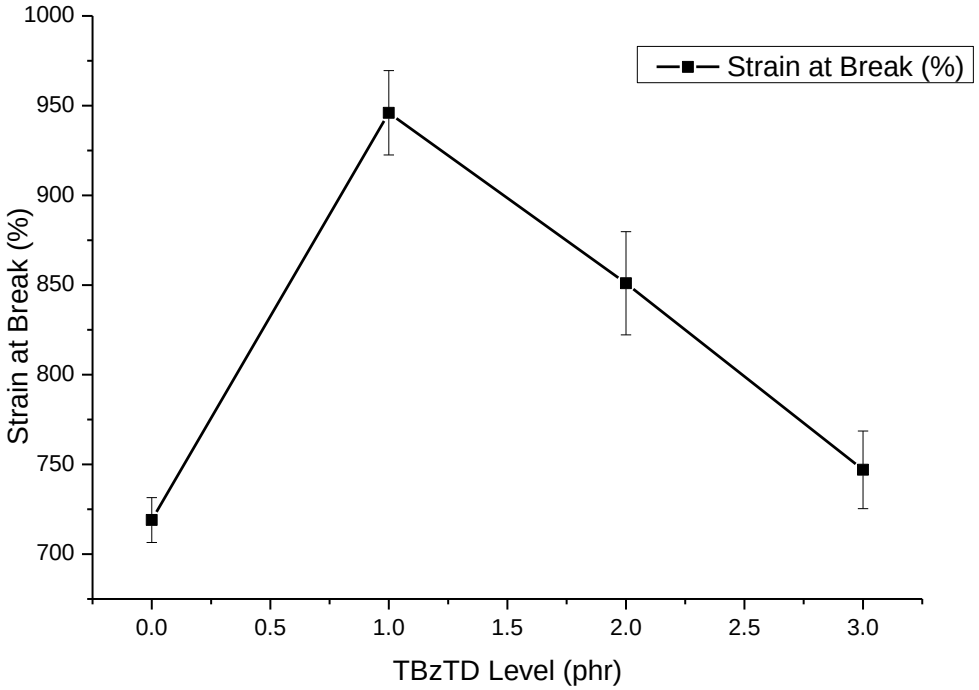


Figure 5.9. Effect on strain at break of varying levels of TBzTD for polychloroprene with 0.75 phr 1,4-diaminobutane. Error bars show one standard deviation from three data sets.

5.3. New Accelerator Studies in Gum Stock and a Master Batch

Having studied the levels required for various additives in gum stock, they were then studied in combination with the new accelerator, PNA5. This was initially done in gum stock with the various additives. Once the additive levels were optimised they were then studied in a filled master batch formulation. In addition to the conventional tensile and rheological tests, the master batch formulations were also tested for ageing, hardness and compression set.

5.3.1. Gum Stock Studies of PNA5-Containing Formulations

The aim of testing PNA5 in gum stock was to ensure its complete compatibility with the other additives present, and also to compare it with ETU-containing formulations. Table 5.8 shows the composition of the formulations tested.

The formulations labelled 5.1, 5.3 and 5.4 had already been tested with regards to the ability of the MFA to reduce the level of ZnO (Section 5.1). Formulation 5.1 is a control containing ETU and formulation 5.3 is a PNA5 control. Both of these formulations are based on standard

amounts of additives (5 phr ZnO, 4 phr MgO and 1 phr stearic acid, with ETU at 1 phr or PNA5 at 2.5 phr). Additional formulations 5.5 to 5.7 were tested to investigate the role of MgO and TBzTD, with formulation 5.5 containing only PNA5 and 1,4-MFA and 5.6 and 5.7 each having the addition of a new additive. This enabled each of the additives to be assessed as to their effect in the formulation.

Table 5.8. Formulations in gum stock containing new accelerator PNA5, and an ETU-containing control. Levels of each additive measured in phr.

Formulation	**5.1 (control)**	**5.3**	**5.5**	**5.6**	**5.4**	**5.7**
ETU	1	-	-	-	-	-
ZnO	5	5	-	1	1	1
MgO	4	4	-	-	4	4
PNA5	-	2.5	2.5	2.5	2.5	2.5
1,4-MFA	-	-	1.5	1.5	1.5	1.5
TBzTD	-	-	-	-	-	0.5
Stearic Acid	1	1	-	-	-	-

The results in Table 5.9 show that the addition of each additive improves the tensile properties of the final material as observed through the increasing 500 % moduli and UTS values (Figure 5.10). These results suggest that each of the additional additives increases the extent of cross-linking, confirming their necessity. It can also be seen that it is not until all of the additives are present that the UTS of a PNA5-containing formulation is higher than that of the ETU control (formulation 5.1).

The rheological changes between the formulations are different to those of the tensile results. Formulation 5.5 contains only PNA5 and 1,4-MFA and appeared to cross-link very well, with a T90 lower than that of the ETU control and with a higher cure rate. When ZnO was added to this (formulation 5.6), the cure rate decreased and the T90 increased, signifying that ZnO had an antagonistic effect on the cross-linking when using PNA5 with 1,4-MFA (Figure 5.11). This has been seen before in the literature where levels of ZnO above 1 phr reduced the physical properties of a vulcanisate which also contained an MFA.[4] This is due to the MFA and PNA5 containing amines which can complex with zinc, to form a tetra-amine zinc complex, reducing the effectiveness of both ZnO and the MFA in cross-linking. Additionally, as both ZnO and amines cross-link through a reaction with the chlorine on the polymer chain,

they will have competing reactions. However, ZnO (even at this low level) will aid in the prevention of ageing of the cross-linked rubber, and would be needed in a filled master batch so was kept in the unfilled polychloroprene. The addition of MgO, and then TBzTD, acted to improve the rheological properties and cross-linking. This could be seen through both additions reducing the T90 and increasing the cure rate. The T90 and cure rate of formulation 5.3 was similar to the ETU control (formulation 5.1), as shown in Figure 5.11, and formulation 5.7 (which contained all of the additives) had a significantly lower T90 and higher cure rate than the control. This indicates that the cross-linking of formulation 5.7 occurred much quicker than that of the ETU control, again confirming the necessity of all additives. Additionally, all of the PNA5-containing formulations have lower scorch times, and (except the PNA5 control) have lower T90 compared to the ETU control (formulation 5.1). Moreover, the PNA systems have similar or higher cure rates, than the ETU control. This indicates that those systems that contain PNA5 cross-link faster than the ETU control. In an industrial setting this would reduce the length of each cure cycle and so could potentially be more cost-effective than an ETU-based system.

Table 5.9. Mechanical properties of various formulations containing PNA5 alongside an ETU control for comparison.

Formulation		**5.1 (ETU control)***	**5.3 (PNA5 control)***	**5.5**	**5.6**	**5.4**	**5.7**
100 % Mod (MPa)		1.22	1.15	0.67	0.79	1.04	1.07
300 % Mod (MPa)		2.02	1.97	1.06	1.27	1.60	1.63
500 % Mod (MPa)		5.59	4.85	1.8	2.34	3.34	3.76
UTS (MPa)		9.8	7.7	9.2	9.5	9.7	12.1
Elongation at break (%)		561	556	741	687	648	656
15 min MDR test at 160 ºC	**MH (lb.in)**	17.58	16.72	8.84	12.13	14.17	15.41
	TS1 (mm:ss)	01:16	01:10	00:52	01:12	00:46	00:38
	T90 (mm:ss)	09:47	10:33	07:50	08:01	05:46	05:28
	Cure (lb.in/min)	3.12	2.8	4.02	2.64	5.16	6.56

*Control formulations contain 5 phr ZnO, 4 phr MgO and 1 phr stearic acid, in addition to the accelerator.

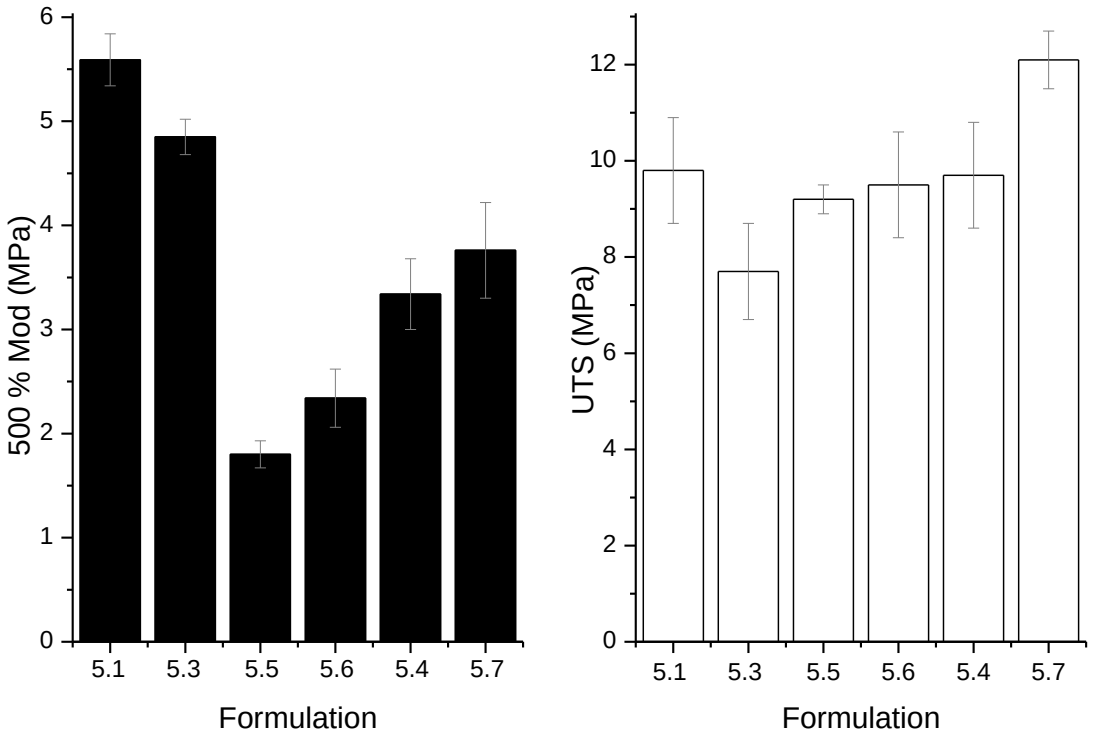


Figure 5.10. Comparison of 500 % modulus and UTS between various formulations with new accelerator PNA5 in, and an ETU control (Formulation 5.1). Error bars show one standard deviation from three data sets.

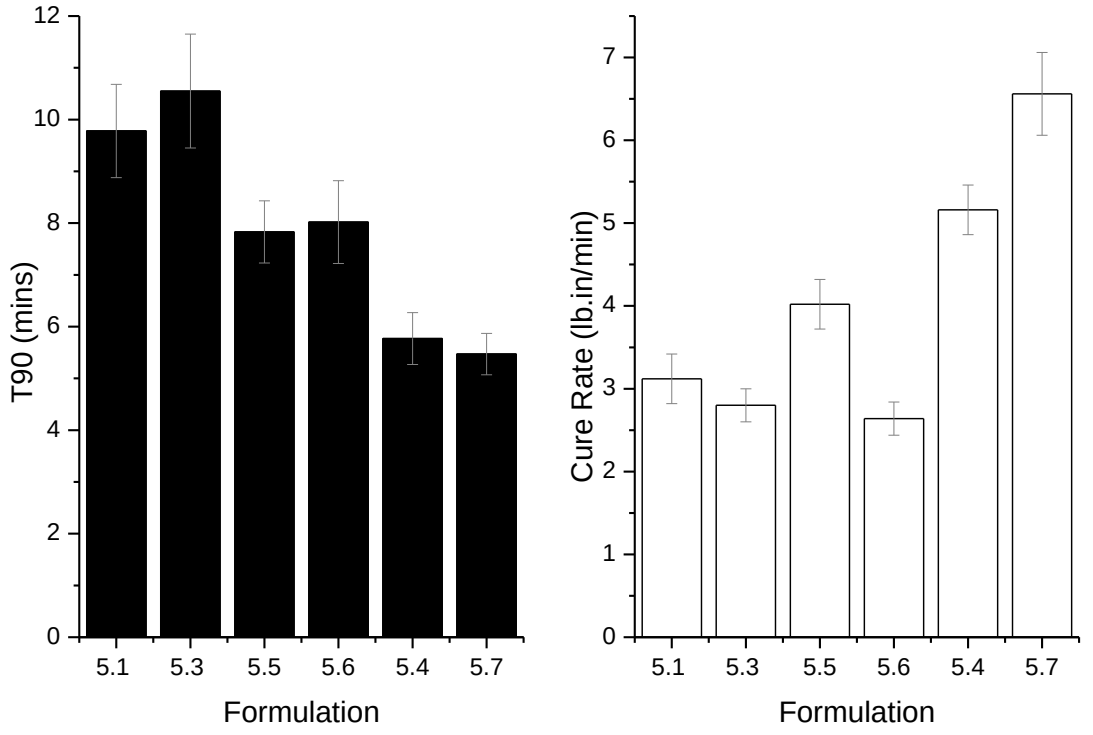


Figure 5.11. T90 and cure rate of various polychloroprene formulations containing PNA5, also shown is an ETU control (Formulation 5.1). Error bars show one standard deviation from three data sets.

5.3.2. Master Batch Studies of PNA5-Containing Formulations

A simple master batch formulation was made by Clwyd Compounders Ltd. that did not contain any metal oxides, accelerators or curatives, into which the remaining additives could be added at various levels (Table 5.10). Building upon the previous work in this chapter an initial formulation containing PNA5 was trialled in the master batch and compared to a standard ETU-containing formulation (Table 5.11). The quantities used were based upon those from the gum stock studies. After initial testing, the quantities of 1,4-MFA, MgO and ZnO were investigated to identify the most appropriate levels for use in a master batch.

Table 5.10. Master batch formulation from Clwyd Compounders Ltd.

Ingredient (trade name)	**Ingredient (chemical name)**	**Purpose**	**Quantity (phr)**
Denka S40V	Polychloroprene	Polymer	100
FEF N550	Carbon Black	Filler	70
Citrofol BII	Acetyltributyl Citrate	Plasticiser	10
ODPA	Octylated diphenylamine	Anti-oxidant	2
WS180	Fatty acid derivatives with silicone	Processing aid	1

Table 5.11. Various formulations tested in the master batch from Clwyd Compounders Ltd. all quantities are in phr.

Formulation	**5.8**	**5.9**	**5.10**	**5.11**	**5.12**	**5.13**	**5.14**	**5.15**
ETU	1	-	-	-	-	-	-	-
ZnO	5	1	1	1	1	1	1	2
MgO	4	4	4	4	4	4	2	4
PNA5	-	2.5	2.5	2.5	2	2	2	2
1,4-MFA	-	1.5	1	0.5	1	0.5	0.5	0.5
TBzTD	-	0.5	0.5	0.5	0.5	0.5	0.5	0.5

Rheological testing (Table 5.12) showed that all of the studied formulations cross-linked the master batch. It can be seen that the cure rate of the ETU control formulation (formulation 5.8) was higher than all of the PNA5-containing formulations. It is also noteworthy that formulation 5.15 had a much lower cure rate than all of the other formulations (Figure 5.12).

This formulation (5.15) contained more ZnO than the other formulations indicating that ZnO is retarding the cure and it can be directly compared with formulation 5.13, which has the same levels of every other additive. When comparing these two formulations, the addition of an extra 1 phr ZnO halves the cure rate, this is as previously mentioned due to the antagonistic effect of ZnO with an amine. The cure rate is, however, unaffected by the change in 1,4-MFA (decreasing in level from formulation 5.9 to 5.11). Formulations 5.12 and 5.13 have a slightly lower cure rate, and these formulations have a reduced level of PNA5 when compared to formulations 5.10 and 5.11, respectively, which have the same levels of the other additives. Similarly, formulation 5.14 has a reduced cure rate; this formulation has a reduced level of MgO but every other additive is the same as formulation 5.13. These two results indicate that both PNA5 and MgO are both important for cross-linking.

Table 5.12. Rheological, hardness and compression set results for formulations 5.8 to 5.15 (see Table 5.11 for formulation details).

	Rheology results (160 °C for 15 mins)				**Hardness (IRHD)**		**24 hours at 70 °C 25% Comp. Set (%)**
	MH (lb.in)	**TS1 (mm:ss)**	**T90 (mm:ss)**	**Cure (lb.in/min)**	**Unaged**	**7 days at 70 °C**	
5.8	55.77	00:34	09:27	11.22	85	84	11.6
5.9	40.48	00:25	08:36	9.74	88	89	26.7
5.10	44.01	00:25	09:30	9.92	84	87	19
5.11	50.67	00:26	09:44	9.26	82	87	22.9
5.12	44.68	00:28	10:42	9.1	82	87	22.1
5.13	48.24	00:26	10:47	8.94	84	84	20.7
5.14	44.12	00:30	09:50	7.4	83	85	22
5.15	34.51	00:44	11:45	4.2	80	82	28.8

The decrease in amount of MFA affects some of the rheological properties, although the cure rate is independent of the level. As the level of MFA in the formulation decreases, both the MH and T90 increase (Figure 5.13). The increase in T90 is due to a longer time taken to cross-link the polychloroprene because of a lower level of diamine present (from the lower level of MFA), this is due to the amine being an activator. Therefore a lower level of activator will increase the time taken for full cross-linking to occur.

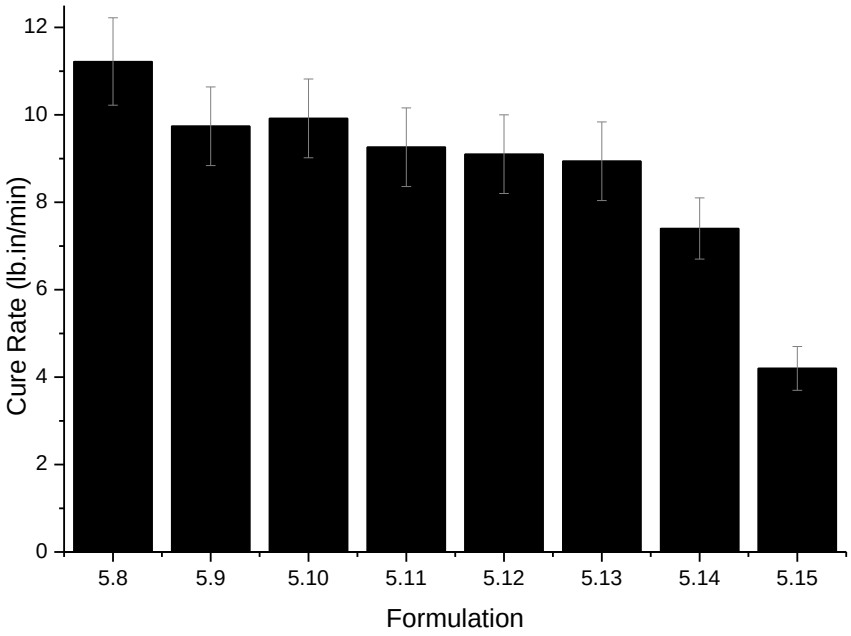


Figure 5.12. Comparison of cure rates between various filled master batch formulations (see Table 5.11 for list of formulation additives). Error bars show one standard deviation from three data sets.

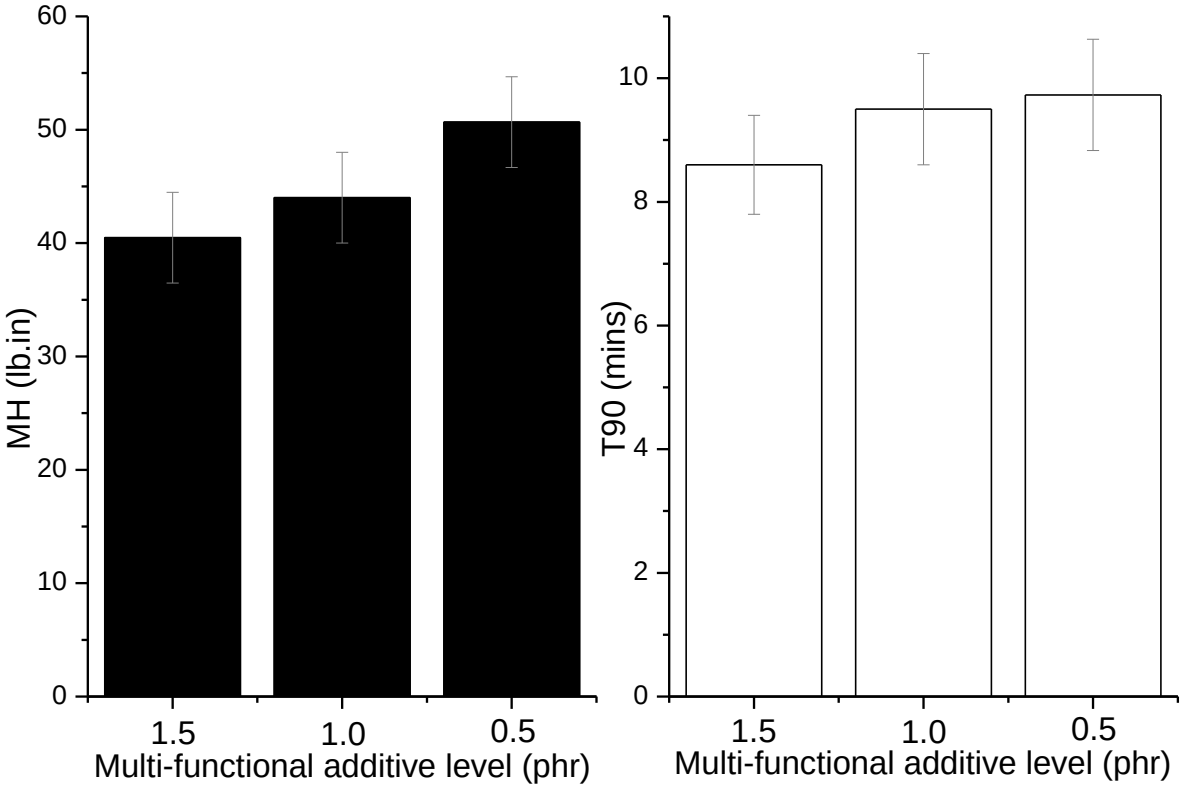


Figure 5.13. Effect of multi-function additive (MFA) level on the maximum torque and T90 in a filled master batch system. Each formulation also contained 1 phr ZnO, 4 phr MgO, 2.5 phr PNA5 and 0.5 phr TBzTD. Error bars show one standard deviation from three data sets.

One property of note in Table 5.12 is that of compression set, it is evident that all of the PNA5-containing formulations tested produced higher compression set than the ETU-containing formulation. Although a typical specification in industry would require a compression set of less than 25 %, which most of the PNA5-containing formulations meet, they are not however as low as formulation 5.8 (ETU control formulation). Nevertheless, the hardness of the various formulations before and after ageing (Table 5.12) was similar, and each only has a slight increase after ageing. These results show, for this physical property, a similarity between the PNA5-containing formulations and the ETU control.

Table 5.13 shows the tensile properties for all of the tested formulations, initially, and after ageing at 70 °C for seven days. Upon examination, it can be noted that all formulations produced similar results, and none of the formulations had a significant decrease in tensile strength after ageing (Figure 5.14). Formulations 5.8 (ETU control) and 5.13 both showed a small increase in tensile strength after ageing, perhaps caused by excess accelerator continuing to cross-link during ageing after the initial cure cycle, they also appear to have the most similar physical properties.

Table 5.13. Tensile properties for formulations 5.8 to 5.15 (see Table 5.11 for formulation details).

	Tensile Results (before ageing)			**Tensile Results (aged 7 days at 70 °C)**		
	100 % Mod (MPa)	**UTS (MPa)**	**Elongation at Break (%)**	**100 % Mod (MPa)**	**UTS (MPa)**	**Elongation at Break (%)**
5.8	12.55	16.3	131	16.04	18	113
5.9	11.6	19.2	159	13.21	15.3	108
5.10	12	17.9	148	13.02	17.1	104
5.11	11.77	16.8	138	14.58	15.2	105
5.12	9.9	17	162	14.67	14.9	109
5.13	13.43	15.7	118	15.56	17.8	115
5.14	10.28	14.9	137	13.34	14.3	108
5.15	10.28	15.9	152	11.63	15.6	135

Therefore, all of the results suggest that formulation 5.13 is the ideal formulation, with the closest tensile results to those of the ETU control formulation, being similar both before and

after ageing for seven days at 70 °C. The rheological properties of formulation 5.13 are slightly different to formulation 5.8 (ETU control), with formulation 5.8 having higher MH and lower T90 and compression set. Nevertheless, the results from formulation 5.13 can still be considered appropriate for commercialisation.

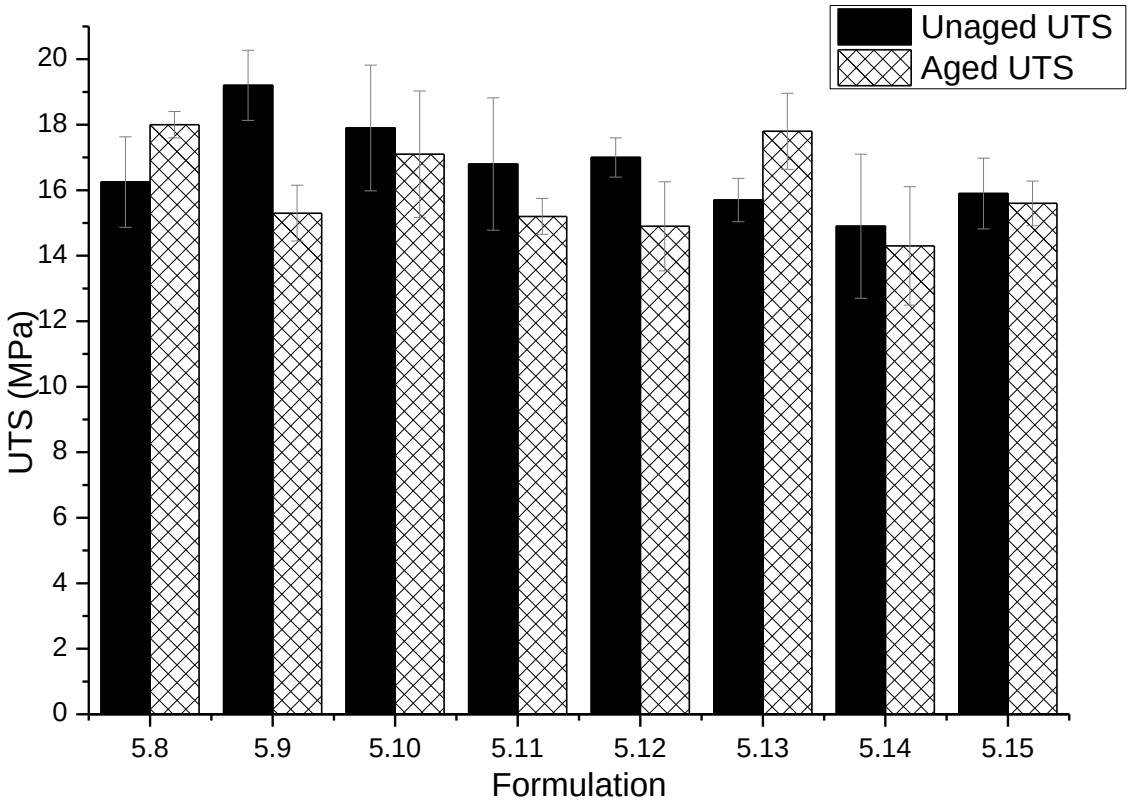


Figure 5.14. Tensile properties of a filled master batch with various different additives (see Table 5.11 for formulation details). Error bars show one standard deviation from three sets of data.

5.4. Study of Diamine Level in New Accelerator

In an effort to improve the properties of the final vulcanised product, the ratio of the two components of PNA5, that is diamine and piperazine-1-carbodithioic acid (PCA), were altered. PNA5 has a ratio of 1:2 of diamine to PCA, respectively, and ratios of 1:4 and 1:1 were examined herein. Once synthesised, the new accelerators were trialled in a master batch formulation similar to formulation 5.13, with PNA5 replaced by an accelerator with a different level of diamine. Physical properties were measured as with previous tested formulations and are shown in Table 5.14.

Table 5.14. Mechanical properties of filled master batch formulations (as formulation 5.13) containing an accelerator with varying ratio of diamine to PCA.

		PCA : diamine ratio		
		1:1	**2:1**	**4:1**
Tensile Results (unaged)	**100 % Mod (MPa)**	13.45	13.43	12.88
	UTS (MPa)	18.4	15.7	19.2
	Elongation at break (%)	138	118	150
Tensile Results (aged 7 days at 70 °C)	**100 % Mod (MPa)**	16.02	15.56	13.76
	UTS (MPa)	18.8	17.8	18.2
	Elongation at break (%)	118	115	134
15 min MDR test at 160 °C	**MH (lb.in)**	45.51	48.24	44.65
	TS1 (mm:ss)	00:22	00:26	00:32
	T90 (mm:ss)	09:42	10:47	11:03
	Cure (lb.in/min)	10.0	8.94	7.42
Hardness (IRHD)	**Unaged**	85	84	83
	7 Days at 70 °C	85	84	84
24 hrs 70 °C 25% Comp. Set (%)		21.6	20.7	19.8

Table 5.14 shows that the tensile results before and after ageing are similar for all three formulations. This indicates that the level of diamine makes very little difference to the strength of the final cured product and does not affect ageing properties. However, the rheological properties (Figure 5.15) show a change in the speed of cure as the level of diamine is altered. This can be seen by an increase in scorch time and T90 and a decrease in the cure rate as the diamine level decreases. The amine is present to activate the polymer chain, therefore as the level of amine decreases there is less activation of the polymer chain. This signifies that initiating and completing cross-linking take longer to be achieved. It can also be seen that a 4:1 ratio produces the lowest compression set (Table 5.14), which was the main property not similar to the ETU-containing formulation. However, the compression set at 19.2 % is still higher with the 4:1 ratio PNA5-containing formulation than was found in the ETU-containing formulation (compression set of 11.6 %), but is closer than previously tested formulations.

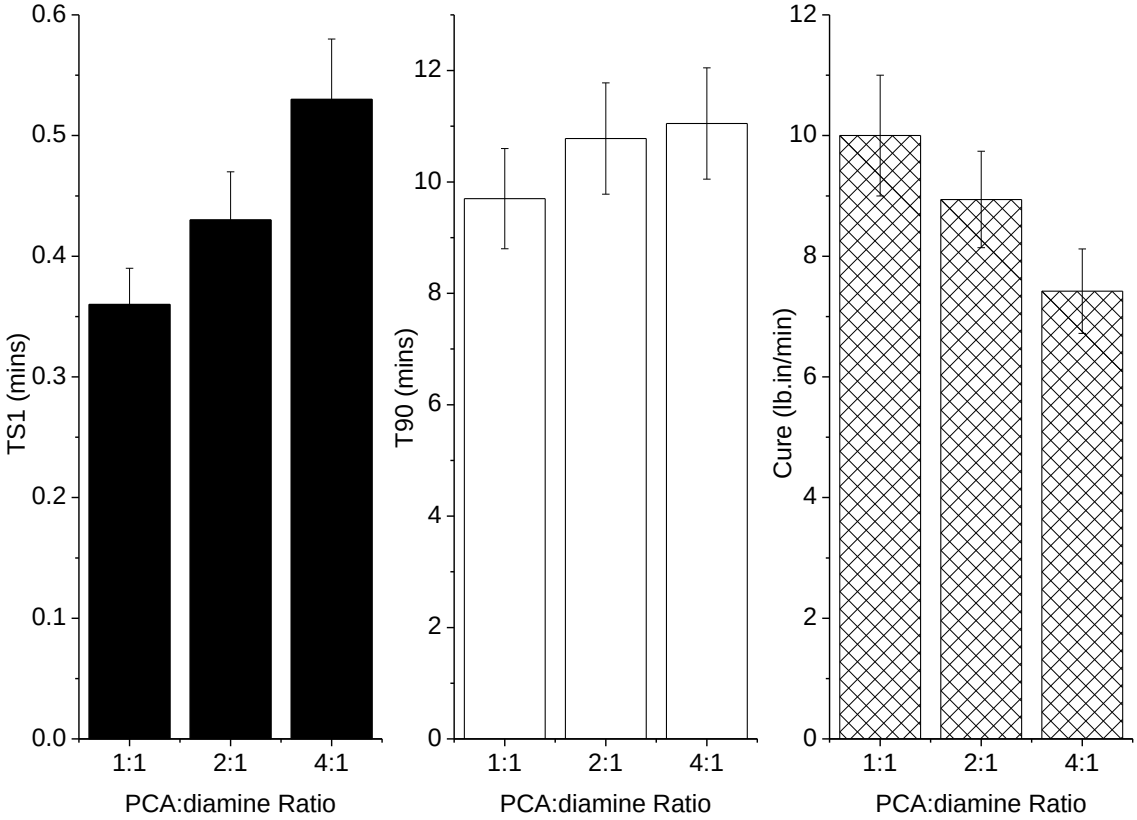


Figure 5.15. Rheological properties of a master batch, comparing the ratio of PCA to diamine in the accelerator. Error bars show one standard deviation from three data sets.

These results have demonstrated the ability of PNA5 to work in a filled commercial master batch. However, there are many different master batch formulations available for different commercial products. Therefore, as with any new product brought to market the exact formulation required for each master batch would have to be tailored to provide the required properties. It has been revealed through the studies herein the options available with PNA5 when in a master batch and that through the examination of the other additives it is possible to match an ETU-containing formulation. This has shown that PNA5 would make a suitable replacement for ETU in a commercial setting.

5.5. Chapter Conclusions

It can be seen through the work in this chapter that the use of multi-functional additives (MFA) enables a reduction in the level of ZnO within all polychloroprene cross-linking systems. From the results gathered, the use of 1,4-diaminobutane with stearic acid (at a ratio of 1:2) appears to be the ideal MFA for activating polychloroprene cross-linking. Results of

formulations with a reduced level of ZnO, which also contained an MFA, produced mechanical and physical results similar to those with no MFA and higher loadings of ZnO. This was seen in formulations accelerated by both ETU and PNA5.

Additionally, the role that both diamines and thiurams play within cross-linking identified that only low levels of each additive are required for cross-linking to occur. Furthermore, above a certain level, the improvement of mechanical and physical properties is minimal. This result enabled the levels of additives compounded with a master batch formulation to be examined. The results closest to those of the ETU control, showed that the ideal formulation contained: 2 phr PNA5, 4 phr MgO, 1 phr ZnO, 0.5 phr TBzTD and 0.5 phr MFA. It has also been shown that the level of diamine present within PNA5 will alter the rate at which cross-linking occurs, but that ageing and tensile properties remain unchanged. These indicated additive levels for the master batch used in this project give a tremendous starting point for other commercial master batches and show that it is possible to match an ETU-containing formulation (the only caveat being that the PNA5 formulations produced a higher compression set). It may be possible with further refinement and in other master batches the high compression set could be overcome. Additionally, not all commercial uses require the level of compression set reached by ETU-containing formulations and those of the PNA5 formulations would be suitable.

Therefore, this project has been successful in finding a safer replacement for ETU. The cross-linked vulcanisates containing this replacement match those of an ETU-containing vulcanisate for physical and mechanical properties, in both rubber gum stock and in an industrial master batch.

References

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CHAPTER 6

CONCLUSIONS AND FUTURE WORK

6. Conclusions and Future Work

This chapter provides a synopsis of the work undertaken in this project as discussed in Chapters 3, 4 and 5, and describes potential future work applicable to each area.

6.1. Conclusions

6.1.1. Cross-linking Mechanisms of Polychloroprene with Ethylene Thiourea and Metal Oxides

The mechanisms by which polychloroprene cross-links in the presence of ethylene thiourea and metal oxides were examined. This was achieved in a novel manner by examining both spectroscopic and mechanical and physical properties of the polymer before and after cross-linking. At least three different distinct mechanisms were found to be occurring. Evidence gathered suggests that the zinc oxide (ZnO)-mediated cross-linking mechanism proceeds in a cationic manner, whereby an unsaturation is formed as part of the new carbon-carbon cross-link structure.[1] The indication for this includes the formation of a new peak in FTIR spectrum at around 1580 cm^{-1} when ZnO is used as a cross-linking agent. For cross-linking polychloroprene with ethylene thiourea (ETU) alone, there is evidence for the mechanism to progress *via* the bis-alkylation mechanism first proposed by Kovacic.[2] This can be reasoned due to the formation of an acidic environment when cross-linking oligomers with ETU (suggesting the formation of HCl), and the formation of a new and distinct peak at ~1550 cm^{-1} in the FTIR spectrum upon cross-linking. This peak is still visible after soxhlet extraction in methanol when performed on the cross-linked rubber, indicating that it is due to a structure formed during cross-linking within the rubber. There is also an indication that other amines, namely linear primary amines and diamines also cross-link in this manner. The mechanism that results obtained herein suggest occurs when both ETU and ZnO are present in polychloroprene is a new pathway. ZnO reacts with the polymer chain first, followed by a reaction between this activated site and the sulfur atom of ETU (Scheme 6.1). This mechanism has similarities to the mechanism proposed by Pariser,[3] except that in the new mechanism ZnO reacts with the polymer chain first to activate it and allow ETU to react *via* its sulfur. In the mechanism proposed by Pariser, the sulfur atom of ETU reacts with the polymer chain first. It has been shown through the results on model compounds and widely used accelerators, herein that sulfur is unlikely to react with the polymer chain alone, and will only do so in the presence of ZnO. This indicates that the ZnO must first activate the chain to

allow cross-linking to occur, as no reaction has been seen to occur between ZnO and ETU. Aside from the results indicating that sulfur is unable to react with the polymer chain unless in the presence of ZnO, achieved through the use of thiols, dithiols and traditional accelerators such as thiurams. Other evidence gathered for this new mechanism includes the formation of both ethylene urea (EU) and zinc chloride; both of which are by-products of the reaction. Additionally, it has been seen that the reduction of the 925 cm^{-1} peak in the FTIR spectra of cured materials, associated with the 1,2-isomer used in cross-linking, is reduced much quicker with ZnO than with other additives, thus indicating it reacts with the polymer chain quickly.

6.1.2. Investigation of New Accelerators to Cross-link Polychloroprene

Chapter 3 provides evidence of the various mechanisms in operation when cross-linking polychloroprene with ETU. Through this, and work carried out with other rubber accelerators, several new potential polychloroprene accelerators were proposed. These accelerators all contained a dithiocarbamate group and were complexed with an amine or diamine. It has been shown that all of the proposed new accelerators were able to cross-link polychloroprene, to a greater or lesser degree. Those most able to cross-link were then trialled in combination with ZnO and tetrabenzyl thiuramdisulfide (TBzTD). On thorough analysis of the molecules, the accelerator which produced the most effective cross-linked rubber was PNA5, a complex between piperazine-1-carbodithioic acid (PCA) and 1,3-diaminopropane (Figure 6.1). The properties of polychloroprene cross-linked with PNA5 found to be most similar to those of the rubber cross-linked with ETU. Furthermore, the addition of TBzTD and ZnO (to either raise or lower the cure rate) has been shown to control the efficiency of PNA5 when tested in a commercial master batch formulation

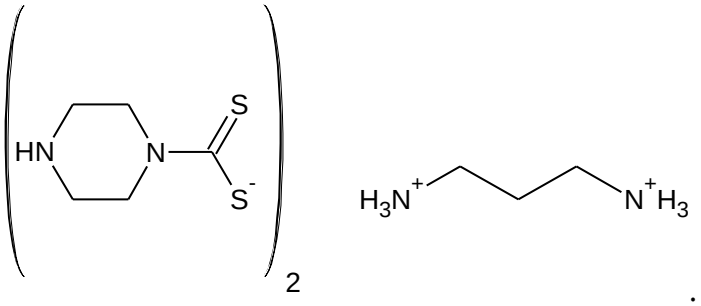
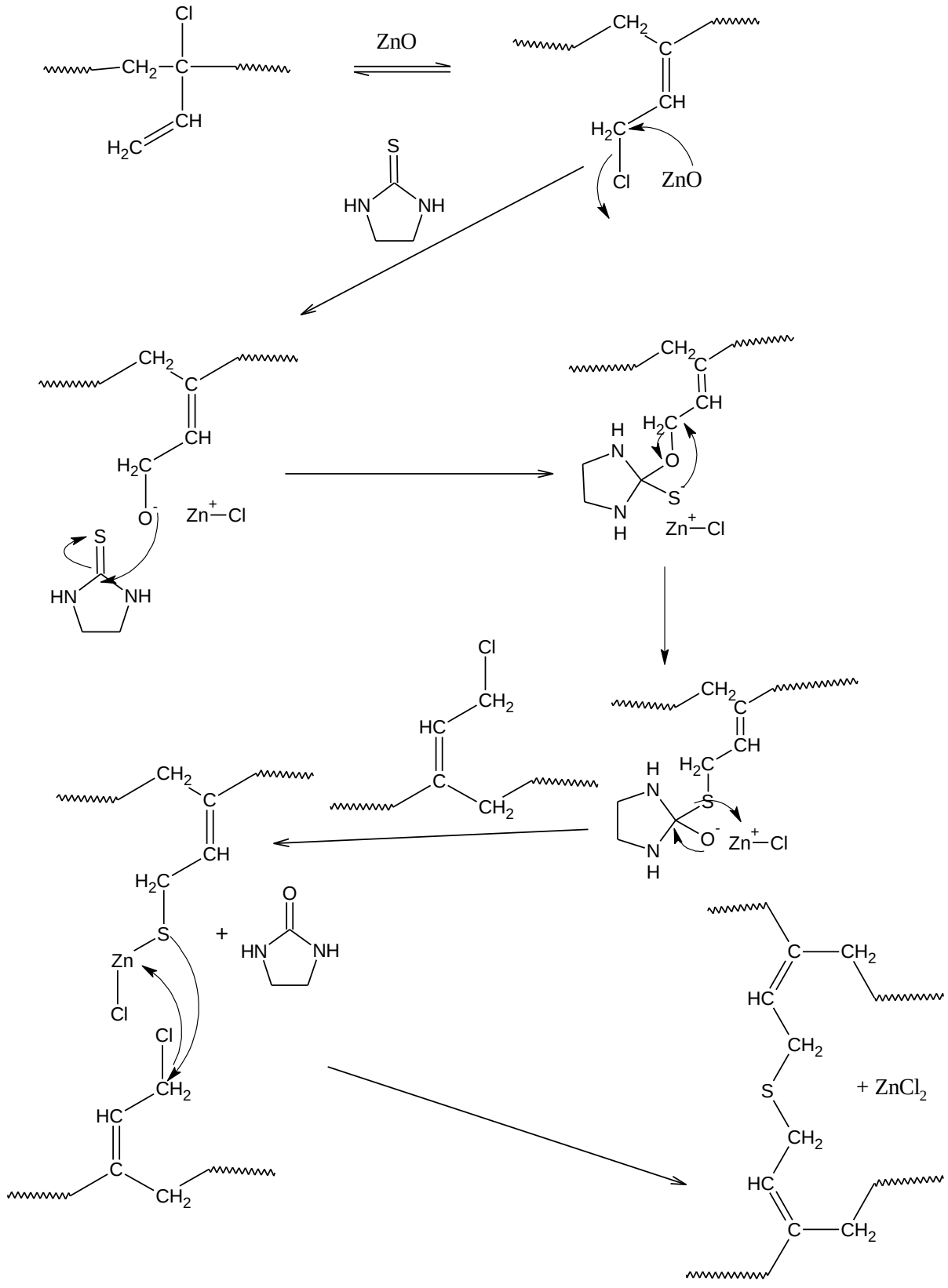


Figure 6.1. Structure of salt complex of piperazine-1-carbodithioic acid and 1,3-diaminopropane (PNA5).



Scheme 6.1. Alternative cross-linking mechanism for polychloroprene with ETU and ZnO, based on the results of the findings herein.

6.1.3. Optimising a New Accelerator for Commercialisation

The role of multi-functional additives (MFA) within polychloroprene cross-linking systems was investigated and it was shown that their use enabled a reduction in the level of ZnO required. ZnO is an environmental toxin, and so there is a need for prospective replacements. The reduction of ZnO through the use of the MFA has been shown in formulations based around ETU in addition to those based around the new accelerator, PNA5. The best MFA was a complex of 1,4-diaminobutane and stearic acid in a 1:2 ratio.

Additionally, it was shown that the levels of diamine and thiuram required for cross-linking with PNA5 system were low; 0.5 to 1 phr. Above these levels there was little improvement to the physical or mechanical properties of the vulcanisate. Following on from these results, the new accelerator was studied in a master batch formulation and it was concluded that the levels of additives required were 2 phr PNA5, 4 phr MgO, 1 phr ZnO, 0.5 phr TBzTD and 0.5 phr MFA. At these levels, the mechanical and physical properties closely matched those of an ETU-containing formulation. It was also shown that by altering the ratio of diamine to piperazine-1-carbodithioic acid (PCA) the rate of cross-linking could be altered, but that the tensile properties remain unchanged.

In summary, it may be said that the project has been successful in that a safer replacement was found for ETU. Additionally, rubber cross-linked with a system based around the new accelerator achieved similar physical and mechanical properties to that cross-linked by a conventional ETU-based system.

6.2. Future Work

6.2.1. Future Work for Cross-linking Mechanisms of Polychloroprene with Ethylene Thiourea and Metal Oxides

There are several different areas in which future study on the cross-linking mechanisms of ETU with polychloroprene could proceed. Model compound studies of molecules containing a sulfur-carbon double bond as appears in ETU, would aid this quest. Examining such compounds within polychloroprene (in both the rubber and oligomer), on their own and in combination with ZnO, would greatly increase the knowledge the role sulfur plays within cross-linking polychloroprene with ETU. Additionally, work on linear dithiols with differing alkyl lengths in combination with ZnO cross-linking polychloroprene could be studied. This

investigation would enable the proposition that the dithiols ‘slot in’ between the polymer chains *via* a ‘bis-alkylation’ cross-linking reaction to be confirmed. Finally, the work completed compared the cross-linking of polychloroprene with differing diamine lengths, would be aided by using a full stoichiometric comparison between the amines.

6.2.2. Future Work in the Investigation of New Accelerators to Cross-link Polychloroprene

Although a brief examination was performed on the relationship between a thiuram-based accelerator and a diamine activator in Chapter 4, more work in this area could fully elucidate their respective roles. It may also be possible to expose a new mechanism with these materials to allow optimisation to occur. Additionally, work on the new accelerators identified the role that the diamine played as an activator. Further study providing a more in-depth investigation into the alkyl length of the diamine could potentially lead to a more suitable replacement for ETU. Moreover, work on the new accelerators was centred on thiuram-based accelerators, however, in Chapter 3 xanthogen-based accelerators were shown to also cross-link in the presence of ZnO. These accelerators (thiuram- and xanthogen-based) were both activated by ZnO, but the new accelerators were all based upon thiurams. Therefore study of accelerator complexes based upon xanthogens may yield a different potential replacement for ETU.

6.2.3. Future Work for Optimising a New Accelerator for Commercialisation

Work on multi-functional additives (MFA), discussed in Chapter 5, was concerned with the reaction between stearic acid and a diamine. It should be possible to create a complex with other lower molecular weight carboxylic acids, such as acetic acid. Due to a reduction in molecular weight between these acids, it would give the resultant MFA greater amine functionality. Stearic acid has a molecular mass of 284 g/mol, therefore an MFA with stearic acid and 1,4-diaminobutane (molecular mass 88 g/mol) in a 2:1 ratio would contain 13 % diamine. Whereas acetic acid has a molecular mass of 60 g/mol, and an MFA with acetic acid and 1,4-diaminobutane would contain 42 % diamine. This would alter the activation ability of the MFA, thus changing its role within a cross-linking system. However, changes in the carboxylic acid used would also change the temperature at which the MFA was activated, and this would need to be thoroughly investigated, before a new MFA could be utilised. Furthermore, only two different diamines where investigated, both of which were linear primary diamines. The ability of other diamines, including those of a different length or that

were secondary or cyclic, such as piperazine, may well improve the feasibility of such an MFA.

The viability of PNA5 (a 2:1 complex between piperazine-1-carbodithioic acid and 1,3-diaminopropane) within a master batch formulation was shown; it was also seen to closely match that of an ETU-containing formulation. However, the master batch formulation used was one created for this project, rather than a standard commercial master batch. Further work in this area, therefore, should utilise the optimum PNA5 system shown in Chapter 5 in a commercially available master batch, and be compared to ETU-based systems. Additionally, other industrial tests, such as bin stability tests (where uncured rubber containing an accelerator system is kept at 40 °C, and the Mooney viscosity is tested every week), would need to be performed on a master batch containing PNA5 and compared to an ETU-containing system.

References

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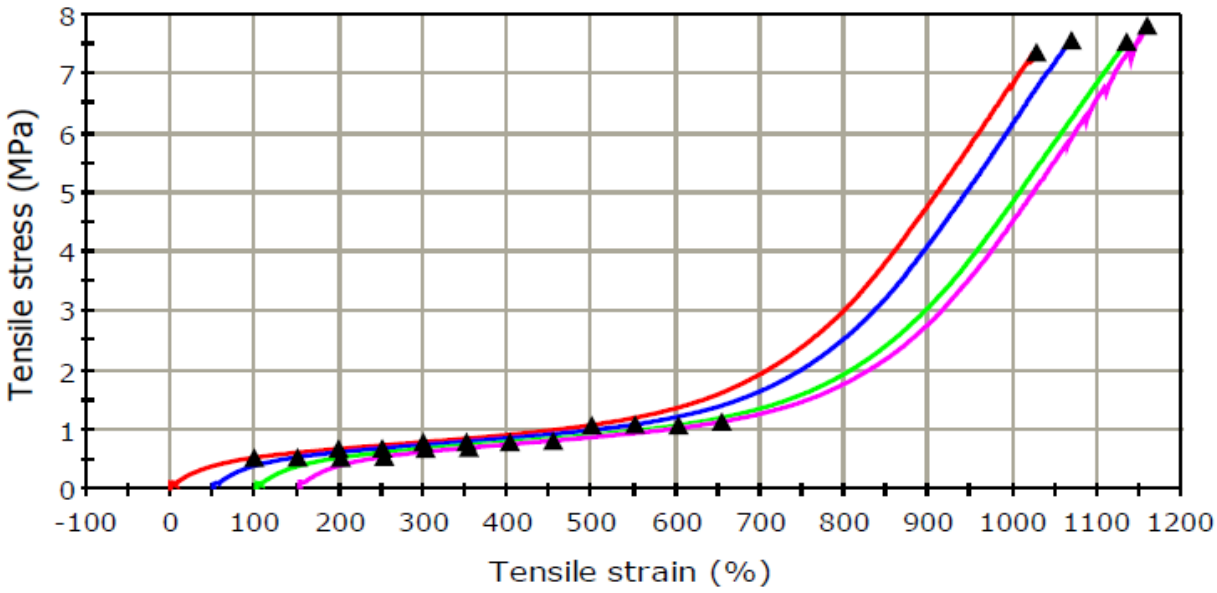
APPENDICES

Appendices

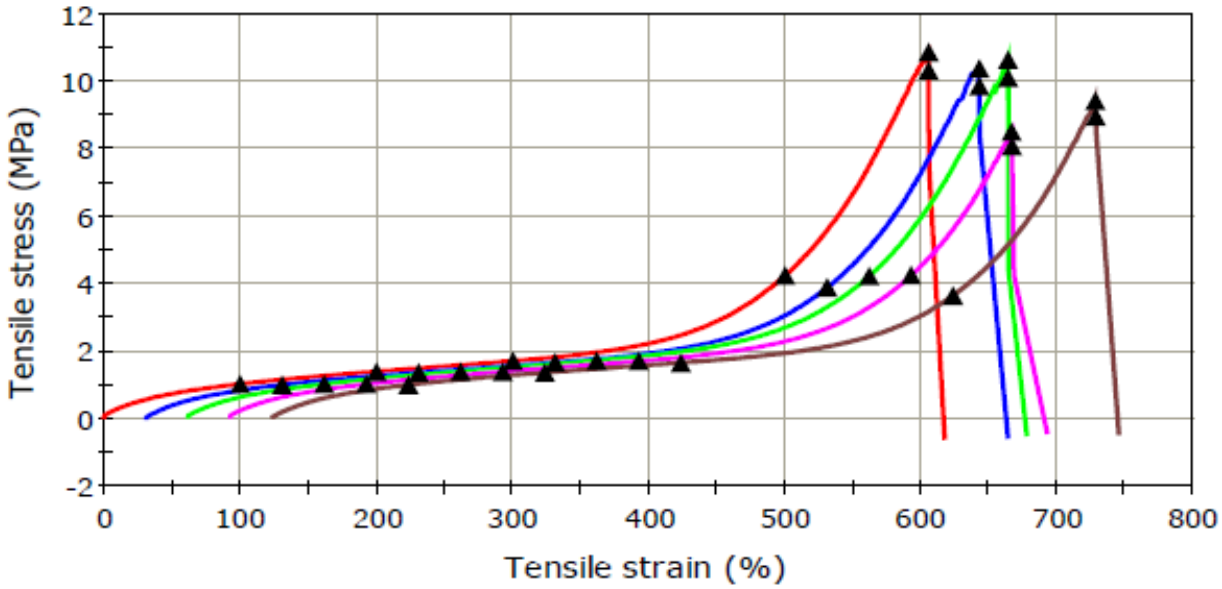
Appendix A: Tensile Testing

Tensile testing was used throughout this project, and in many instances the ultimate tensile strength (UTS) is quoted. The UTS is the stress of the material being tested when it breaks. However, in some cases in this project the UTS quoted is the final measured tensile stress as opposed to the tensile stress at break. This is the case for those samples that did not break (DNB) where the UTS quoted is technically the tensile stress at 1000 % extension. Appendix 1.1 shows a lightly cross-linked sample that does not break at full extension, a more highly cross-linked sample is shown in Appendix 1.2. Tensile samples in master batch formulation are shown in Appendices 1.3 and 1.4.

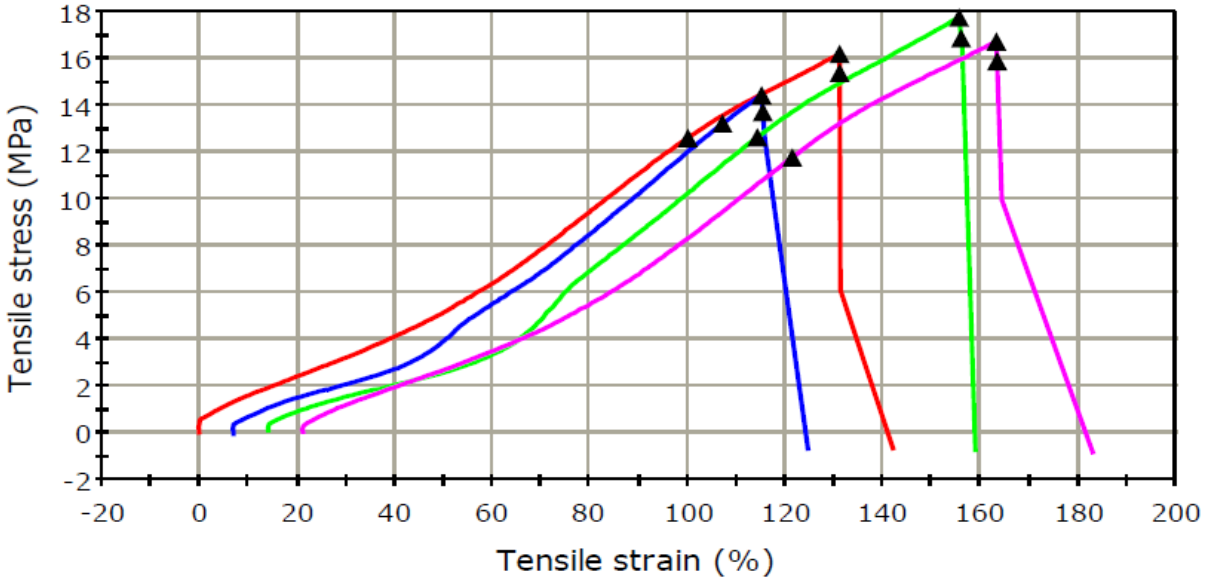
Appendix 1.1. Tensile graph of polychloroprene gum stock cured with only 2 phr ETU, showing the curve for a lightly cross-linked sample.



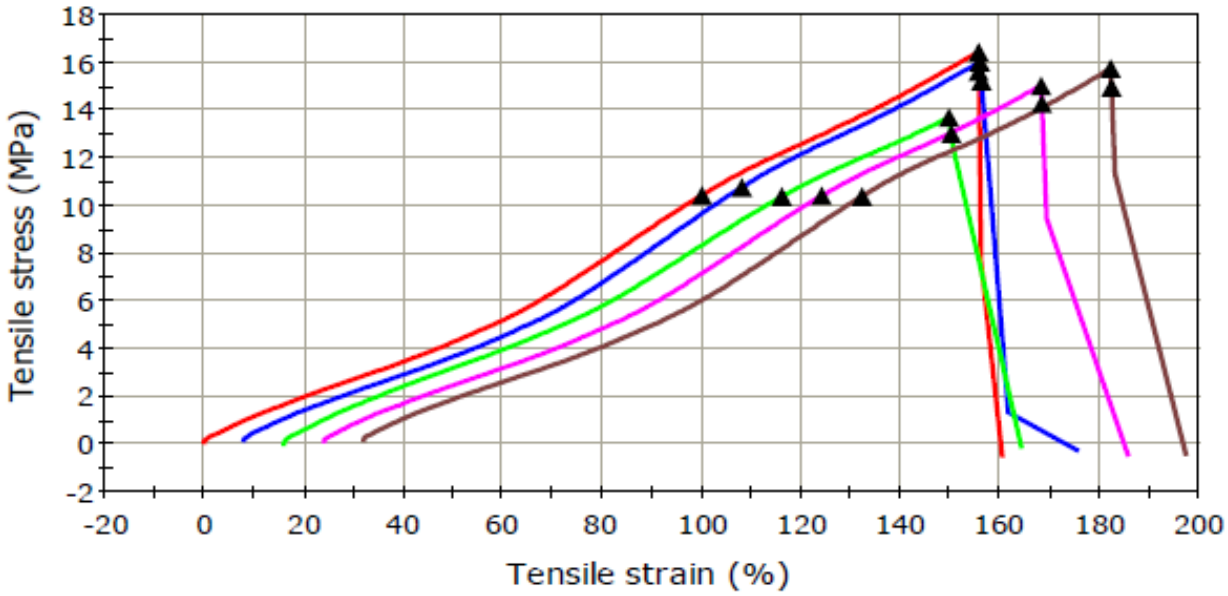
Appendix 1.2. Tensile graph of polychloroprene gum stock cured with 2 phr ETU and 5 phr ZnO, illustrating a highly cross-linked sample



Appendix 1.3. Tensile graph of the master batch containing 1 phr ETU, 5 phr ZnO and 4 phr MgO.

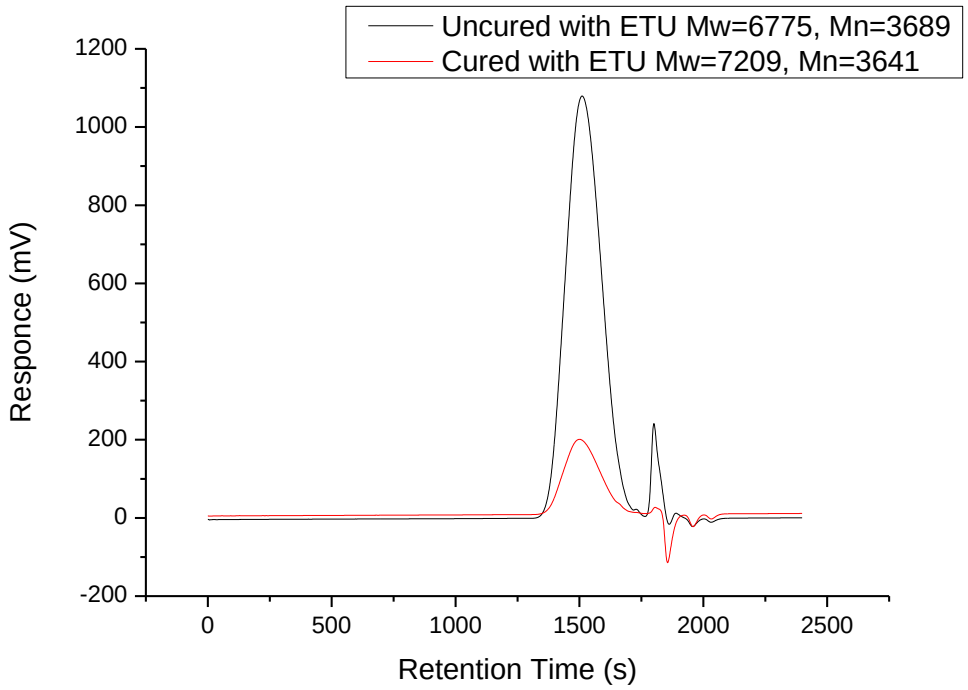


Appendix 1.4. Tensile graph of the master batch containing 2 phr PNA5, 1 phr ZnO, 4 phr MgO, 0.5 phr 1,4-MFA and 0.5 phr TBzTD.

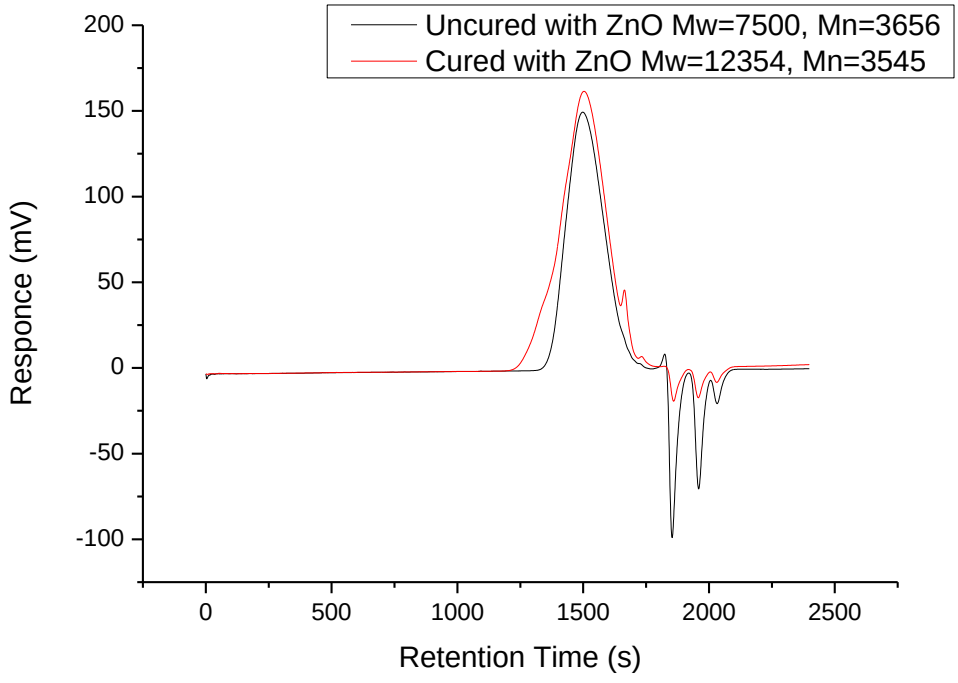


Appendix B: Oligomer Testing

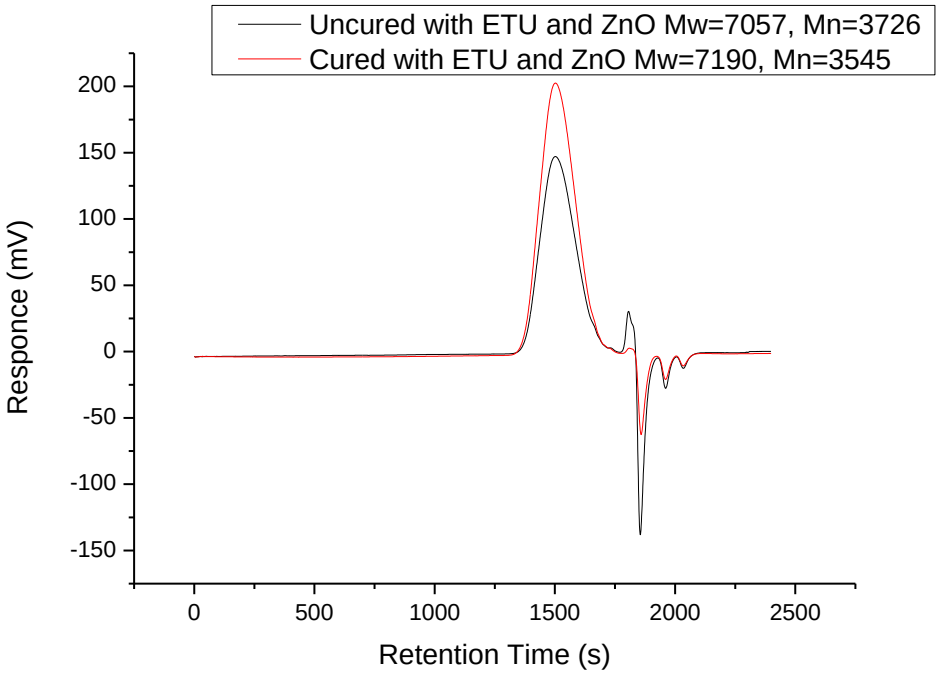
Appendix 2.1. GPC trace of oligochloroprene with 2 phr ETU before and after heating to 160 °C for 60 minutes.



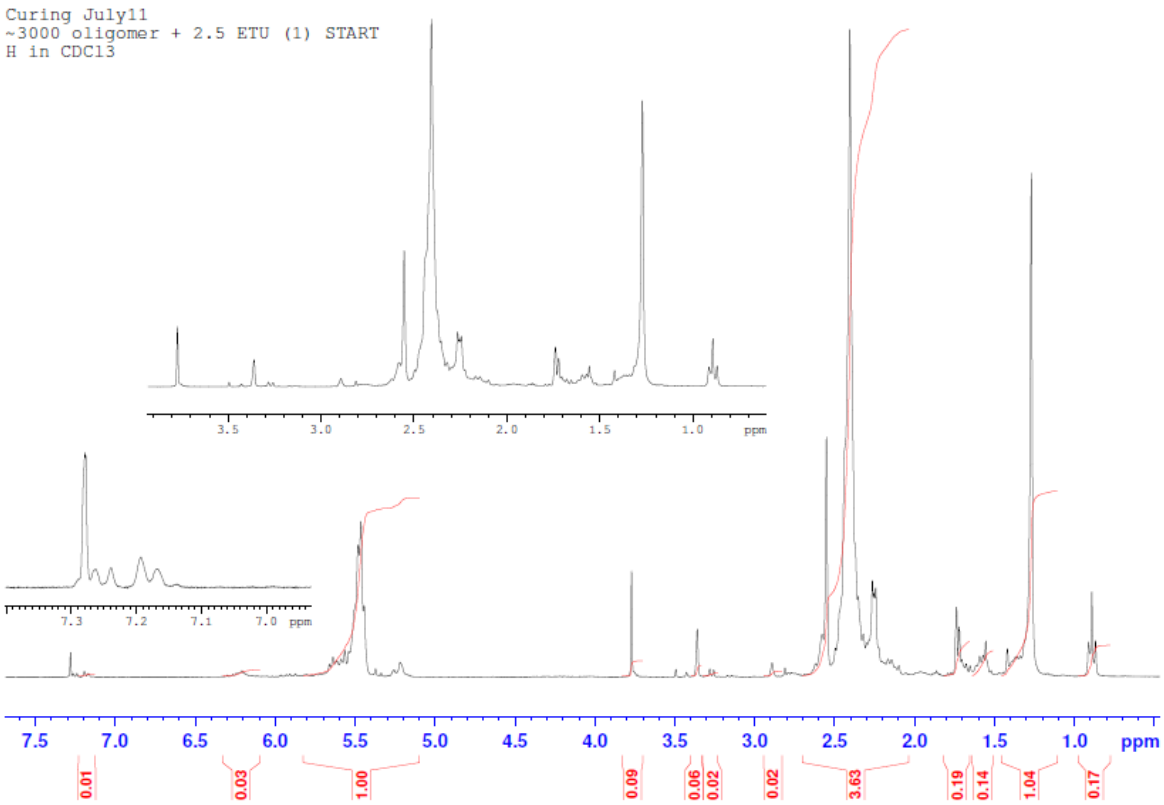
Appendix 2.2. GPC trace of oligochloroprene with 1 phr zinc oxide active before and after heating to 160 °C for 60 minutes



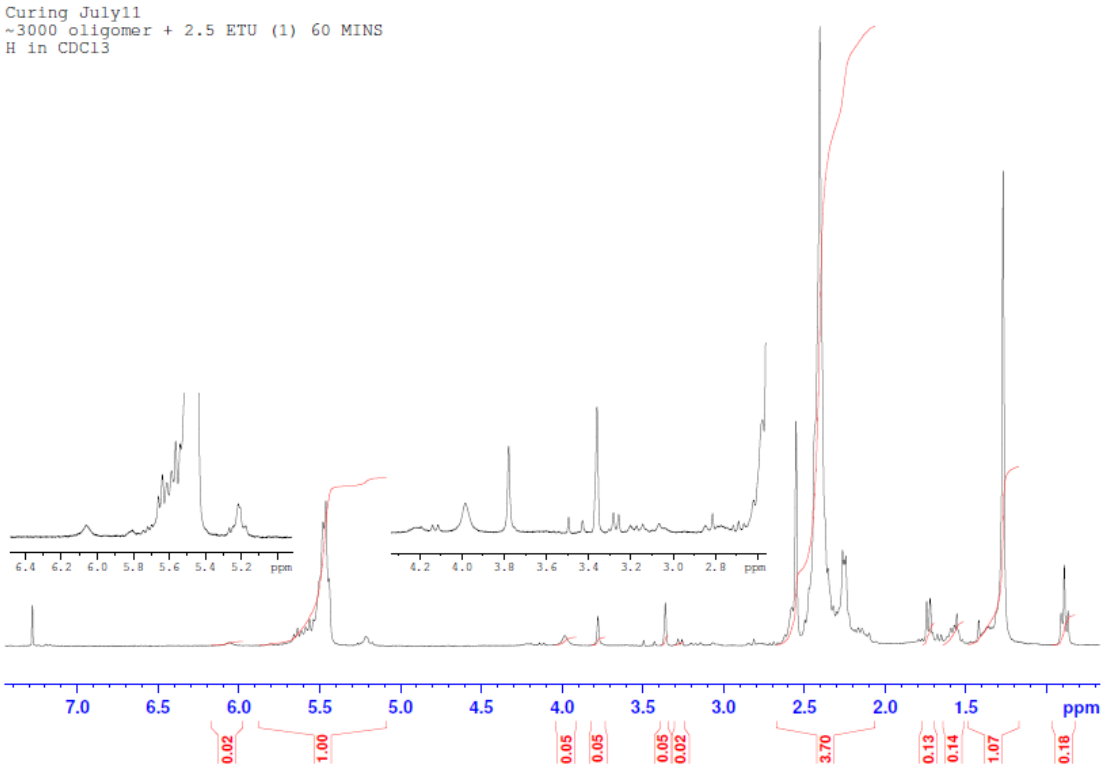
Appendix 2.3. GPC trace of oligochloroprene with 2 phr ETU and 1 phr zinc oxide active before and after heating to 160 °C for 60 minutes



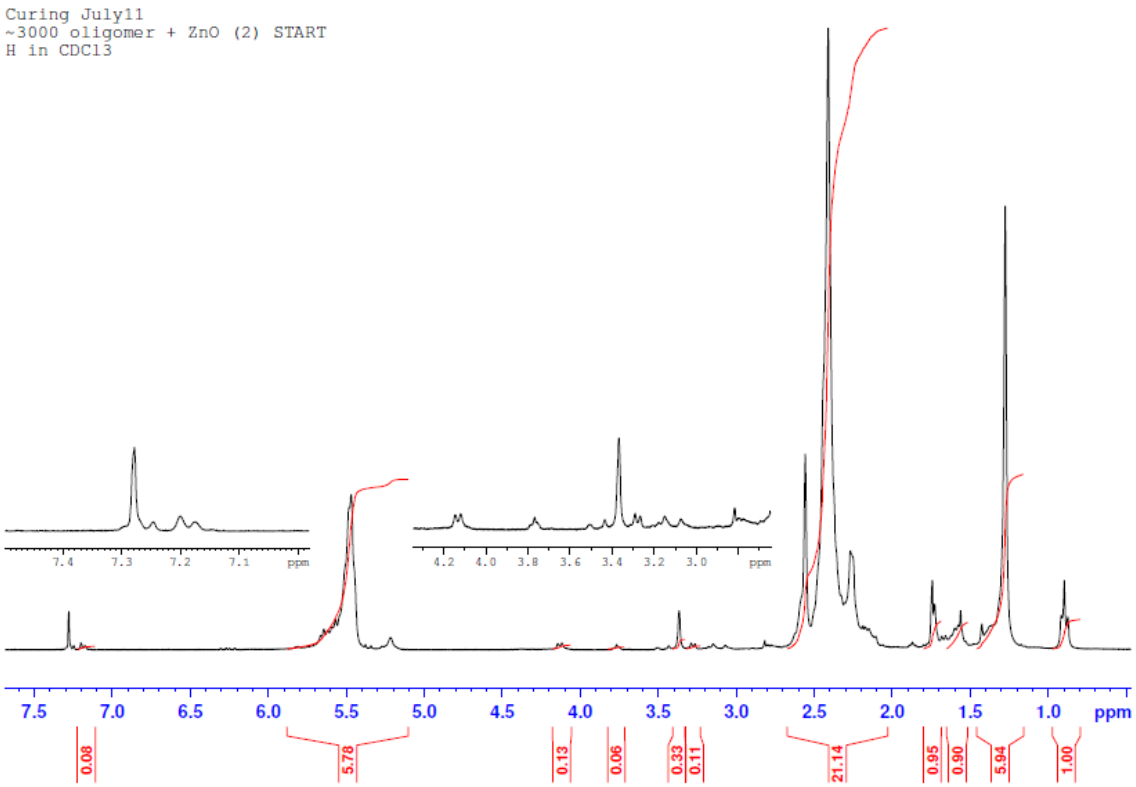
Appendix 2.4. ^{1}H NMR spectrum of oligochloroprene with 2.5 phr ETU before heating



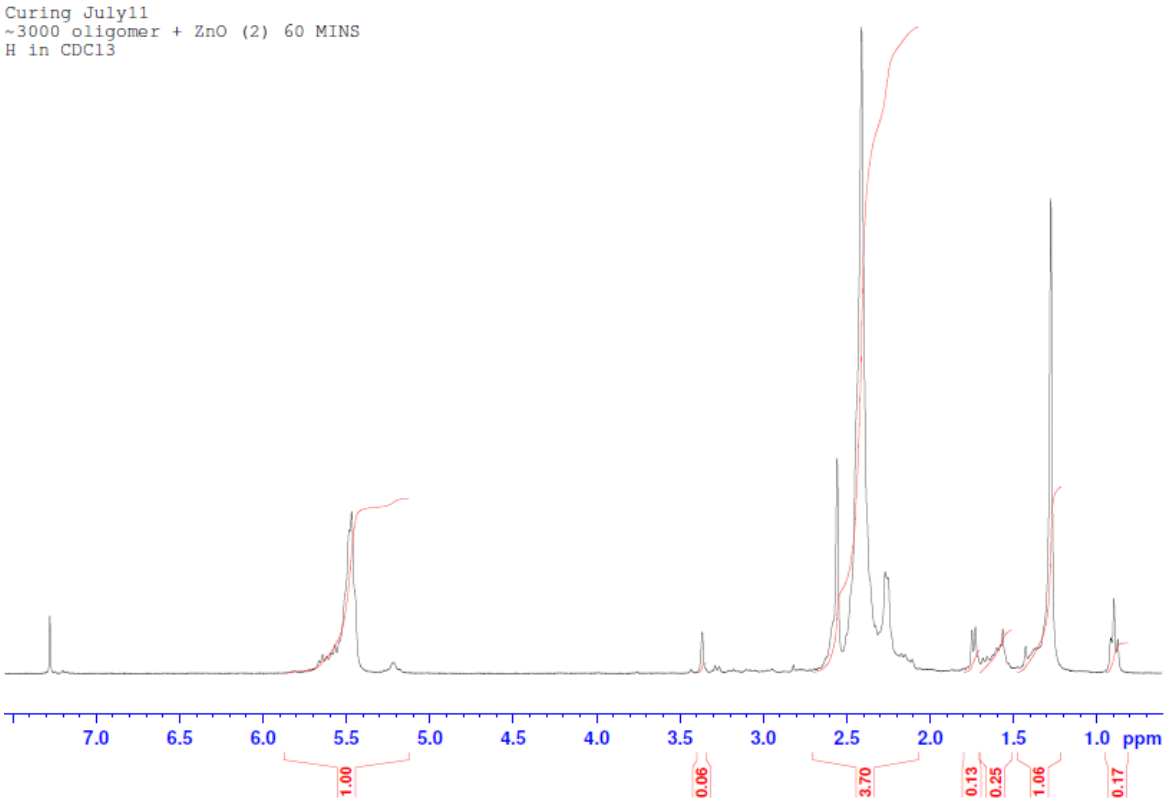
Appendix 2.5. ^{1}H NMR spectrum of oligochloroprene with 2.5 phr ETU after heating to 160 °C for 60 minutes



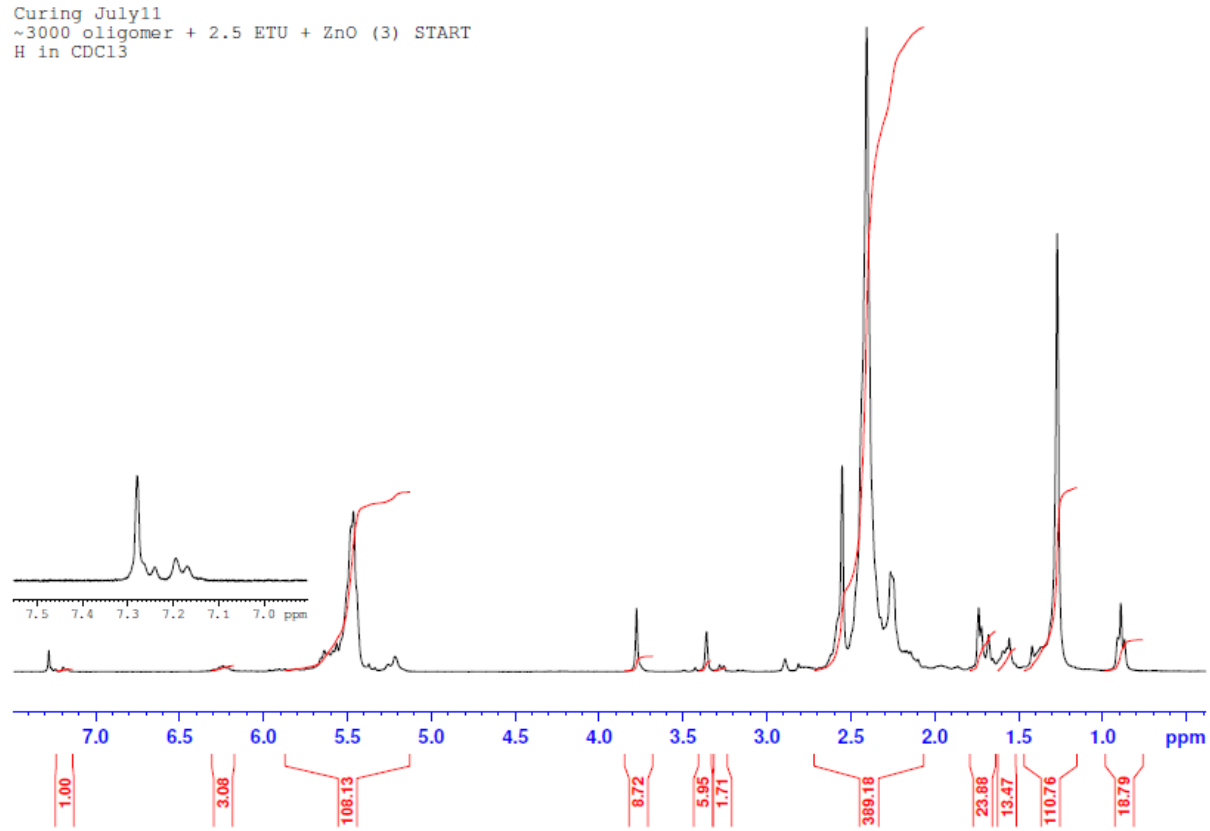
Appendix 2.6. ^{1}H NMR spectrum of oligochloroprene with 1 phr ZnO active before heating



Appendix 2.5. ^{1}H NMR spectrum of oligochloroprene with 1 phr ZnO active after heating to 160 °C for 60 minutes



Appendix 2.6. ^{1}H NMR spectrum of oligochloroprene with 2.5 phr ETU and 1 phr ZnO active before heating



Appendix 2.5. ^{1}H NMR spectrum of oligochloroprene with 1 phr ZnO active after heating to 160 °C for 60 minutes