To the memory of my late father

Daniel Ajayi Omikorede.

A STUDY OF NITROXYL RADICAL PRECURSORS AS PHOTOSTABILISERS FOR POLYMERS

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Submitted for the Degree of Doctor of Philosophy

The University of Aston in Birmingham

November 1984

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SUMMARY

The effects of different compounds on the melt stabilisation and the subsquent photostabilisation of Polypropylene have been studied under various processing conditions. Better melt and photo-stabilisation were obtained in the polymer films processed with the additives under restricted oxygen conditions than in the presence of oxygen excess.

4-hydroxyl-2,2,6,6 tetramethyl piperidinyl-1-oxyl and its hydroxylamine were very efficient melt and photostabilisers. The mechanism of melt stabilisation by the former involved the conversion of the nitroxyl radical to the free hydroxylamine with the formation of ethylenic unsaturation with processing time. Evidence for consumption and regeneration of nitroxyl radicals in both cases is presented. Photostabilisation by both compounds was by alkyl radical trapping.

2-methyl-2-nitroso propane and N-nitroso diphenylamine were found to be melt and photostabilisers. They generated the corresponding nitroxyl radicals during processing which in turn are responsible for the subsequent photo stabilisation.

2-methyl-2-nitro-propane, trimethylol nitromethane and trimethylol amino methane were not nitroxyl radical precursors either during processing or subsequent photo-oxidation. They are not effective as melt stabilisers for Polypropylene. The photostabilising effect of trimethylol nitromethane was very good, but less so for 2-methyl-2-nitro propane, whereas, trimethylol amino methane was not a good photostabiliser.

Esters of trimethylol nitromethane were not as good melt or photostabilsers as the nitro alcohol itself. They also antagonise with HOBP in Polypropylene while all other classes of compounds synergise with HOBP.

KEYWORDS: Polypropylene, nitroxyl radical precursors, photostabilisation nitro alcohol, synergism.

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The work described in this thesis was carried out between October 1981 and October 1984. It has been done independently and submitted for no other degree.

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CHAPTER ONE

1. INTRODUCTION

1.1 General aspects of polymer oxidation

All polymers are vulnerable to deterioration when exposed to the environment. Perishing of rubbers, weathering of plastics, tendering of fibres, fatigue failure in tyres are all different aspects of macromolecular oxidation.(1) Of the chemical processes that affect the physical, chemical and electrical properties of polymers, oxidation by elemental oxygen is the most deleterious(2). Other factors of accelerating influences include heat, light, contamination by metal ions, ozone and mechanical deformation(3).

Degradation of polymers usually occurs in two principal stages(3); during processing/fabricating operations in which the polymer is subjected to high temperature and mechanical stresses, and during the subsequent service life of the fabricated articles, when exposed to different environmental conditions. This results in deterioration of physical, chemical and mechanical properties such as loss of tensile strength, impact strength, resistance to fatigue, optical clarity, time to embrittlement, etc.

The nature of the degradation process varies in rate and extent, depending on the chemical and physical structures (4,5) of the polymer, the presence of impurities (6,7) which serve as sites of autoxidation and the environment to which they are exposed.

Poly propylene for instance, contains tertiary hydrogen atoms which constitute weak spots open to attack by oxygen. This is particularly severe at high temperatures and under the effect of ultraviolet light. This weakness is aggravated by the presence of impurities such as metal ions and hydroperoxides which may be formed during manufacture and processing operations.

1.1.1 Mechanism of thermal oxidation of Polyolefins

It is now universally accepted that oxidative degradation processes of polyolefins, like other hydrocarbon polymers, proceed through a radical chain auto-oxidation mechanism originally proposed by Bolland and his co-workers$^{(8-10)}$ as shown in the general reaction scheme below:-

Reaction Scheme 1.

Initiation $R - R \xrightarrow{\text{Shear}} 2R^{\bullet}$ -(1)

$RH + X^{\bullet} \longrightarrow R^{\bullet} + XH$ -(2)

$ROOH \longrightarrow RO^{\bullet} + {}^{\bullet}OH$ -(3)

$2\,ROOH \longrightarrow ROO^{\bullet} + H_2O + RO^{\bullet}$ -(4)

Propagation $R^{\bullet} + O_2 \longrightarrow ROO^{\bullet}$ -(5)

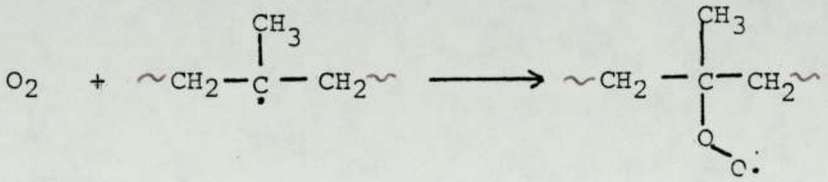
$ROO^{\bullet} + R'H \longrightarrow ROOH + R'^{\bullet}$ -(6)

Termination $2ROO^{\bullet} \longrightarrow$ Disproportionation products -(7)

$R^{\bullet} + ROO^{\bullet} \longrightarrow ROOR$ -(8)

$R^{\bullet} + R^{\bullet} \longrightarrow R - R$ -(9)

Evidence suggests(11-21) that polymeric hydroperoxides are mainly responsible for polymer degradation at least during initial stages of the oxidation process. These hydroperoxides are either formed by catalysed air oxidation during storage or by oxidation during the processing operation, during which macro-alkyl radicals combine with oxygen to give macroperoxyl radical (21) as shown below for polypropylene.

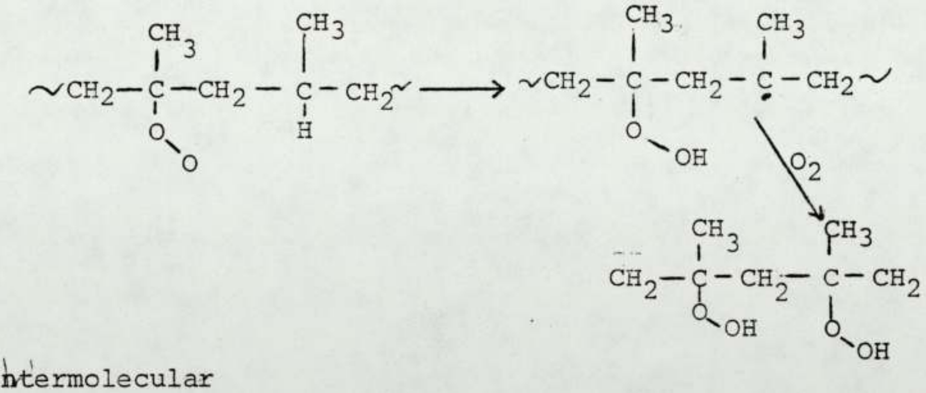


$$O_2 + \sim CH_2-\overset{CH_3}{\underset{\bullet}{C}}-CH_2\sim \longrightarrow \sim CH_2-\overset{CH_3}{\underset{O-O\cdot}{C}}-CH_2\sim \qquad -(10)$$

The macroperoxy radicals then abstract hydrogen atoms either intramolecularly or intermolecularly to give hydroperoxide as shown in reactions (11) and (12).

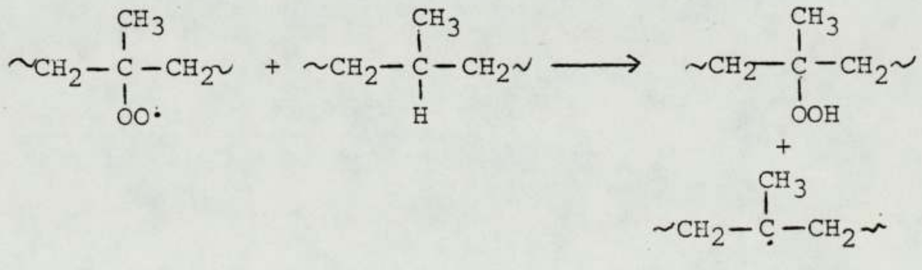
Reaction Scheme 2:

Intramolecular



$$\sim CH_2-\overset{CH_3}{\underset{O-O}{C}}-CH_2-\overset{CH_3}{\underset{H}{C}}-CH_2\sim \longrightarrow \sim CH_2-\overset{CH_3}{\underset{O-OH}{C}}-CH_2-\overset{CH_3}{\underset{\bullet}{C}}-CH_2\sim \xrightarrow{O_2} CH_2-\overset{CH_3}{\underset{O-OH}{C}}-CH_2-\overset{CH_3}{\underset{O-OH}{C}}-CH_2 \qquad -(11)$$

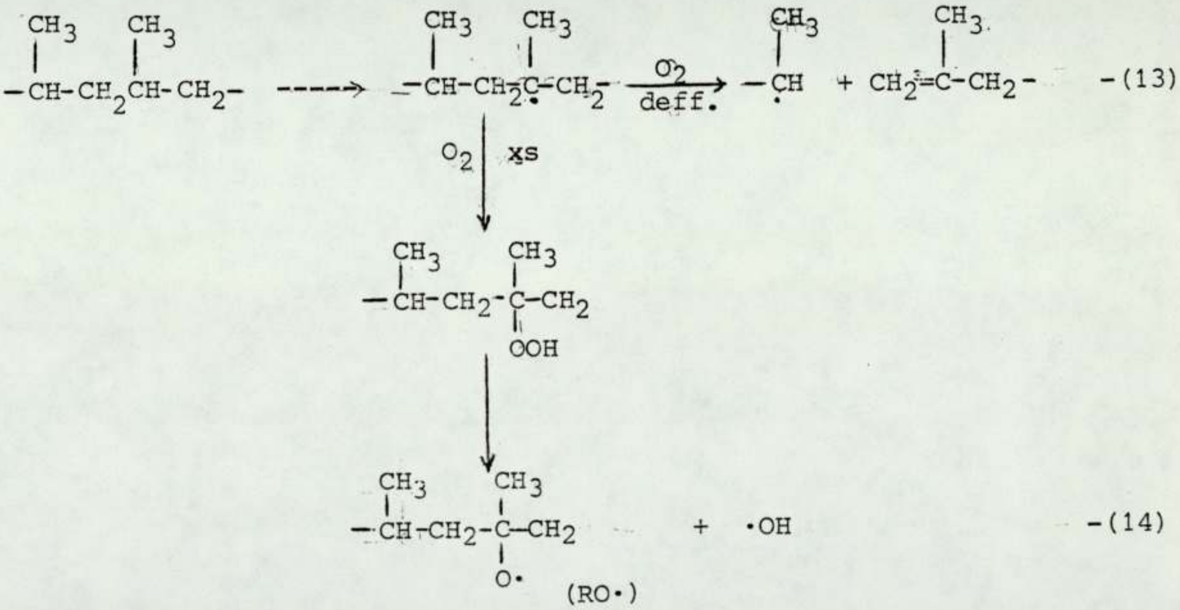
Intermolecular



$$\sim CH_2-\overset{CH_3}{\underset{OO\cdot}{C}}-CH_2\sim + \sim CH_2-\overset{CH_3}{\underset{H}{C}}-CH_2\sim \longrightarrow \sim CH_2-\overset{CH_3}{\underset{OOH}{C}}-CH_2\sim + \sim CH_2-\overset{CH_3}{\underset{\bullet}{C}}-CH_2\sim \qquad -(12)$$

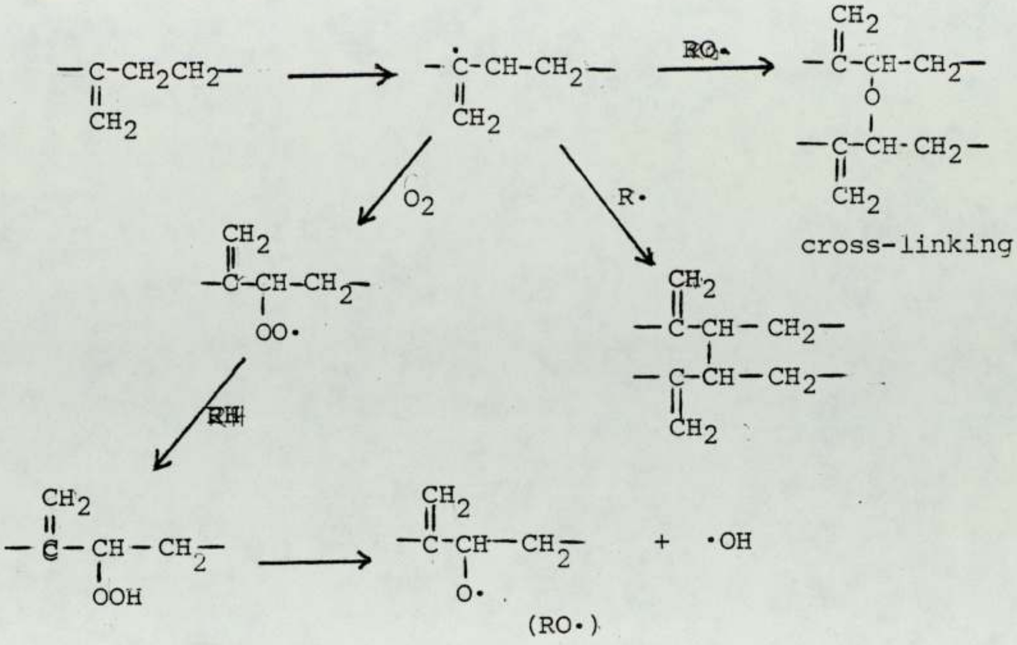
Indeed, there's evidence (22) to show that the products of thermal oxidation (or u.v. initiated photo-oxidation) of polypropylene are polymeric hydroperoxides as the main product (about 75 mole %)(22) together with lesser amount of alcohol, carbonyl and peroxide groups. Hydroperoxides thus formed may undergo thermolysis during thermal processing in restricted oxygen to give hydroxyl and alkoxyl radicals, but in the absence of oxygen, and at normal processing (or higher) temperatures, radical-induced depolymerisation may also occur as shown in Reaction Scheme 3.

Reaction Scheme 3:



Similarly, in Polyethylene, thermolysis of formed hydroperoxides occurs to give hydroxyl and alkoxyl radicals but in a deficiency of oxygen, the macroalkyl radicals cause cross-linking. However, in excess oxygen, much higher concentrations of hydroperoxides are formed with subsequent thermolysis resulting in chain scission(21)- as shown in scheme 4.

Reaction Scheme 4:

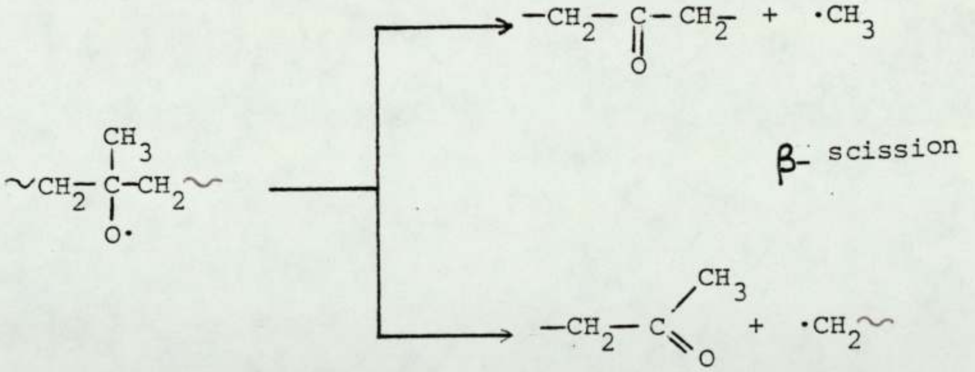


-(15)

-(16)

-(17)

Evidence shows(23-25) that the alkoxyl radical formed in the case of Polypropylens (reaction 14) undergoes cleavage by β -scission to give a ketone and a primary alkyl radical.

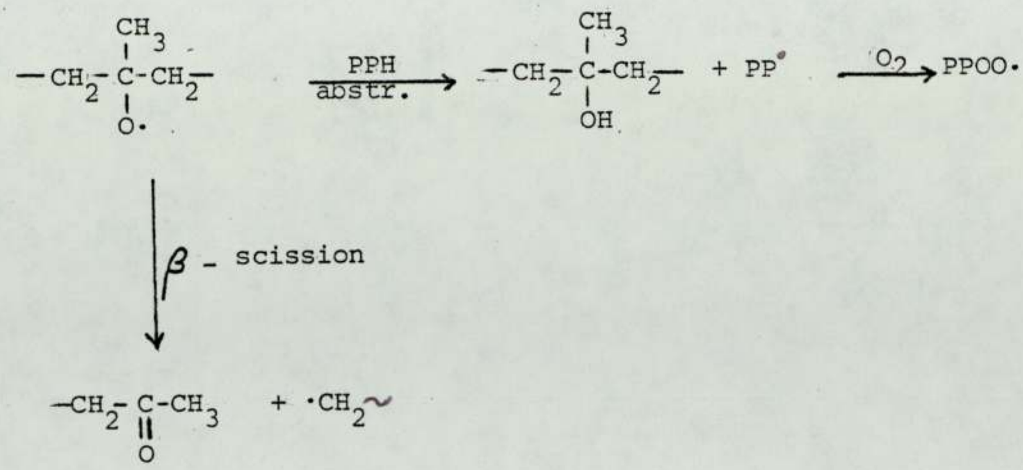


- (18)

-(19)

This was later supported by Decker and Mayo(26), who concluded that about 65% of the alkoxyl radicals (in polypropylene) undergo β - scission while the remainder attack the polypropylene matrix to give alcohol groups and eventually regenerate peroxyl radicals through alkyl radicals.

Reaction Scheme 5:



-(20)

-(21)

Thus the easier the abstraction of a hydrogen from the polymer matrix, the faster the rate of oxidation(27). The role of the ketones in subsequent oxidation processes will be discussed in a later section.

The initial products of autoxidation are alkyl and alkylperoxyl radicals and hydroperoxides. At normal oxygen pressures hydroperoxides are predominant (through alkylperoxyl radical intermediates) hence termination processes involving alkylperoxyl radicals (reaction scheme 1 reactions 7 and 8) are favoured while at limited oxygen pressures, processes involving macro-alkyl radicals are favoured (scheme 1 reaction 9).

1.1.2 Photo oxidation

Photo-oxidation involves the same radical sequence as thermal autoxidation except that the rate of initiation in the former is faster. This is attributed to the rapid cleavage of the initially formed hydroperoxides under u.v. light$^{(28)}$. Thus, the rate of termination is faster and consequently the kinetic chain length is shorter.$^{(29)}$

Polypropylene is a branched alkane and should not absorb light beyond 180nm$^{(30)}$. However, it is highly photo-sensitive when exposed to sunlight ($\lambda > 190$nm): this has been attributed to impurities such as peroxide and carbonyl groups $^{(31,32)}$ which are introduced into the polymer by air-oxidation during manufacture or/and processing operations or by 'impurities-catalysed' oxidation at room temperature during storage. Although peroxide and carbonyl groups absorb u.v. light in the region 290-330 nm$^{(34)}$, the true nature of the impurities depend on the conditions of manufacture (polymerisation), extrusion mode, as well as the presence of deliberately introduced species such as pigments in the polymer.$^{(22)}$

1.1.2.1. Mechanism of photo-oxidation of Polyolefins

The behaviour of polyolefins, as other polymers, upon exposure to u.v. light depends on the thermal oxidation history. Scott$^{(35)}$ suggested that chromophores are produced in higher concentrations during processing/fabrication and thus contribute more to the photoinitiating step than those produced during manufacture.

Ample evidence$^{(11-21,35-37)}$ indicate that hydroperoxides produced during thermal processing are the main photo-initiators at the early stages of u.v. irradiation, rather than other chromophoric groups e.g.

carbonyl group which are formed as a result of thermal- and photo-decomposition of the hydroperoxides. However, carbonyl groups are also believed to contribute to photo-initiation at later stages(16,38). And since carbonyl groups could readily be identified (easier than hydroperoxides) in saturated hydrocarbon polymers(39), some workers(40) believed that hydroperoxides are not involved in the photo-initiation process. But, this argument has been out-weighed by evidence which support hydroperoxide photo-initiation which can be summarised as in reaction scheme 6.

Reaction Scheme 6:

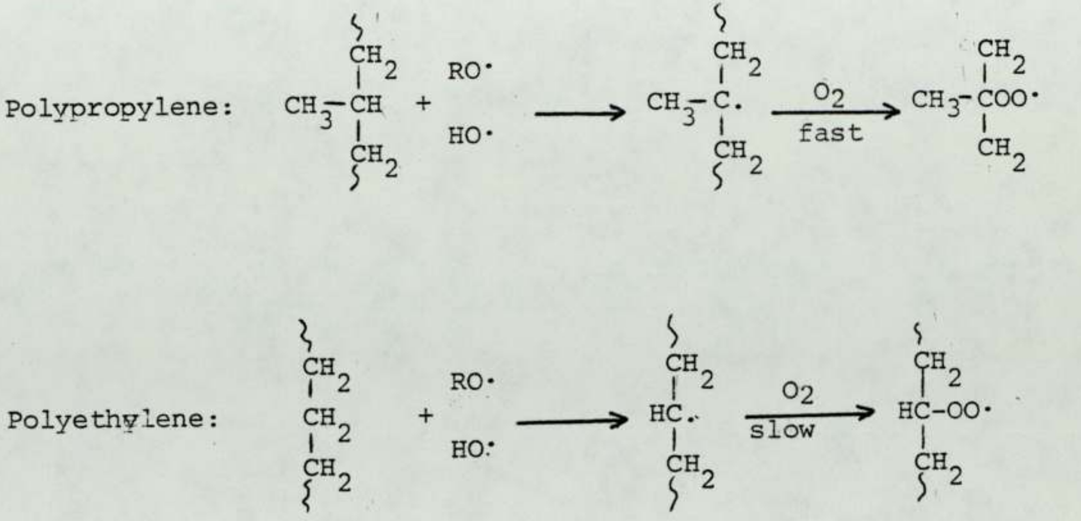
$$\mathrm{ROOH} \xrightarrow{h\nu} \mathrm{RO}^{\bullet} + {}^{\bullet}\mathrm{OH} \qquad -(22)$$

$$\mathrm{R'H} + \mathrm{RO}^{\bullet} \longrightarrow \mathrm{ROH} + \mathrm{R'}^{\bullet} \qquad -(23)$$

$$\mathrm{R'H} + {}^{\bullet}\mathrm{OH} \longrightarrow \mathrm{H_2O} + \mathrm{R'}^{\bullet} \qquad -(24)$$

The rates of reactions (23) and (24) vary from polymer to polymer. Veseley(41) and his co-workers thus attributed the greater light stability of Polyethylene to the slow rate of attack by radicals (reactions (23) & (24)) compared to the rather fast rate in polypropylene (Reaction scheme 7).

Reaction Scheme 7:



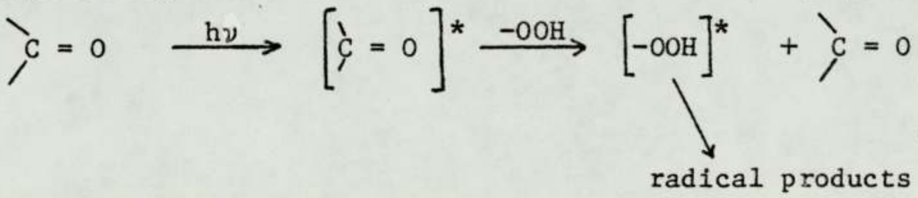
-(25)

-(26)

In addition the intra-or intermolecular abstraction of the labile hydrogen in Polypropylene (Scheme 2, reactions 11 & 12) by the macroperoxyl radical to form hydroperoxides occurs at a faster rate than in Polyethylene. (Intramolecular abstraction predominates in polypropylene).

1.1.2.2 The role of carbonyl groups in photo-oxidation

Carbonyl groups are introduced into the polymer by air-oxidation during manufacture and as a result of thermal- and photodecomposition of hydroperoxides during fabrication and exposure to the environment respectively. They are believed(42) to be photosensitisers in the later stages of photo-oxidation. Their energy is transferred to -OOH groups through their excited states as in reaction (27).

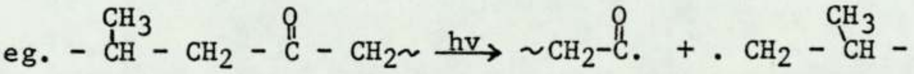


-(27)

The rate of photo-oxidation however, has been found(43) to be independent of the concentration of carbonyl groups in the polymer at the initial stages.

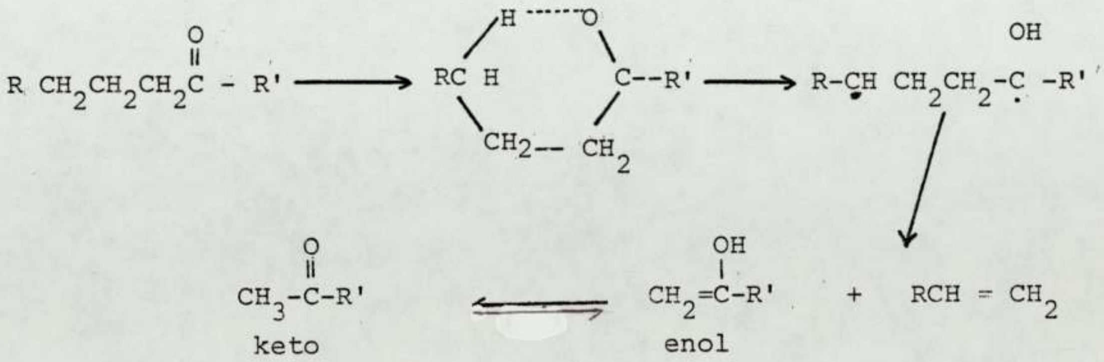
Photochemical studies of carbonyl groups (44-47) containing hydrogen on the carbon atom in the α- position suggest that Norrish 1 and Norrish 2 reactions are important in the photo-oxidation mechanism of polymer as they both lead to scission of bonds in the main polymer chain. In the Norrish 1 type, the bond between the carbonyl group and adjacent α- carbon is homolytically cleaved, resulting in two radicals.

$$RCOR' \longrightarrow \begin{cases} RCO\cdot + R'\cdot \longrightarrow R. + CO + R'. \\ R\cdot + R'CO \longrightarrow R. + R' + CO \end{cases} \qquad - (28)$$

eg.  - (29)

$$\text{eg.}\ -\overset{CH_3}{\overset{|}{C}H} - CH_2 - \overset{O}{\overset{\|}{C}} - CH_2\sim \xrightarrow{h\nu} \sim CH_2-\overset{O}{\overset{\|}{C}}. \ + \ .\ CH_2 - \overset{CH_3}{\overset{\backslash}{C}H} - \qquad - (29)$$

In Norrish 2 type, a non-radical intramolecular process occurs with the formation of a six membered cyclic intermediate that eventually yields an enol (which rearranges to ketone) and an olefinic group.

 -(30)

These reactions were used to explain the sensitization of photo-oxidation of Polyethylene(48), oxidation of unsaturated hydrocarbon(49) and hydrogen abstraction from a hydrocarbon chain(50), a process that contribute to the light-sensitivity of Polypropylene compared to Polyethylene.

1.1.2.3 Metal Impurities and other chromophores in photo-oxidation

Metal impurities in polyolefins are mainly catalyst residues e.g. Titanium, left behind during polymerisation. They are thought(51) to sensitize photo-oxidation of polyolefins by a mechanism that generates free radicals on photo-oxidation.

$$M^{n+}X^{-} \xrightarrow{h\nu} \left\{M^{(n-1)*}X\right] \longrightarrow M^{(n-1)+} + X^{\cdot} \qquad -(31)$$

$$ROOH + M^{n+} \longrightarrow RO. + M^{(n+1)} + OH^{\cdot} \qquad -(32)$$

However, no pro-oxidant effect was observed for titanium, and there is no correlation between titanium content and photostability(52).

Other chromophoric groups include unsaturation, formed during manufacture; polynuclear aromatic compounds, derived from exposure to polluted atmospheres; singlet oxygen produced either from termination of peroxyl radicals or by electron transfer from excited states e.g. carbonyl; oxygen - polymer charge transfer complexes. Although Allen and Fatinikun(53) observed a relationship betwen unsaturation and induction period in the photo-oxidation of poly-propylene, the role of these chromophores as initiators are insignificant, compared with hydroperoxides(39). The contribution of various chromophoric groups in Polypropylene(52) to the overall photoinitiation step is in the order of

$$\mathrm{ROOH} > \mathrm{Ti} > \mathrm{PNA} > \rangle C = O > \mathrm{PP} \ldots O_2$$

Generally, the prior thermal history of the polyolefins, to a large extent, determines their subsequent photo-oxidative behaviour. For example, in Polypropylene, the increase in MFI observed with increasing processing severity e.g. in an open mixer of a torque rheometer is a consequence of the high concentrations of hydoperoxides formed at longer processing times. (Scheme 3) while under oxygen deficient conditions a less dramatic increase in MFI is observed(39) and this is related to the lower concentration of hydroperoxides formed under this condition. The same is true for polyethylene (Scheme 4).

1.2 Stabilisation of Polyolefins

Stabilisation of polyolefins is essential against high processing temperatures and against both high temperatures and u.v. irradiation during service life. Stabilisation may be approached by one or a combination of the following.(54-56)

a) removal of impurities that initiate degradation e.g. metal ions

b) incorporation of compounds that retard oxidation e.g. metal-chelating additives, and

c) modification of polymer structure, giving more resistant product e.g. by co-polymerisation.

Of these, additive incorporation is the most widely used, and it depends on a number of factors such as the intrinsic activity(57), additive solubility in the polymer, and solubility in any medium it may be in contact with during service life, additive migration and subsequent volatilisation (at high temperature) etc. Bilingham and Calvert(58) have demonstrated that additives are mainly lodged at the spherulite boundaries of the amorphous phase of polypropylene. This is favourable, as the amorphous phase is the most oxidation - sensitive part of the polymer matrix.(59)

1.2.1 Antioxidant mechanisms

Antioxidants are classified according to their mode of functions and how they interfere chemically with the polymer. Since oxidation of polymers proceeds through the formation of hydroperoxides by a radical chain process, and their subsequent breakdown into free radicals, any additive that interferes with either or both of these processes is desirable. Thus there are two major mechanisms of antioxidant action - a chain breaking mechanism which involves the deactivation of chain propagation species ($R^{\bullet}$ and $ROO^{\bullet}$) and preventive mechanism that involves inhibition of chain reactions by the removal (usually through decomposition into inert products) of the radical generating species, hydroperoxides.

1.2.1.1 Chain breaking mechanisms

Alkylperoxyl radical deactivators are reducing agents or electron donors (hence CB-D) while alkyl radicals are oxidised to carbonium ions by acceptance of an electron from the antioxidant(60).
(hence CB-A)

$$\begin{tikzcd} R^{\cdot} \arrow[r, "O_2"] \arrow[d, "-e"] & ROO^{\cdot} \arrow[d, "+e"] \\ R^{+} & ROO^{-} \\ (CB\text{-}A) & (CB\text{-}D) \end{tikzcd} \qquad -(33)$$

(i) Chain- breaking donor (CB-D) mechanism

CB-D antioxidants function by donating electron(s) to alkylperoxyl ($ROO^{\cdot}$) radicals resulting in the eventual consumption of the inhibitor. The presence of a reactive N-H and/or O-H functional groups in hindered phenols and secondary amines suggest that they compete with the polymer for the $ROO^{\cdot}$ radicals. The transfer of a hydrogen atom to $ROO^{\cdot}$ radical effectively deactivates it; forming hydroperoxide and a radical from the antioxidant. which may react with another $ROO^{\cdot}$ through radical trapping.(61)

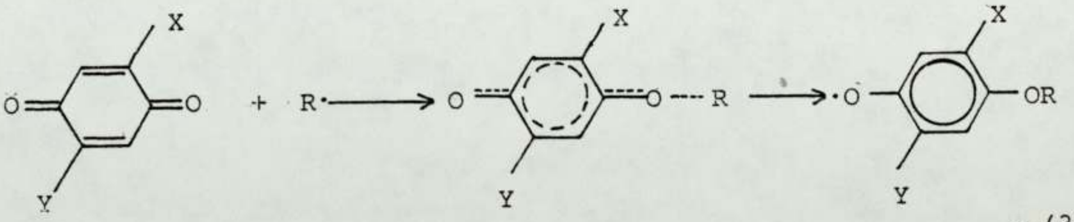
$$ROO^{\cdot} + Ph_2\,N - H \longrightarrow ROOH + Ph_2\,N^{\cdot} \qquad -(34)$$

$$Ph_2N. + ROO^{\cdot} \longrightarrow PH_2N\theta. + RO^{\cdot} \qquad -(35)$$

Thus electron releasing groups such as alkyl, alkoxyl attached to the ortho- or para- positions of hindered phenols or amines increase antioxidant activity more than those in m-positions, while electron-attracting groups such as nitro groups and halogens decrease the antioxidant activity.(62) Also, α -branched alkyl groups in ortho-positions increase antioxidant activity while those is para-positions decrease it.

(ii) **Chain-breaking acceptor (CB-A) mechanisms**

Macro-alkyl radicals are readily oxidised by electron-acceptors. Thus, an oxidising agent that can remove alkyl radicals from an autoxidising system (in preference to ROO$^\bullet$) should have antioxidant activity. Compounds in this group include quinones, nitro compounds, phenoxyls(63) and nitroxyl compounds(64,65). Quinones and nitro compounds have been successfully used for rubber stabilisation during processing(66) although they are unable to compete with oxygen in high oxygen pressures. Their transition states are believed(60) to involve charge separation.



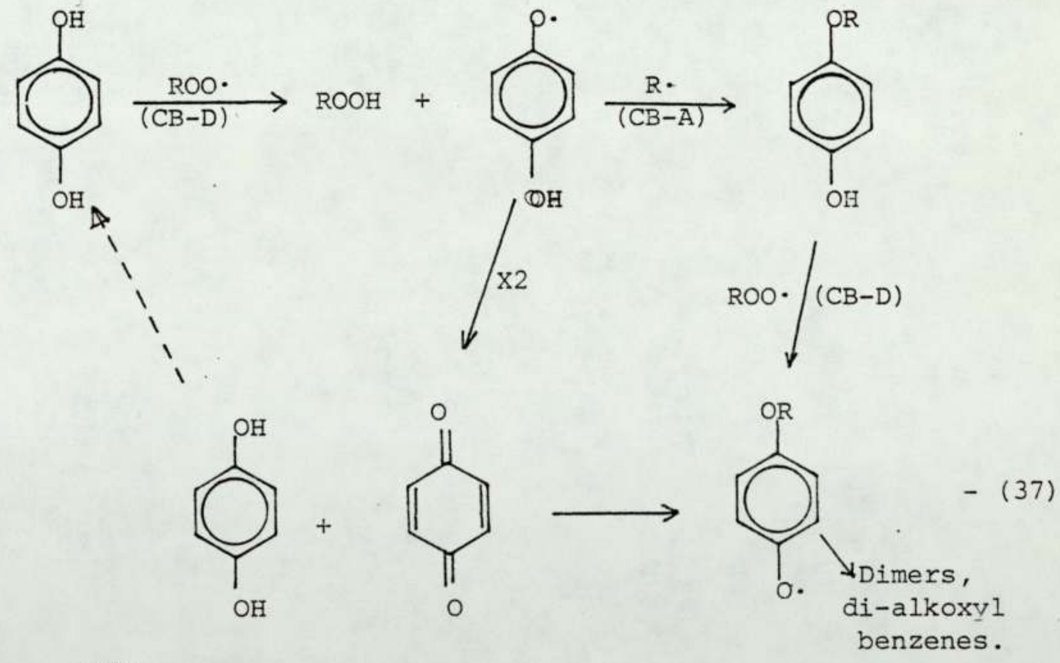
- (36)

Thus electron withdrawing and delocalising substituents increase alkyl radical affinity, hence antioxidant activity.

(iii) Complimentary mechanism of CB-A and CB-D antioxidants

The CB-D and CB-A mechanisms are efficient in systems in which the chain propagating species present in high concentrations are ROO$^\bullet$ and R$^\bullet$. Any antioxidant that possesses the ability to function by both mechanism will therefore have an advantage over either. One of the best known examples is hydroquinones. In the presence of ROO$^\bullet$ radicals, it is converted to benzoquinone by CB-D mechanism which in itself is an alkyl radical 'trap' by a CB-A mechanism giving eventually inactive products as shown in scheme 8.

Reaction Scheme 8.



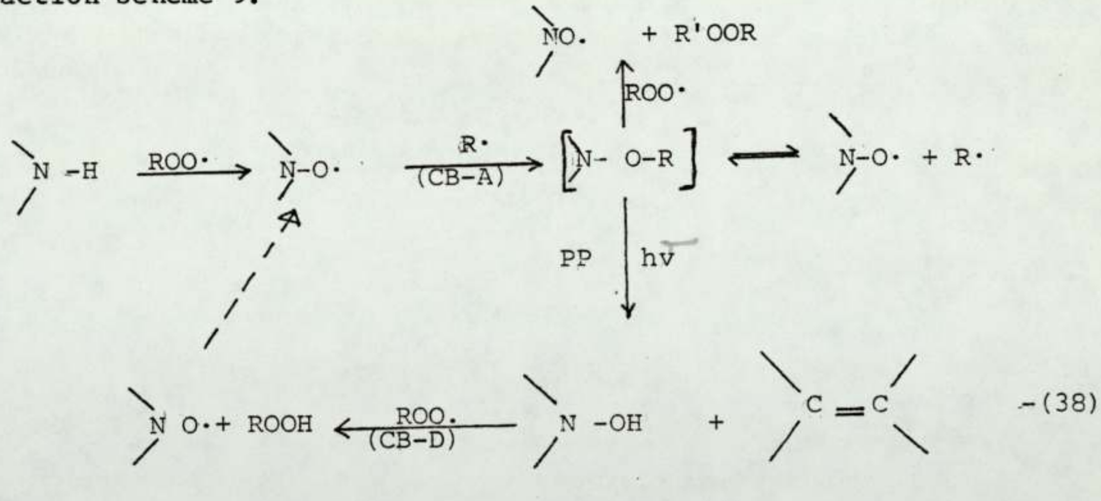
- (37)

Henmann(67) therefore concluded that it is this ability of the benzoquinones derived from hydroquinones to effectively trap alkyl radicals in conditions of restricted oxygen access that is responsible for melt stabilisation of polypropylene under the same condition.

(iv) Regenerative chain breaking mechanism

Some antioxidants can alternate between their oxidised and reduced states, thereby exhibit regenerative behaviour under conditions where both R$^\bullet$ and ROO$^\bullet$ radicals are present. Examples include transition metal ions which have been successfully employed during photo oxidation of drying oils;(68) and as thermal antioxidants in polyamides and polyesters. Nitroxyl radicals derived from hindered piperidines is another class of compounds,(69-71) which has been thought to act through a regenerative mechanism. They are believed to be effective radical traps (CB-A mechanism). Free hydroxylamine is oxidised by ROO$^\bullet$ (CB-D mechanism) to regenerate the nitroxyl radicals as shown in scheme 9.

Reaction Scheme 9.



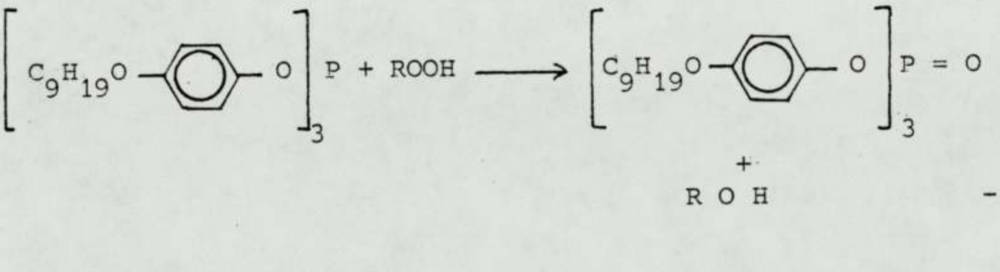
Thus, the transformational products of the parent amine are thought to be the effective "traps" and not the parent amine itself.(71)

1.2.1.2 Preventive mechanism of peroxide decomposition

Since hydroperoxides are key initiators for polymer oxidation, any compound that deactivates or removes hydroperoxides in a non-radical process effectively inhibits polymer oxidation. These are called preventive antioxidants and may include peroxide decomposers, metal ion deactivators, u.v. absorbers, u.v. quenchers. A whole family of sulphur-containing compounds fall into this class. Examples are sulphides (mono-and di-) and dithiolates(72-74) which have been used in polyolefins. Peroxide decomposers are classified as catalytic or stoichiometric(75-76) according to their mode of action. Phosphite esters(60,77) and a variety of sulphur compounds are examples of stoichiometric and catalytic peroxide decomposers respectively which act as melt, heat and light stabiliser.

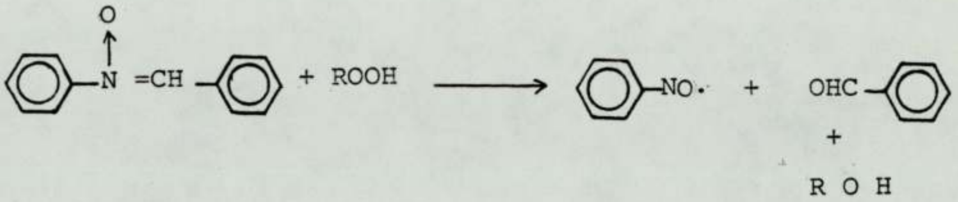
(i) Stoichiometric peroxide decomposer (PD-S)

The only requirement of compounds in this group is the ability to reduce hyroperoxides stoichiometrically to alcohols in a non-radical process. Notable among this group is tris nonyl phenyl phosphite (a phosphite ester) which is a commercial stabiliser for rubber(78).



- (39)

A smilar mechanism is involved in the thermal antioxidant action of α, N diphenyl nitrone(79), in which the subsequent nitroxyl radical can additionally 'trap' alkyl radicals thus exhibiting autosynergism.



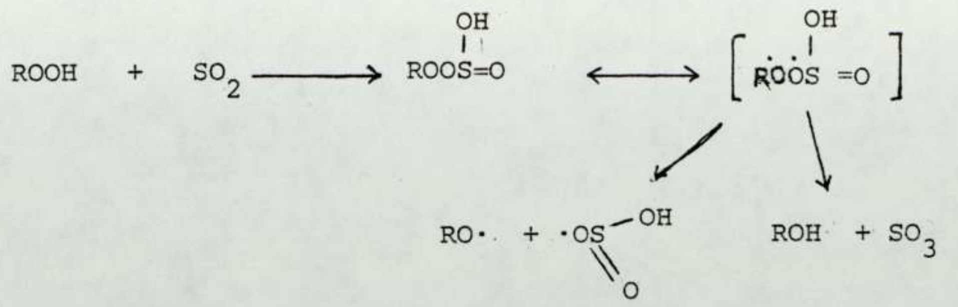
-(40)

Transformation products of phosphite esters (phosphate esters) are in themselves antioxidants.(80).

(ii) <u>Catalytic peroxide decomposers (PD-C)</u>

Compounds in this group destroy hydroperoxides catalytically through the formation of acidic products in a radical generating process. A variety of sulphur compounds fall into this group. Antioxidant activity is normally proceeded by a pro-oxidant stage. In dithiolates however, the pro-oxidant effect is only transient and of no effect on the long term antioxidant action(81).

It was suggested(82) that SO_2 acts as a catalyst for the decomposition of hydroperoxides to alcohols and ketones, but more recent evidence(83) show that SO_2 rather than being a catalyst, reacts with hydroperoxide stoichiometrically in a homolytic process, giving rise to SO_3 which is a powerful catalyst for hydroperoxide decomposition.



-(41)

Thus regeneration is responsible for the catalytic effect of SO_3 on hydroperoxide decomposition.

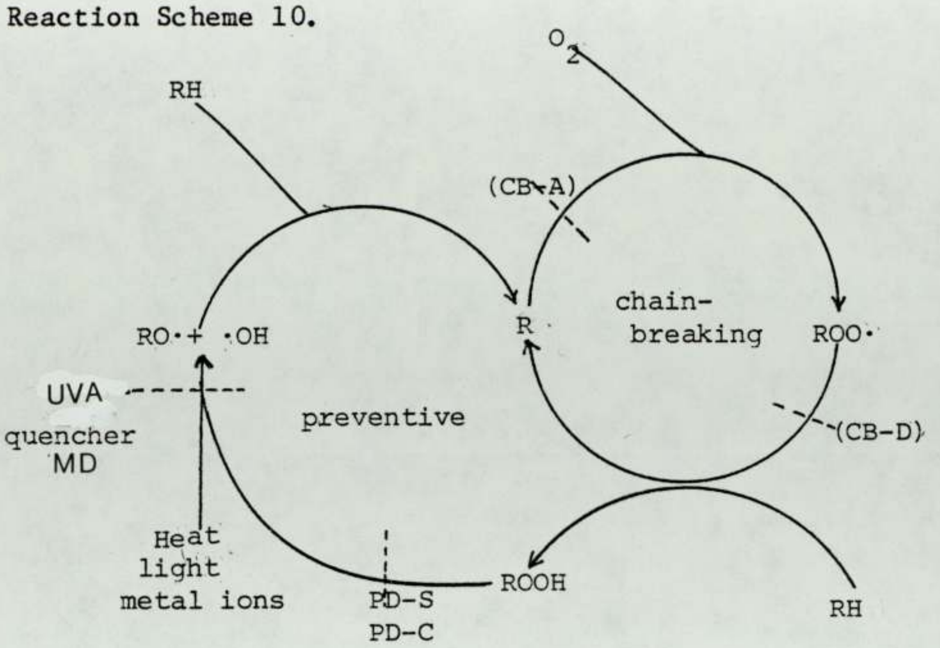
Many sulphur-containing compounds which are peroxidolytic antioxidants are also able to trap $ROO^{\bullet}$ hence have lower pro-oxidant effect than simple sulphides and many of them, (e.g. Nickel complexes of dithioic acid) function by many other stabilising mechanisms(84) e.g. u.v. absorption and u.v. screening. They are therefore not only thermal antioxidants but also useful as photostabilisers.

A variety of metal complexing agents are effective in stabilising polyolefins against the effect of metal ions. Metal thiolates for example, effectively deactivate metal ions, and, also exert a positive antioxidant effect,(85), due to their ability to decompose hydroperoxides by a non radical mechanism.

1.2.2 Photostabilisation of Polymers

The key steps in polymer photo-oxidation are as shown in reaction scheme 10 (39). Essentially, these include (a) Formation of polymer radicals ($R^{\bullet}$ and $ROO^{\bullet}$) and (b) Formation of radical generators of which hydroperoxides are the most important.

Reaction Scheme 10.



The photo-oxidising system contains radicals such as R$^{\cdot}$, ROO$^{\cdot}$, RO$^{\cdot}$ and $^{\cdot}$OH which all take part in the photodegradation process. Reducing the number and/or activity of these radicals is a means of effective photostabilisation. Based on this fact, u.v. stabilisers have been classified into four main types as follows:-

(i) chain breaking antioxidants
(ii) peroxide decomposers
(iii) u.v. absorbers
(iv) excited state quenchers

The mechanism of chain-breaking and peroxide decomposition in photostabilisation is not different from that of conventional antioxidants. Hindered piperidines are good photostabilisers (through their intermediate nitroxyl radicals)(86-92) while phenolic antioxidants are of little value as they are destroyed under the effect of u.v. light(52,93). Their activity however is enhanced when grafted to the polymer through acrylic groups.(94) e.g. 3,5 ditert butyl, 4-hydroxyl benzyl acrylate.

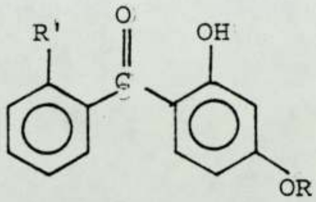
A comparison of u.v. stabilising activity of a typical chains-breaking antioxidant (Irganox 1076), a u.v. absorber (HOBP) and peroxide decomposers Nickel diethyl dithio carbamate (NiDEC) and Zinc diethyl dithio carbamate (ZnDEC) showed(95) the order of:

$$\text{NiDEC} > \text{HOBP} > \text{Irganox 1076} > \text{ZnDEC}\,.$$

The difference in u.v. stabilising activity of NiDEC and ZnDEC is not related to the peroxide decomposing ability but that NiDEC is more stable under u.v. irradiation than ZnDEC(32) hence a better u.v. stabiliser.

1.2.2.1 U.V. absorbing mechanism

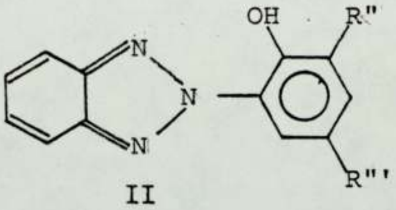
The requirement of compounds in this group is the ability to absorb u.v. light without destruction of their structure ; and to emit the absorbed light in a non-destructive way (radiation). The absorbed light energy may be released as flourescence or as phosphorescence which are of less degradative effect. Prominent examples of compounds in this group include 2-hydroxy benzophenones (I) and 2-hydroxy benzotriazoles II.



I

R = n-alkyl

R'= H



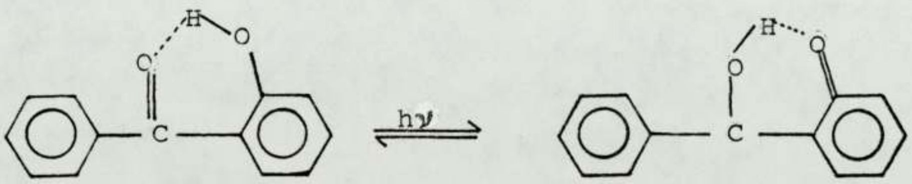
II

R" = t-Butyl

R"' = methyl, t-butyl.

It was thought(96) that the longer the R group in (I) the better the u.v. absorbing capability due to better compatibility and probable reduction in migration. However, studies(97) on diffusion and compatibility of homologous series of 2 — hydroxy-4-alkyloxy-benzophenones in isotactic polypropylene show that migration (hence surface blooming/evaporation) decreases with alkyl chain length R but compatibility is independent of the chain length.

The effectiveness of hydroxybenzophenones as u.v. absorbers is associated with the internal hydrogen bond between hydroxyl and carbonyl groups(98), which enhance the dissipation of u.v. light via keto-enol tautomerism in excited states.



-(42)

The same mechanism may be true for hydroxytriazoles.

1.2.2.2 Mechanism of quenching of excited states

This involves a direct transfer of excitation energy from the polymer molecule to an acceptor molecule. Thus, the quencher (acceptor) molecule must have excited state energy levels lower to that of the polymer and must also be able to dissipate its accumulated energy harmlessly.(99)

The photo-excited state of carbonyl groups if quenched by O_2 in its triplet state (to form longer life singlet state oxygen(48) which may react with double bond of polyolefins to give hydroperoxides) may indirectly initiate degradation. An effective quencher must therefore deactivate the carbonyl excited state, preventing Norrish type 1 & 2 reactions in the polymer (reactions 17 and 19) as well as deactivating singlet oxygen and subsequently preventing hydroperoxide formation.

Nickel (II) chelates(81,88,95,100) have been reported to be effective quenchers of excited singlet oxygen and of photo excited states generally. Their u.v. stabilising effectiveness however, is due to the peroxide decomposing ability, and to a lesser extent, radical scavenging by their transformation products.

In the light of above photo stabilisation mechanisms, factors that must be considered in the choice of u.v. stabilisers include,

(i) Photostability of the additive and its transformation products.

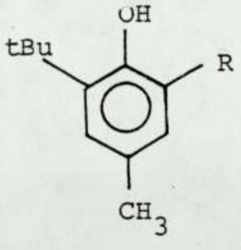
(ii) Chemical changes in the additive that may occur during processing which may affect the photostability.

(iii) Compactibility/solubility of the additive in the polymer. The stabiliser must not be lost by migration/volatilisation.

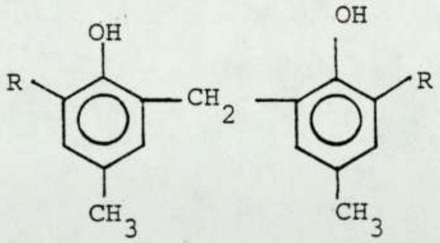
(iv) The nature of the environment of the polymer during service life: photo-oxidative, or thermal-photo-oxidative.

1.3 Antioxidant substantivity

This phenomenon had been overlooked until recently. Surprisingly, the motivation to investigate the relationship between antioxidant structure and substantivity came from the plastic rather than rubber industry. It was found that simple low molecular weight phenolic antioxidant used in rubber (e.g. III and IV) were effective melt stabilisers for polypropylene during processing but failed upon accelerated oven ageing tests.

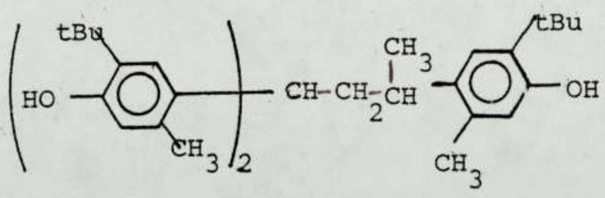


III

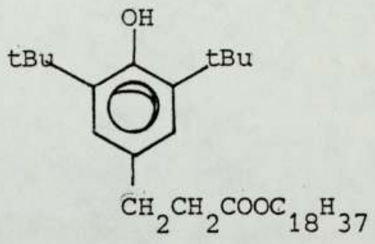


IV

This failure was associated to loss of antioxidant by volatilisation (at high temperature). High molecular weight anti-oxidants were therefore developed of which commercial samples include Topanol CA (V), Irganox 1076 (VI)



V



VI

Billingham(101) suggests that additive loss from the polymer depends on two factors: (i) the rate of removal from surface due to dissolution, precipitation and evaporation. (ii) the rate of replacement by diffusion from bulk, which is analogous to heat loss by conduction/emission. Under severe conditions therefore, antioxidant volatilisation is more important than its intrinsic activity. Billingham therefore suggested four strategies to overcome additive volatilisation:

(i) maximise solubility, this eliminates bloom and reduce vapour pressure.

(ii) reduce volatility, by employing high molecular weight substituents.

(iii) reduce diffusion co-efficient by employing polymer bound additives in copolymerisation/grafting.

(iv) Super saturation of additive, provided it does not greatly alter the polymer structure to a disadvantage. This results in a diffusion-controlled loss.

1.4 Synergism and Antagonism

When the combined effect of two or more antioxidants is greater than the sum of individual effects of the antioxidants, the phenomenon is refered to as synergism and the two or more antioxidants are synergists. Synergism is economical and desirable. The mechanism is not fully understood but it is believed that mutual protection by synergists are involved.

HOBP (a u.v absorber) and its analogues, synergise effectively with both chain breaking antioxidants (e.g. Irganox 1076) and peroxide decomposers(95) (.e.g. NiDEC) under u.v. exposure. Hindered phenols containing benzylic sulphur have been shown(102) to be more effective than conventional hindered phenols at the same molar concentration in combination with HOPB. Propionate esters are unstable under u.v. light but are effectively used as synergistic thermal stabilisers with phenolic antioxidants.

Antagonism is the reverse of synergism and suggests that there is interaction between the two or more compounds to form complexes which are inactive to alkyl or alkylperoxyl radicals(103). On the other hand, there may be cross-termination reactions(104) between radicals of inhibitors, thus decreasing the inhibiting power.

$$A. + .A' \longrightarrow A — A' \qquad -(43)$$

1.5 Review of nitroxyl radicals and precursors as photostabilisers for polymers

Aromatic secondary amines give secondary oxidative products that are themselves powerful antioxidants. In particular, nitroxyl radicals have assumed a position of importance in the photo stabilisation of polyolefins particularly polypropylene and in rubbers.(37,52,70).

Free nitroxyl radicals having no α- hydrogen atoms are stable(105-107). In sterically hindered nitroxyl compounds such as 2,2,6,6 tetramethyl piperidin-1-oxyl, the methyl groups not only stabilise the ring but also prevent valence tautomeric transformations which lead to hydroxylamine and nitrone formations.

Nitroxyl radicals inhibit chain reactions of oxidation of hydrocarbons and polymer(65,90,108-11). This inhibition was attributed to the "trapping" of active alkyl radicals by the nitroxyl radicals in a CB-A process (see scheme 9). However this 'trapping' theory is not sufficient to explain the effectiveness of nitroxyl radicals as antioxidants. The derived alkyl hydroxylamines ($>$N-OR) are known(112) to be thermally unstable and there is no evidence that they survive the processing operation without decomposition. Moreover, solvent extraction of polypropylene films processed with nitroxyl radicals reduces photostability substantially(111,113) almost to the level of an unstabilised analogue.

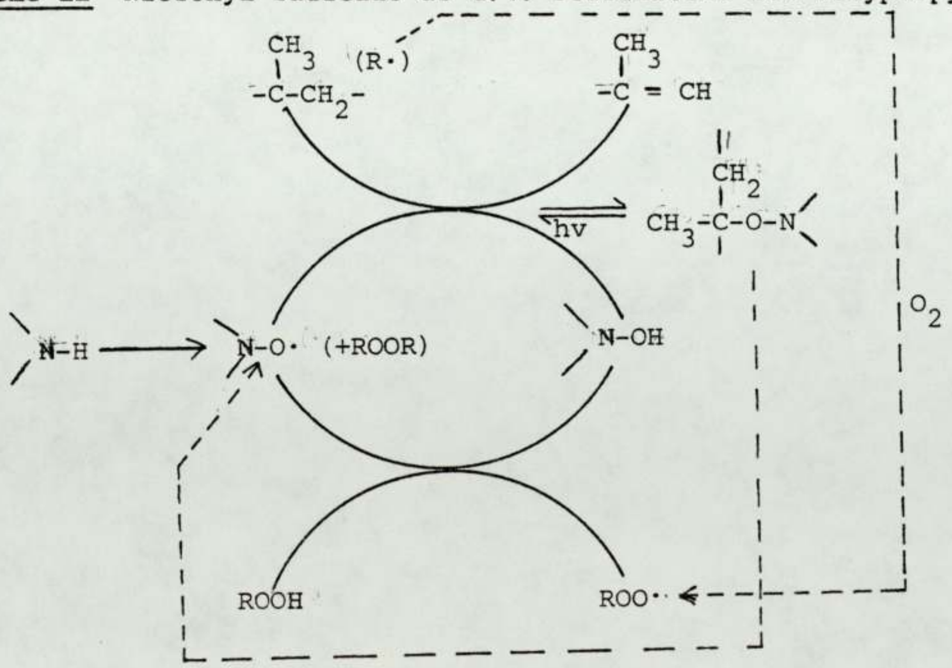
Nitroxyl radical regeneration had been proposed to account for their effectiveness as photostabilisers. It was suggested(114,115) that the derived alkyl hydroxylamine reads with alkylperoxyl ($ROO^{\bullet}$) radicals during photo oxidation, thus regenerating the nitroxyl and a macromolecular dialkyl peroxide results.

$$>N-OR + ROO^{\bullet} \longrightarrow >N-O^{\bullet} + ROOR \qquad (-44)$$

But, the rate of the reaction (44) is not high enough(37) for this reaction to proceed.

An alternate regeneration process has now been suggested(39) with appropriate evidence(116,117) that nitroxyl radicals are continously regenerated in a cyclic mechanism involving the corresponding hydroxylamines as shown in scheme 11.

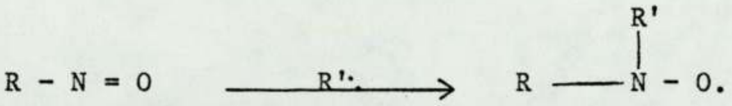
Scheme 11 Nitroxyl radicals as u.v. stabilisers for Polypropylene.



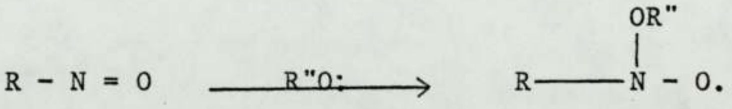
This scheme is the best representation yet of the mechanism of nitroxyl regeneration although the role of the alkyl hydroxylamine remains a matter of controversy. A recent spectroscopic study (FTIR) concludes(118) that substituted (alkyl) hydroxylamine are the dominant reservoir of photostabilising species during photo oxidation. But evidence(113) shows that solvent extraction of films containing nitroxyls results in a reduced photostability.

Nitroxyl radicals were thought to scavenge alkyl radicals alone(116) but there is evidence that aromatic nitroxyl radicals such as diphenyl nitroxyl radicals react with both alkyl and alkylperoxyl radicals.(69)

Some precursors of nitroxyl radicals such as nitroso and nitrone compounds are known to react with alkyl and alkoxyl radicals giving substituted nitroxides as products(119,120). Such reactions have actually been utilised to detect and identify radicals present in reaction systems and are termed "spin traps".

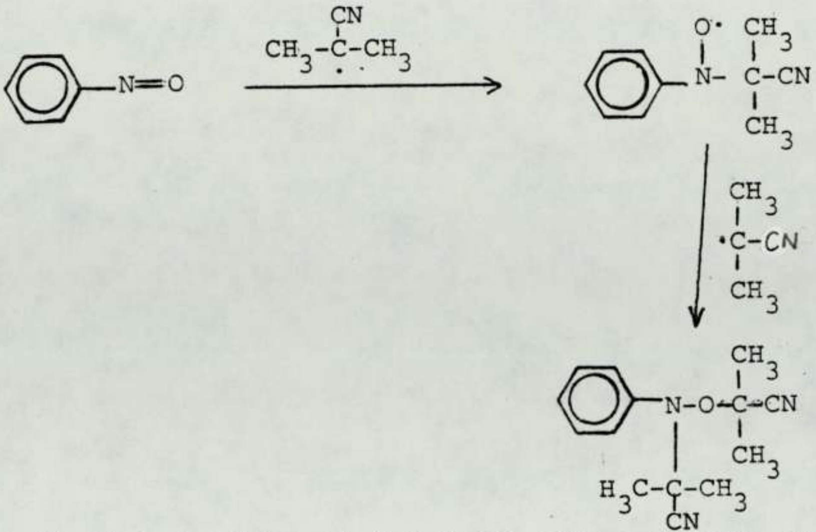


$$R - N = O \xrightarrow{R'\cdot} R - \overset{R'}{\overset{|}{N}} - O\cdot \qquad -(45)$$



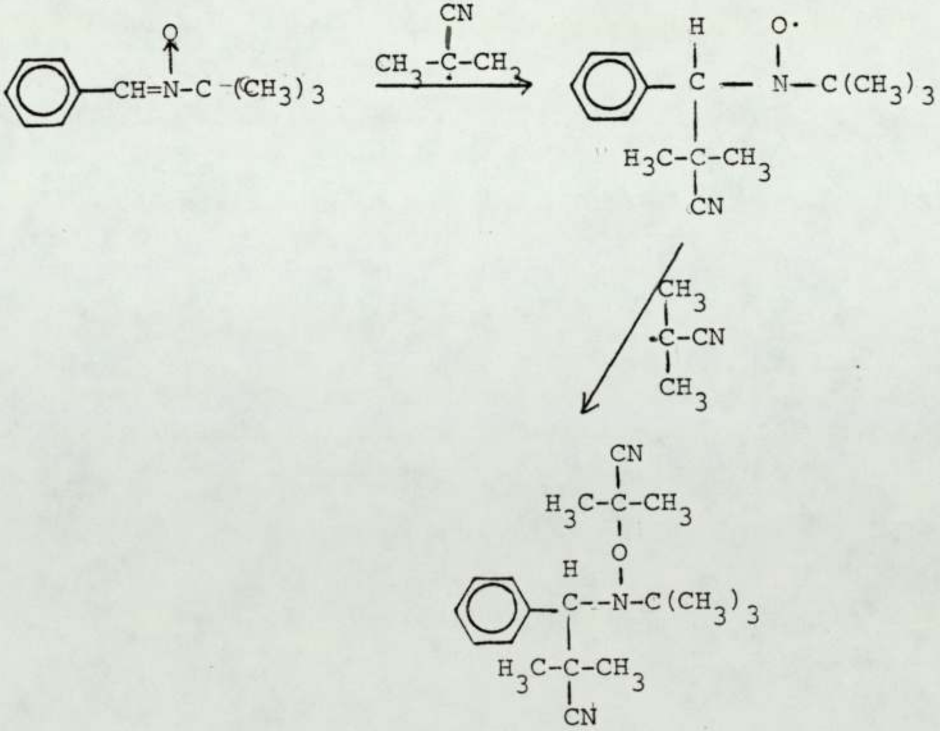
$$R - N = O \xrightarrow{R''O\cdot} R - \overset{OR''}{\overset{|}{N}} - O\cdot \qquad -(46)$$

The derived nitroxyl radical can then scavenge another radical to give the substituted hydroxylamine. Thus when an excess of azo-bis-isobutyronitrile (AIBN) was reacted with nitrosobenzene(121) nitroxyl radical was not detected but di-t-alkyl phenyl hydroxylamine was obtained in about 75% yield.



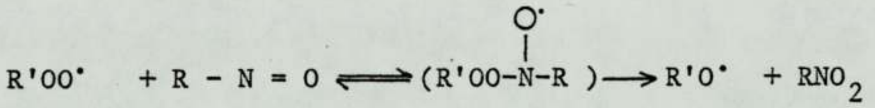
-(47)

Similarly, reaction of N-t-butyl nitrones with alkyl radicals give stable nitroxyl radicals. For example, reaction of AIBN(122) with α - phenyl, N-t-butyl nitrone in xylene at 110°C gives stable nitroxyl radical derivates which on further reaction gives substituted hydroxylamines.

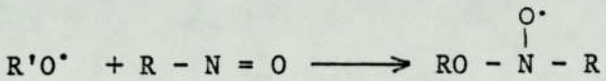


-(48)

'Trapping' of peroxy radicals rather than alkyl radicals by nitroso and nitrone compounds gives rise to alkoxy rather than alkylperoxy nitroxide(120). PFab(123) shows the mechanisms to be according to reactions 49 and 50 below;



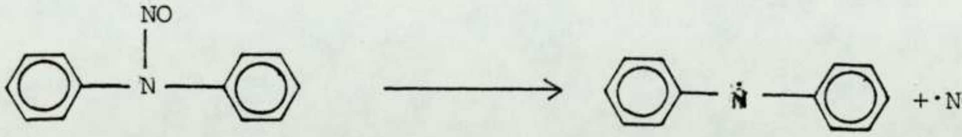
$$R'OO^{\bullet} + R-N=O \rightleftharpoons (R'OO-\overset{\overset{\Large O^{\bullet}}{|}}{N}-R) \longrightarrow R'O^{\bullet} + RNO_2 \qquad -(49)$$



$$R'O^{\bullet} + R-N=O \longrightarrow RO-\overset{\overset{O^{\bullet}}{|}}{N}-R \qquad -(50)$$

Generally, nitroso compounds appear to be more efficient traps for n-alkyl radicals than nitrones(124) and aromatic nitroso compounds are better traps than nitroso alkanes.

Other common nitroxyl generators include N-nitrosoamines, although they are generally not stable and are easily decomposed thermally or upon u.v. irradiation giving nitric oxide and a radical. It is believed(121,125) that the N-N bond breaks and the nitric oxide produced is reactive.



-(51)

$$(CH_3)_2\,N-N=O \longrightarrow (CH_3)_2N^{\bullet} + {}^{\bullet}NO \qquad -(52)$$

These reactions have been exploited in the photo stabilisation of Polypropylene(126) in which the nitric oxide produced is thought to react with the polymer.

1.6 SCOPE AND OBJECT OF RESEARCH

Nitroxyl radicals stabilise polyolefins during thermal processing and during photo-oxidation by "trapping" the macro-alkyl radicals produced, resulting in alkyl hydroxylamines and/or free hydroxylamines. The exact nature and the role of each of the products is still controversial. An initial objective of this research was to examine the mechanism of the reaction in order to throw light into how the alkyl hydroxylamines fit into the reaction mechanisms; if they are formed at all; and their concentrations relative to nitroxyl radicals and free hydroxylamine. Methods of estimating all these species were developed, using analytical and chemical techniques, together with chemical methods for estimating unsaturation and hydroxylamine concentrations and attention was focussed on the identification of products formed during processing which were responsible for the melt and u.v. stabilising effect.

A second object of this work was to examine simpler nitroxyl radical generators as photostabilisers for polymers (PP). Two classes of compounds that showed considerable promise are the nitroso, and nitro tertiary alkanes e.g. 2-methyl-2-nitroso propane (tBuNO) and 2-methyl-2-nitro propane ($tBuNO_2$). tBuNO is a known radical trap(119,152,154) while $tBuNO_2$ is not. Attention was again focussed on identifying the product formed during processing and during photo oxidation which was responsible for the stabilising effect. Other classes of compounds examined include a nitroso-amine (N-nitroso diphenyl amine, NDPA), a nitro alcohol (trimethylol nitromethane, TN) and an amino-alcohol (trimethylol aminomethane). These compounds have found different applications, as retarders for vulcanisation(116)

(NDPA) in rubber and cross-linking agents(151) in moulding plastics but their activity as photostabilisers in polymers have not been investigated. Attempts were made to examine the mechanism of their action as photostabilisers for Polypropylene.

Long alkyl chain esters of trimethylol nitromethane (TN) were also synthesised and investigated as photostabilisers for PP in order to establish the contribution of the different alkyl chain lengths to the photostabilisation of PP, compared to trimethylol nitromethane itself.

Synergism (or antagonism) of some of the classes of compounds above with commercial antioxidants (e.g. Tinuvin 770) and u.v. stabilisers (e.g. HOBP) was also investigated at different synergistic combinations and attempts made to explain the mechanism of their co-operative action (synergism or antagonism).

CHAPTER TWO

2. PREPARATION OF CHEMICAL COMPOUND AND GENERAL EXPERIMENTAL TECHNIQUES

2.1 Materials

Polypropylene used in this work was unstabilised and supplied in powdered form by Imperial Chemical Industries (ICI) Plastics Division Ltd. as "Propathene HF 22" with a density of 0.905 gm/Cm^3 and a melt flow index of 3.9g/10 minutes.

Tables 2.1 and 2.2 contain lists of all chemical compounds prepared (as described in the following section) and those commercially procured respectively. Unless otherwise stated, all solvents used in preparation of compounds in this work are of standard laboratory (general purpose) grade. For model compound studies, 'spectroscopic grade' solvents were employed (in u.v. spectrophotometry) with purities of above 98%.

All commercial stabilisers listed in Table 2.2 were used as supplied without any further purification.

2.2 Preparation of Chemical compounds

2.2.1 4-hydroxyl, 2,2,6,6 tetramethyl piperidine-1-oxyl, I (4OHTMPNO.) (65)

14g of 4-hydroxyl-2,2,6,6 tetramethyl piperidine, X, was dissolved

Table 2.1. List of chemical compounds prepared, structure, and code names

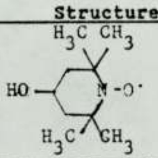
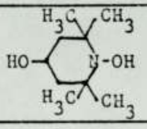
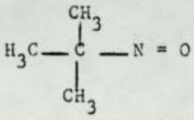
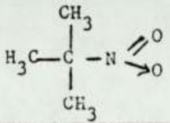
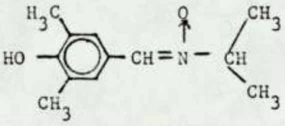
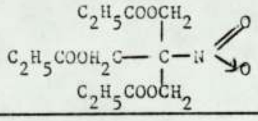
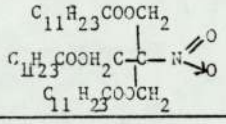
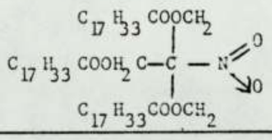
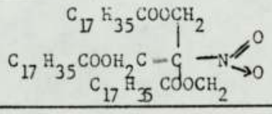
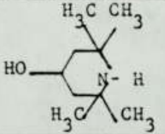
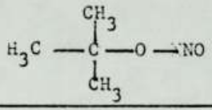
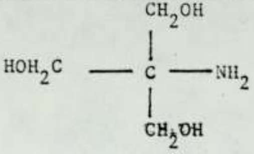
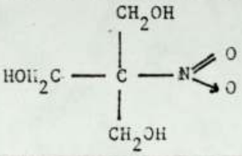
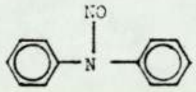
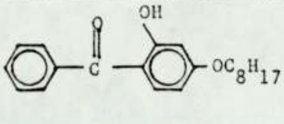
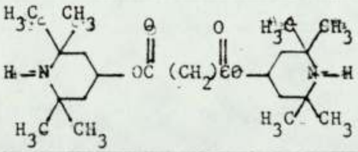
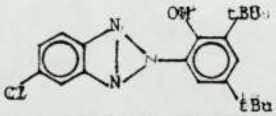
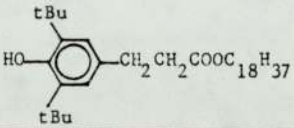
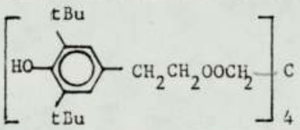
Chemical name	Structure	Code Name	No
4-hydroxyl,2,2,6,6 tetramethyl piperidiny-1-oxyl		4-OHTMPNO·	I
4-hydroxyl,2,2,6,6 tetramethyl piperidiny-1-ol		4-OHTMPNOH	II
2 methyl,2-nitroso propane		tBuNO	III
2 methyl,2-nitro propane		tBuNO$_2$	IV
α,3,5,dimethy-4-hydroxyl-phenyl-N-isopropyl nitrone		DHPIN	V
Trimethylol nitromethane tripropionate		PTN	VI
Trimethylol nitromethane tri laurate		LTN	VII
Trimethylol nitromethane trio oleiate		OTN	VIII
Trimethylol nitromethane tri stearate		STN	IX

Table 2.2. List of commercially procured compounds

Chemical name	Structure	Code Name	No.	M.pt.C	Supplier
4-hydroxyl,2,2,6,6 tetra methyl piperidine		4-OHTMPNH	X	129° (129-131)	Ciba-Geigy
2-methyl-2-nitrite propane		tBuONO	XI	62°* (61-63)	Fluka AG
Trimethylol amino-methane		T Am[a] (Tris amino)	XII	167° (171-172	Angus Chemie GmbH
Trimethylol nitromethane		TN (Tris nitro)[a]	XIII	147° (165-175)	Angus Chemie GmbH
N-nitro diphenylamine		NDPA	XIV	60° (63°)	Vulnax International
2-hydroxyl-4-octyloxy benzophenone		HOBP	XV	47° (47°)	American Cyanamid Corporation
Bis (2,2,6,6 tetramethyl-4-piperidinyl) Sebacate		Tinuvin 770[a]	XVI (81-86)	81°	Ciba-Geigy
2-(2'-hydroxyl,3'5'di-tert-butyl-phenyl) 5 - chloro benztriazole		Tinuvin 327[a]	XVII		Ciba-Geigy
Octadecyl,3,5 di-tert-butyl- 4-hydroxyphenyl propionate		Irganox 1076[a]	XVIII	49° (49-54)	Ciba-Geigy
(3,(3,5 ditert-butyl-4-hydroxiphenyl) propionate		Irganox 1010[a]	XIX	112° (110-125)	Ciba-Geigy

\+ figures in brackets are those quoted by the suppliers

* boiling point

a are commercial names as well

in 140 ml of distilled water and 1.4g of Sodium tungstate ($Na_2WO_4.2H_2O$) was added. 35 mls of 30% hydrogen peroxide was added slowly over a period of 10 minutes. The reaction mixture was magnetically stirred overnight at room temperature. Upon prolonged agitation, the solution turned reddish orange. The solution was then saturated with sodium chloride and repeatedly extracted with di-ethyl ether. The ether phase was dried over anhydrous Magnessium sulphate ($MgSO_4$) for about an hour. the solution was then filtered to remove $MgSO_4$ and ether was removed on a rotary evaporator, giving orange crystals in about 75-85% yield. Recrystallisation from di-ethyl ether gave long orange crystals with a melting point of 68°C (lit 65-68°C)(65)

Analytical data:

(i) Infra-red analysis: KBr disc" disappearance of band at 3230cm^{-1} (N-H stretch) in parent amine; strong N-O stretch at 1355 cm^{-1} (Fig. 2.2 (a))

(ii) e.s.r. analysis (solid sample): triplet, splitting factor (a_N) = 15.26, g-value 2.0065. (See fig. 2.1)

(iii) The elemental analysis of this and other compounds prepared in this work is shown in table 2.3.

2.2.2 4-hydroxyl 2,2,6,6 tetramethyl piperidine-1-ol, II (4-OHTMPNOH) (127)

0.6g of 85% hydrazine (0.01 mole) was added to a solution of 4-hydroxyl 2,2,6,6 tetramethyl piperidine-1-oxyl, I, (1.722g; 0.01 mole)

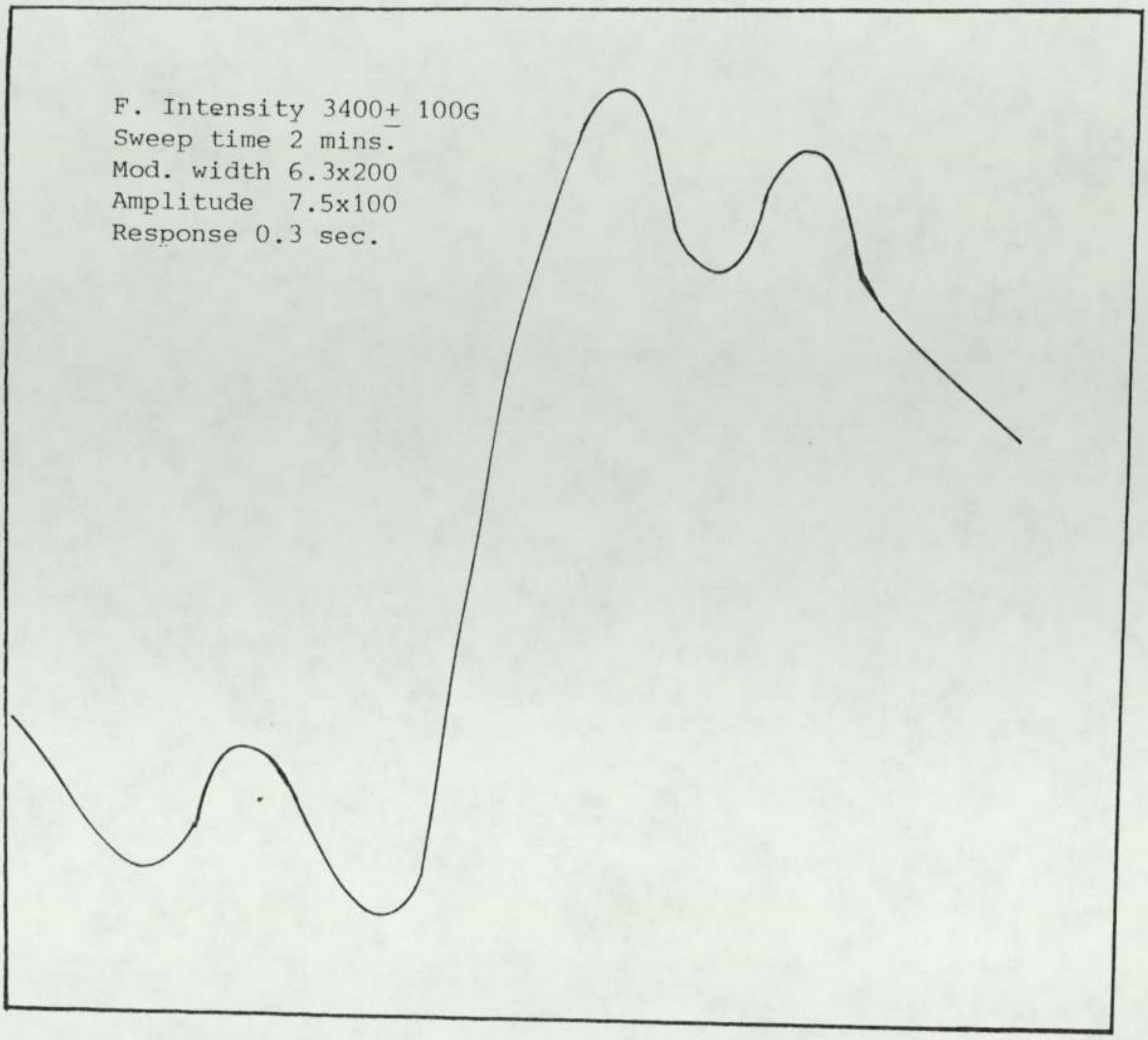


Fig. 2.1.: E.s.r.spectrum of 4OHTMPNO· (solid) g-value= 2.0065, a_N 15.26

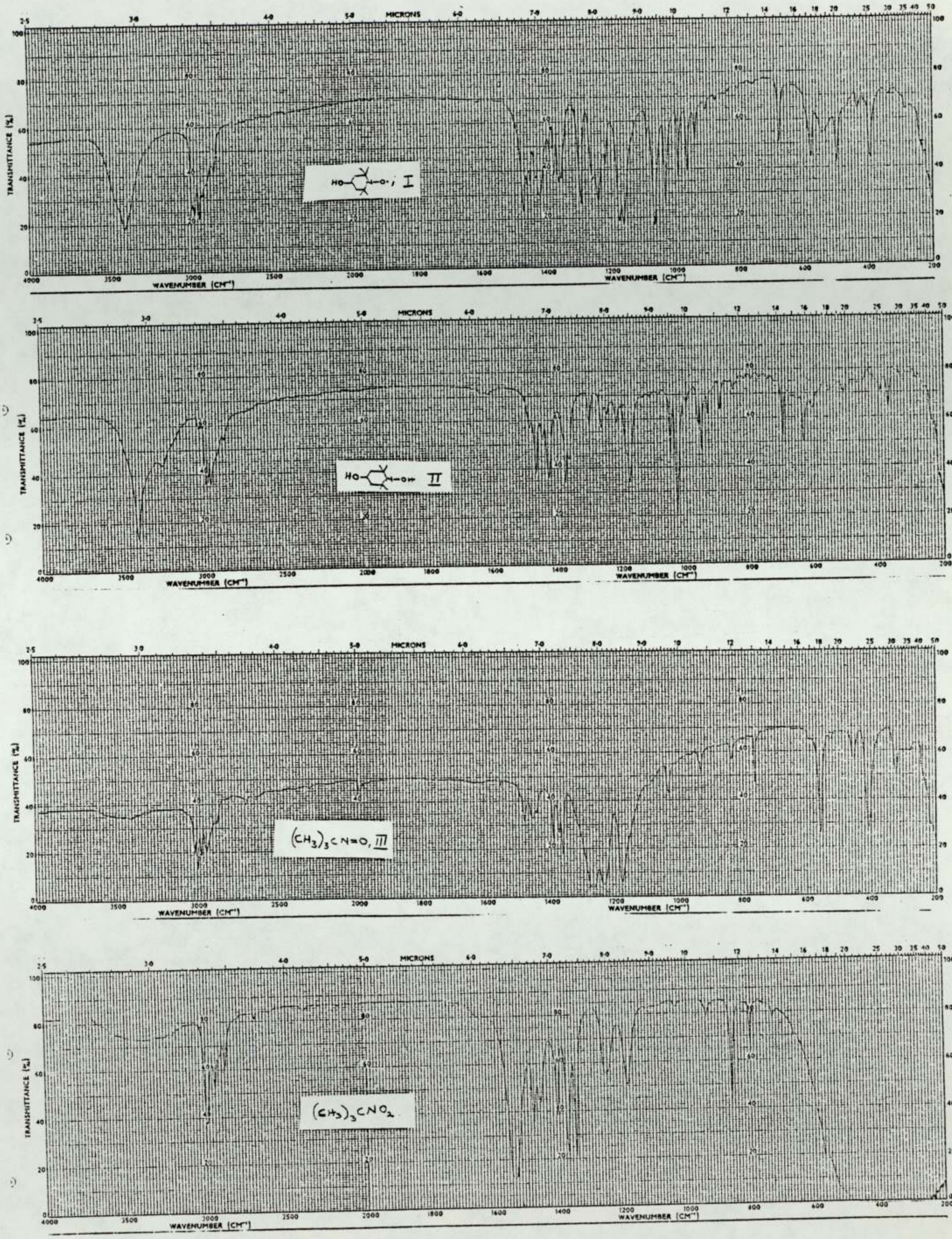


Fig. 2.2. Infra-red spectra of (a) 4OHTMPNO· (b) 4OHTMPNOH (c) tBuNO (d) tBuNO$_2$.

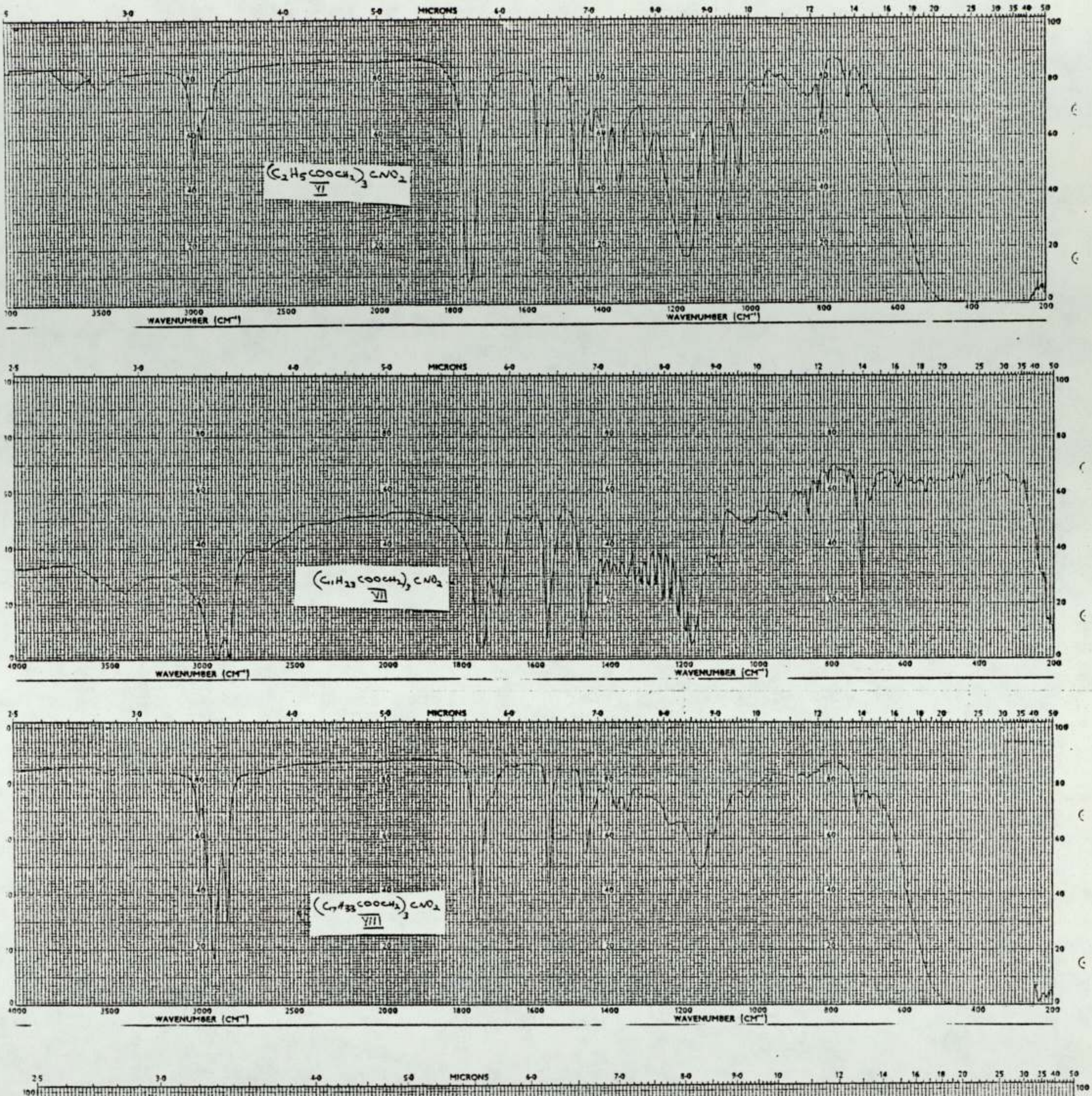


Fig. 2.3. Infra-red spectra of (a) PTN (b) LTN (c) OTN (d) STN.

in 10 mls of methanol. The reaction mixture was refluxed for 24 hours and until completely decolourised at 70°C. the methanol was evaporated at room temperature under vaccum. The white residue was recrystallised from a mixture (1:1) of ether and benzene. Colourless needles were obtained with a yield of about 90%, melting point 156°C (lit 157°C).(121)

Analytical data:

(i) Infra-red analysis: KBr disc: disapearance of 1355 cm^{-1} (N-O$^\cdot$stretch); strong. 1470 cm^{-1}(N-OH stretch). (See fig. 2.2b)

(ii) E.S.R = No signal.

(iii) Elemental analysis: Table 2.3

2.2.3 <u>2-methyl-2-nitroso propane, III (tBuNO)</u> (128)

A solution of tertiary butylamine (36.6g; 0.50 mol) and sodium tungstate $Na_2WO_4.2H_2O$ (4g) in 50 mls of distilled water was cooled in an ice-bath. To this, 113.3g of 30% (1.0 mole) hydrogen peroxide was added dropwise over 1.3 hours at 15-20°C with stirring. Hydrogen peroxide addition was stopped whenever temperature reached 20°C. After complete addition, the reaction mixture was stirred for a further 30 minutes at 20-25°C and about 3g of sodium chloride was added to break the emulsion. A blue organic layer was formed. This was separated and washed twice with 25 mls portions of dilute HCl, then dried over anhydrous magnessium sulphate. Distillation gave a dark blue organic compound (b.p. 50-55°C). The distillate was kept in an ice-bath until solidification (dimer form), giving 10g (22%) of colourless crystals. m.pt 73°C (lit 74-75°C)(128).

Analytical data:

(i) Infrared analysis: (K.Br disc) strong N=O stretch - 1555 cm^{-1}

(ii) (Fig. 2.2(c)).

(iii) Elemental analysis: Table 2.3

2.2.4 2-methyl-2-nitro propane, IV ($tBuNO_2$) (129)

A solution of tertiary butylamine (36.6g; 0.50 mol), sodium tungstate, Na_2WO_4 $2H_2O$ (4.0g) and 25 ml distilled water was cooled in an ice-bath. 30% hydrogen peroxide (170g, 1.50 mol) was added dropwise over a period of 2 hours with stirring.

The first 100g was added at 15-20°C; 100 mls of methanol was then added and the hydrogen peroxide addition was continued at 25-30°C. After complete addition, stirring was continued for an additional hour at room temperature. The organic layer was separated and the water layer was extracted with three 25 ml portions of ether. The combined organic layer and the extract was dried over anhydrous $MgSO_4$ and distilled to afford 35.4g (70%) of 2-methyl-2-nitro propane; b.pt 125-127°C (lit 126-127°C)(129). This method has the advantage of a greater yield, than the continued distillation of the residue as described in section 2.2.3, which yields only 34%.

Analytical data:

(i) Infra-red analysis (neat) NaCl disc: strong asym. N-O stretch - 1540 cm^{-1} and sym.N-O stretch - 1350 cm^{-1} (Fig. 2.2 (d))

(ii) Elemental analysis: Table 2.3.

2.2.5 α,3,5-dimethyl-4-hydroxyl phenyl, -N- isopropyl nitrone, V (DHPIN) (130)

DHPIN was prepared from the reaction of 3,5 dimethyl -4-hydroxyl-benzaldehyde with N-isopropyl hydroxylamine. The aldehyde was prepared as follows:

Boric acid (35g), hexamethylene tetramine (25g) and ethylene glycol (100 mls) were placed in a beaker and the mixture was heated to 130°C with stirring. 2,6, xylenol (12.2g; 0.1 mole) was slowly added over a period of 10 minutes, after which time heating was continued for a further 30 minutes. A colour change to deep orange was observed. The beaker was removed from heat source and cooled slightly. 30% sulphuric acid (150 ml) was then added and the mixture was left to stand for one hour. The aldehyde separated and was filtered off. Recrystallisation from aqueous methanol gave long needles, 11.5g (77%) and m.pt 113°C (lit 112-112.6)$^{(131)}$.

For the N-isopropyl hydroxylamine, 2 nitropropane (72g; 0.808 mol), and ammonium chloride (30g) were dissolved in 400 mls of distilled water and cooled to below 20°C. 137.5g zinc dust was added gradually with stirring over a period of 2 hours. The temperature was not allowed to rise above 20°C. After complete addition, the reaction mixture was further stirred for 45 minutes at room temperature and filtered repeatedly until removal of all particles of zinc oxide was obtained. The filterate containing N-isopropyl hydroxylamine hydrochloride was used directly to prepare the nitrone as follows:

To the aqueous filterate, 3,5 dimethyl--4-hydroxyl benzaldehyde (20 g; 0.133 mole) dissolved in 2N sodium hydroxide solution (100 mls) was added and stirred magnetically for 1 hour. The reaction mixture was then made to pH8 (BDH litmus paper) by dropwise addition of conc. HCl and then stirred overnight. A pale yellow precipitate was formed. This was separated and recrystallised from methanol giving about 15.9g (68% yield) and a melting point of 193°C (lit 192-195°C)$^{(130)}$.

Analytical dta:

(i) Infra-red analysis: KBr disc: OH broad. 3200 cm^{-1}; CH_3- bending 1375 cm^{-1}; C = N stretch 1580 cm^{-1} (strong) N - O stretch 1170 cm^{-1} (strong)

(ii) Elemental analysis: Table 2.3

2.2.6 Trimethylol nitromethane tripropionate VI (PTN)-$^{(126)}$

To a 1-litre flask, (equipped with a stirrer, thermometer, nitrogen inlet tube and a reflux condenser fitted with a "Dean and Stark" water separator) was added 15.1g (0.1 mol) of tris nitro, (XIII), 22.2g (0.3 mol) of propionic acid, 250 mls of toluene and 2g of toluene-p-sulphonic acid catalyst. The reaction mixture was refluxed under nitrogen at about 125°C until 5.4g (0.3mol) of water was collected in the azeotrope receiver (usually this takes between 18-24 hours). The toluene solution of the ester was then filtered to remove any small amount of tris nitro, and then heated under reduced pressure to remove the solvent. The liquid residue was then washed twice with 25 mls portion of water and then dried over anhydrous $MgSO_4$. The liquid ester was yellowish with a boiling range of 168-176°C (5-10 mm of Hg), (lit 170-185)$^{(133)}$; density 1.15 at 23°C (lit 1.17 at 25°C)$^{(133)}$.

Analytical data:

(i) Infra-red analysis (neat) NaCl disc: C=O stretch 1750 cm^{-1}; asym. N-O stretch. 1560cm^{-1} and sym. N-O stretch 1350cm^{-1} (Fig. 2.3 (a))

(ii) Elemental analysis: Table 2.3

2.2.7 Trimethylol nitromethane trilaurate. VII (LTN)

The same procedure as in section 2.2.6 above was employed, using 60g (0.3 mol) of lauric acid, 15.1g (0.1 mol) of tris nitro, XIII, 250 ml of toluene and 2g toluene-p-sulphonic acid catalyst. The reaction mixture was refluxed until 5.4g (0.3 mol) of water was collected. Toluene and the traces of tris nitro were removed as described above. Upon cooling, the solid ester obtained was washed repeatedly (room temperature) with 50 mls portions of distilled water to remove traces of residual catalyst and then dried at reduced pressures in a vaccum oven to obtain the pure solid eter in about 90% yield. M-Pt 33°C

Analytical data:

(i) Infra-red analysis: KBr disc C=O stretch 1750 cm^{-1}; N-O stretch 1570 cm^{-1} and 1350cm^{-1}; (Fig. 2.3(b))

(ii) Elemental analysis: Table 2.3

2.2.8 Trimethylol nitromethane trioleiate. VIII (OTN)

15.1g (0.1mol) of tris nitro, XIII, 84.6g (0.3 mol) of oleic acid, 250 mls of toluene and 2g toluene-p-sulphonic acid were refluxed (for about 12 hours) as described above until 5.4g (0.3 mol) of water was obtained. The solvent was removed by boiling under reduced pressure and the resultant brown liquid ester was washed repeatedly with water at room temperature and dried over anhydrous $MgSO_4$ to obtain the pure ester in about 91% yield. Boiling range 78-94°C (5-10mm of Hg); density 0.935 at 23°C.

Analytical data:

(i) Infra-red analysis: NaCl disc (neat) C=O stretch 1750 cm^{-1};N-O stretch 1560 cm^{-1}; and 1350cm^{-1}; (Fig. 2.3(c))

(ii) Elemental analysis: Table 2.3

2.2.9 Trimethylol nitromethane tristearate, IX (STN)

As above, 15.1g (0.1 mol) of tris nitro, XIII, 85.2g (0.3 mol) stearic acid, 250 mls toluene and 2g toluene-p-sulphonic acid were refluxed under nitrogen until 5.4g (0.3 mol) of water was collected (18-24 hours). The solvent was removed by boiling under reduced pressure. The solid residue was cooled and washed repeatedly with water and then dried under pressure. Pure solid ester was obtained in about 85% yield m.pt 59°C.

Analytical data:

(i) Infra-red analysis: KBr disc C=O stretch 1755 cm^{-1}; N-O stretch 1560 cm^{-1}; and 1350cm^{-1}; (Fig. 2.3(d))

(ii) Elemental analysis: Table 2.3

Table 2.3: Elemental analysis of synthesized compunds

Compound	Code Name	Formula	C%		H%		N%	
			Calc.	Found	Calc.	Found	Calc.	Found
2-methyl-2-nitroso propane	tBuNO	C_4H_9NO	55.17	55.2	10.34	10.10	16.09	15.40
2-methyl-2-nitro propane	$tBuNO_2$	$C_4H_9NO_2$	46.60	46.2	8.74	8.50	13.59	14.0
4-hydroxyl-2,2,6,6 tetramethyl piperidine-1-oxyl	4-OHTMPNO.	$C_9H_{18}NO_2$	62.79	62.75	10.47	11.15	8.14	8.30
4-hydroxyl-2,2,6,6 tetramethyl piperidine-1-ol	4-OHTMPNOH	$C_9H_{19}NO_2$	62.43	61.90	10.98	10.40	8.09	7.90
α,3,5 dimethyl-4-hydroxyl phenyl-N-isopropyl nitrone	DHPIN	$C_{12}H_{17}NO_2$	69.57	68.8	8.21	8.30	6.76	7.0
Trimethylol nitromethane tripropionate	PTN	$C_{13}H_{21}NO_8$	48.90	47.70	6.58	6.70	4.39	4.20
Trimethylol nitromethane trilaurate	LTN	$C_{40}H_{75}NO_8$	68.87	69.40	10.76	11.40	2.01	1.95
Trimethylol nitromethane trioleiate	OTN	$C_{58}H_{105}NO_8$	73.81	73.80	11.13	12.0	1.48	1.50
Trimethylol nitromethane tristearate	STN.	$C_{58}H_{111}NO_8$	73.34	73.9	11.70	12.1	1.48	1.80

2.3 General experimental techniques

2.3.1 Processing of polymer and film preparation

Polypropylene (with or without additives) was processed using a prototype Hampden RAPRA Torque rheometer head, fitted on a Brabender plasticorder motor. Essentially, the torque rheometer is a mixing chamber, containing two counter-rotating screws. The rotor speed could be varied but for effective and efficient mixing, a speed of 65 revolutions per minute was used. The mixing chamber is oil-heated by means of a pump. The torque required for mixing, the temperature of the melt and the speed of mixing could be monitored by an integrated recorder attached to the rheometer. The mixing chamber may be left open or closed during processing by use of a compressed-air-controlled pneumatic ram. For closed-chamber mixing, (limited amount of oxygen) a full charge of the chamber, (35g of Polypropylene) is required. In open chamber mixing however, when oxygen access is required, a charge less than full (e.g. 25g of Polypropylene) is used, leaving the ram open.

Before processing with additives, the polymer and the required concentration of the additive were tumble-mixed at room temperature. Unless otherwise stated, the temperature of the heating oil during processing throughout this work was 180^{o}C (melt temp in the closed mixer was about 177-178^{o}C while that of the open mixer was about 170-172^{o}C). After processing, the hot polymer melt was quickly removed within 5-15 seconds and chilled in cold water to avoid uncontrolled thermal oxidation. For reliable results, only the first few grams of polymer removed from the mixing chamber were used.

Films of processed polymers were made by compression moulding by means of an electric press. The procesed polymer was placed between two sheets of special grade, heat-resistant cellophane- used as a mould-release agent, which were themselves located between stainless steel glazing plates. The plates were then inserted between two platens of the already heated press, and the platens were moved into contact with both plates for about 30 seconds to 1 minute to preheat and soften the polymer. The desired pressure of 25 tons on a ram of 6 inch diameter was applied slowly over a period of another minute and allowed to remain so far another 1.5-2 minutes. The mould was then water-cooled to well below transition temperature (about 70°C for PP) removed for cutting and testing. Control of film thickness was achieved by using an appropriate polymer weight. For instance, about 6-7g of Polypropylene, produced a thickness of approximately 0.008 inch (200 um) under a pressure of 25 tons on a ram of 6 inch diameter.

2.3.2 Accelerated u.v. exposure

Polymer films were mounted on special "Multisampler" sample mounts and irradiated in a u.v. cabinet. The cabinet consists of a circular rotating sample drum with a circumference of about 15 cm from the periphery of the radiation source. The radiation source consists of a cylindrical array of 1:3 combination of sun lamps and actinic blue lamps (28 in all), each of 20 watts. By this arrangements, the light beam fell perpendicularly on the surface of the polymer films. The distribution spectra showed that the maximum in the relative intensity is at 317 nm for the sun lamps and 374nm for the blue lamps. (Average temperature in the cabinet during irradiation is 33-35°C).

2.3.3 Extraction of Films

The removal of unreacted (unbound) additives and low molecular weight materials from polymer samples was accomplished by continous hot extraction in a soxhlet extractor apparatus using a suitable solvent (dichloromethane). The cut samples were put in extraction thimbles and put in the extractor under a steady steam of nitrogen for about 10-12 hours. After extraction, the samples were dried under vacuum at room temperature for about 24 hours. The solvent of the extract was removed on a rotary evaporator and the product, kept for spectroscopic and chemical analysis.

2.3.4 Infra-red spectroscopy of oxidised films

The nature of structural changes occuring during polymer oxidation, the oxidation products formed and the kinetics of the growth/decomposition of funçtional groups were monitored by infra-red spectroscopy. A reference peak (absorbance) was chosen which corresponds to an absorption band that does not change with oxidation. In Polypropylene, the band at 2720 cm^{-1} was used. The build-up or decomposition of different functional groups were measured as indices in relation to the reference peak; and are the ratios of the absorbance of the functional groups to that of the reference peak. Thus,

$$\text{Carbonyl Index} = \frac{\text{Absorbance of carbonyl group}}{\text{Absorbance of reference peak}} = \frac{A\ (1710\ cm^{-1})}{A\ (2720\ cm^{-1})}$$

The use of a reference peak, minimises errors due to variations in film thickness as well as instrumentation errors. For all infra-red spectroscopy in this work, a Perkin-Elmer grating spectrophotometer model 599 was used, and the spectra of oxidised films were taken at intervals, from 4000 cm^{-1} to 600 cm^{-1} on the same chart paper for comparison purposes. The spectrophotometer was calibrated to 100% transmittance before use.

2.3.5 Ultra-violet spectroscopy

Ultra-violet spectroscopy of polymer films with incorporated additives were recorded using PYE-UNICAM SP800 uv/visible spectrophotometer. In order to obtain the spectra of the additives in films, a film of unprocessed, additive-free polymer of identical thickness was used (as a compensator) in the reference beam. In solutions however, quartz cells of 1 cm pathlength were used with the pure solvent as compensation in the reference beam.

2.3.6 Measurement of Melt Flow Index

Melt flow index (MFI) is defined as the amount of polymer in gramme weight extruded through a standard orifice (die diameter of 0.0465 in) in a given time (e.g. 10 minutes) under a standard load. This measurement is related to, and inversely proportional to the molecular weight of the polymer. MFI measurement was carried out on a "Davenport Polythene grader" as follows.

The barrel was charged with about 4-5 gm of the processed polymer within 1 minute. A piston was then placed in the barrel and allowed to remain for four minutes during which the polymer was uniformly heated at the desired temperature of extrusion (230°C ± 0.5°C). At the end of the four minutes a 2.16 kg weight was placed on the piston and the extruded samples were cut at regular intervals with a sharp-edged knife. Usually, samples were taken at 30 second or 1 minute intervals. The first one or two cut-offs were rejected, and at least 5 cut-offs were taken for average weight measurement. When the rate of extrusion was high, due to a drop in molecular weight, shorter time intervals e.g. 15 seconds were used. The average weight of extruded samples per time interval was then calculated for 10 minutes. Where the MFI was less than 25g/10 minutes, a standard die with an internal diameter of 0.465 inch bore was used as recommended(134) but where MFI was above 25g/10 min. a smaller die with a tenth bore of the standard bore diameter was used.

2.3.7 Measurement of Hydroperoxide in Polymer Films

Chemical method:

This is a modification of the methods employed by Manasek(135) and his co-workers and Geddes(136) as follows:

0.5 - 1 g of polymer film was cut into small pieces and introduced into 21.7 mls of deaerated chloroform and purged with nitrogen for 30 minutes. This was then allowed to swell for 18 hours. 3.3 mls of glacial acetic acid was then added and the solution was purged with nitrogen for five minutes before and after addition of 2 mls of a freshly deaerated 5% (w/v) solution of sodium iodide in methanol. (All solvents were deaerated in bulk prior to use and sealed by rubber seals)

After storage for about 2 hours in the dark for complete reaction, the liberated iodine was titrated using standard 0.01N sodium thiosulphate. This was a more reliable method than the spectrophotometric method employed by Allen(137) and co-workers as this eliminates the problems of oxidation and interference from stabilisers.

2.3.8 **Measurement of unsaturation in polymer films** (138)

0.5g of polymer film was introduced into 75 mls of deaerated chloroform in a conical flask and left to stand for 48 hours. (Alternatively it could be refluxed for 30-45 minutes). After swelling, (or if refluxed, after cooling) 5 mls of 20% solution (w/v) of trichloroacetic acid in chloroform was added followed by 25 mls of 0.1N iodine solution. 25 mls of 5% solution (w/v) of mercuric acetate in glacial acetic acid was then added. The mixture was swirlled gently and stored in the dark for about 2 hours. 75 mls of 75% potassium iodide solution was then added and the excess iodine in the mixture was titrated with 0.1N sodium thiosulphate solution, using starch end point in the aqueous layer. The same procedure was repeated without the polymer film for reference (blank). The mole per cent unsaturation (defined as mole per cent of monomer units containing double bonds)(138) was calculated as:

$$\text{Mole \% unsaturation} = \frac{(B-S)\ (N)\ (M)\ (100)}{(\text{gram of sample})\ (3000)}$$

where B = Vol. of thiosulphate for blank (mls)

S = Vol. of thiosulphate for sample (mls)

N = Normality of thiosulphate

M = molecular weight of structural unit of polymer (for Polypropylene = 42)

This method is preferable to the infra-red spectroscopic method as the olefinic unsaturation at 1640-1690 cm^{-1} may be completely overlapped by stronger carbonyl absorption at 1710 cm^{-1}.

2.3.9 Hydroxylamine detection (139)

Detection of hydroxylamine that may be formed during the processing of polypropylene and a nitroxyl radical was carried out upon extraction of the polymer film and concentration of the extract: To 1 ml of the extract (dissolved in dichloromethane) a few drops of dilute HCl were added, followed by 1 ml of 1% solution (w/v) of oxine (8-hydroxy quinoline) in ethanol and then 1 ml of 2N sodium carbonate solution was added. The mixture was well shaken; development of green colouration (indo-oxine formation) indicated the presence of hydroxylamine).

2.3.10 Determination of hydroperoxide decomposition by additives in solution

Stock solutions of 8 x 10^{-2}M of Cumene hydroperoxide (CHP) and 2 x10^{-2}M of the test compound were made in chlorobenzane (puriss) espectively and reaction ratios were taken from these stock. For example, for a 1:1 reaction ratio is a total of 8 mls of reaction volume, 1 ml of CHP solution, and 3 mls of chlorobenzene solvent were required. The solvent was first placed in a stoppered test tube equipped with a nitrogen inlet which was placed in a heating medium at 100°C. After about 2 minutes, the hydroperoxide solution was added, followed by the addition of the test-compound-solution (after another three minutes). 1 ml, of the reaction mixture was then quickly removed (at required intervals), to which 10 mls of acetic acid solution in isopropanol (25 mls acid in 250 mls isopropanol) was added, followed by 10 mls of sodium iodide solution in isopropanol (7g NaI in 250 mls isopropanol. This reaction mixture was then warmed up with stirring for about 1 minute and titrated with 2×10^{-3}M sodium thiosulphate solution, thus determining the concentration of undecomposed hydroperoxide.

2.3.11 Electron Spin Resonance (e.s.r.) spectroscopy

Electron spin resonance spectroscopy was used to identify radicals and to determine radical concentrations in processed polypropylene films. E.s.r. spectra were obtained using a JEOL-PE spectro-meter, which was calibrated by a marker sample of MnO powder containing thermally diffused Mn^{2+} ions. The radical is normally characterised by its g-value and hyperfine splitting value (aN). As the sharp hyperfine structure of Mn^{2+} consisting of six lines could be observed, g-values of radicals were measured using the Mn^{2+} as reference. Samples of polypropylene films of 4 cm x 1 cm (about 0.09 g) were cut into strips and placed into a quartz tube. The tube was then immersed into the cavity of the spectrometer. After the spectrum of each sample was obtained, the sample was replaced by the marker and the spectrum recorded under the same conditions. The g-value could then be calculated with respect to the third and fourth lines of Mn^{2+} according to the spectrometer manual.

2.3.11.1 Determination of g-values

The line position of an e.s.r. spectrum is denoted in terms of "g-value." Thus, the g-Factor (spectroscopic splitting factor - which is dimensionless) determines the field at which the spectrum occurs, and it is a measure of amount of spin-orbit coupling. g-value is expressed as a function of microwave frequency and magnetic field at resonance. Energy of interaction of magnetic field and magnetic moment of an electron is given as:

$$\Delta E = g \beta H$$

$$\text{Thus,} \quad h\nu = g \beta H$$

$$\therefore \quad g = \frac{h\nu}{\beta H}$$

Assuming that the spectrum of the sample and marker were obtained simultaneously (spectr of most organic radicals fall betwen the 3rd and 4th lines of Mn^{2+} as in fig. 2.4;

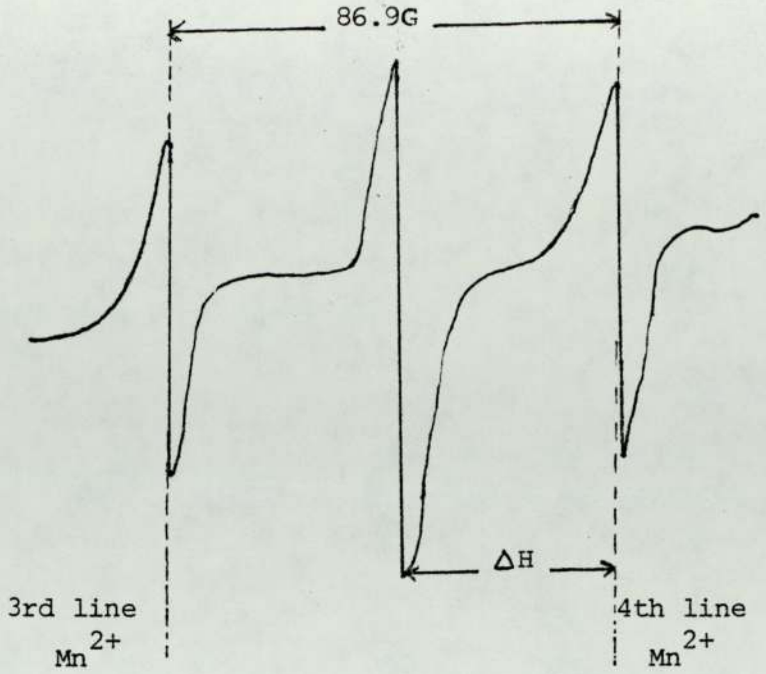


Fig. 2.4

and assuming that:

a) the g-value of the fourth line of Mn^{2+} counted from the low magnetic field is g = 1.981 (140), and it does not vary significantly between frequency range 9200- 9400 mHz.

b) microwave frequency remains between 9200-9400 mHz thus keeping the g-value of 4th line of marker constant, and

c) the distance between the third and fourth lines of the marker sample (Mn^{2+}) is 86.9 gauss.

ΔH represents the distance between the sample spectrum and fourth line of marker spectrum which could easily be obtained by proportional calculation. Once H has been obtained, the g-value of the unknown sample can be calculated as;

$h\nu = g_1\beta H_o$ For marker sample

$h\nu = g\beta(H_o - \Delta H)$ For unknown sample

Therefore $$g = \frac{h\nu}{\beta(H_o - \Delta H)} = \frac{\frac{h\nu}{\beta}}{\frac{h\nu}{g_1\beta} - \Delta H}$$

where β = Bohr magneton

h = planck's constant

g = g-value of unknown sample

g_1 = g-value of marker sample

Substituting ν for 9300 mHz (mean of 9200-9400 mHz)

$$g = \frac{6651}{3357 - \Delta H}$$

The g-values are useful in the identification of different radical types but not useful in differentiating between members of the same group of radicals, thus the hyperfine splitting factor is used. Hyperfine structure arises from interaction of unpaired electrons with neighbouring nuclei which have non-zero spin.

The hyperfine splitting constant of a radical which gives triplet signals can be calculated as follows.

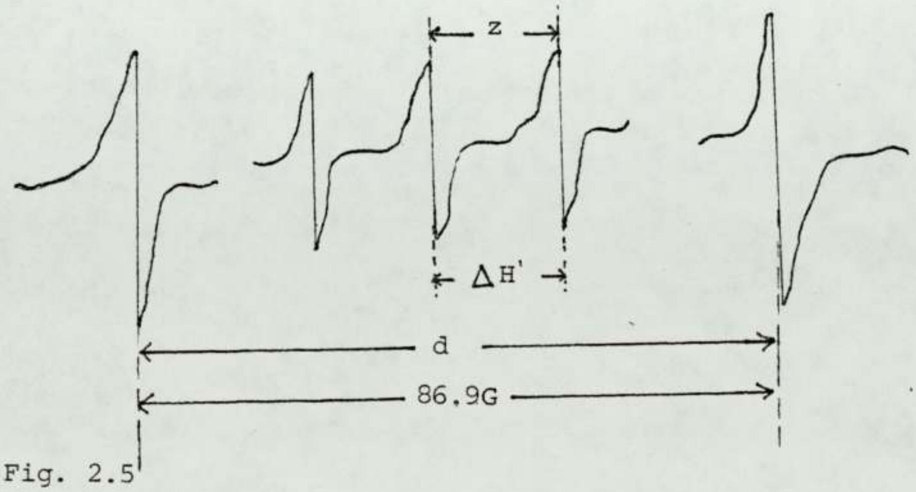


Fig. 2.5

If we assume (Fig. 2.5) that d is the distance between the third and fourth lines of Mn^{2+} and z is the separation between the two hyperfine lines of the detected signal, the splitting constant will be:

$$a_N = \Delta H' = \frac{z}{d} \times 86.9$$

2.3.11.2 Measurement of radical concentration

Concentration of radicals was measured as a ratio of a known reference. The reference sample used was copper sulphate solution of known concentration. 10 μl of 0.1M $CuSO_4$ solution was put in a capillary tube and sealed at both ends. This was fastened to the outer surface of the quartz tube in which the polymer samples were placed. Both spectra (polymer and reference) were thus recorded simultaneously.

This was essential for the reproducibility of results. The radical concentration was calculated by comparing the ratio $Y'm\ (\ Hpp)^2$ for the polymer samples to that of the reference as in Fig. 2.6.

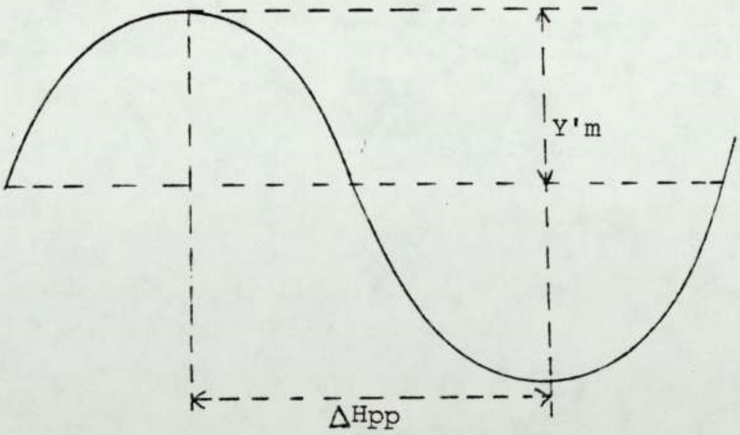


Fig. 2.6

$$\frac{Y'm\ (\Delta Hpp)^2\ \text{sample}}{Y'm\ (\Delta Hpp)^2\ \text{reference}} = \frac{\text{radical concentration in sample}}{\text{radical concentration in reference sample}}$$

where Y'm is in cm and Hpp is in gauss

This method was found to be a close approximation of the summation method of Wyard(141) and which has also been successfully used by other workers(142).

2.3.12. **Estimation of embrittlement time**

Embrittlement times of irradiated polymer films were estimated by flexing the polymer films of the same thickness forward and backward through an angle of 180°. The observation of a crack marked embrittlement of the polymer film.

2.3.13 **Oxidation of extracts**

The conversion of the hydroxylamine to its corresponding nitroxyl radical was effected, using the method of Durmis and his co-workers(110).

Approximately 0.5g of the PP films processed with 1.16×10^{-3} mol/100g of 4OHTMPNO./4OHTMPNOH was extracted in a soxhlet extractor under nitrogen with dichloromethane at 35°C for 12 hours. To the extract, 0.5 g of m-chloroperbenzoic acid was added and the mixture was allowed to boil for a further 2 hours. A solution test on the extract, as described previously (see 2.3.9) confirms the complete conversion of the hydroxylamine to the corresponding nitroxyl radical, (by disappearance of the green colouration).

CHAPTER THREE

A NITROXYL RADICAL AND ITS CORRESPONDING HYDROXYLAMINE AS PHOTOSTABILISERS FOR POLYPROPYLENE

3.1 INTRODUCTION

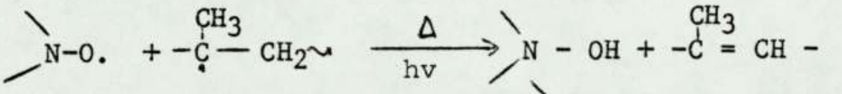
Nitroxyl radicals are known(92,143) to scavenge alkyl radicals in a CB-A process, resulting in the formation of alkyl hydroxylamines

$$>N - O. + R^{\cdot} \longrightarrow >NOR \qquad - (1)$$

The alkyl hydroxylamine is then believed to undergo a reaction with peroxyl radicals to regenerate the nitroxyl radical (115)

$$>N - OR + R'OO^{\cdot} \longrightarrow >N - O. + R'OOR \qquad - (2)$$

However recent work(113,144) has shown that during photo irradiation of polyolefin stabilised with stable nitroxyl radicals, ethylenic unsaturation was formed in the polymer matrix by the following reaction mechanism.



$$>N\text{-}O. + -\overset{CH_3}{\underset{\cdot}{C}} - CH_2\sim \xrightarrow[hv]{\Delta} >N - OH + -\overset{CH_3}{C} = CH - \qquad - (3)$$

$$>NOH + R'OO. \longrightarrow >N - O\cdot + R'OOH \qquad - (4)$$

The role of alkyl hydroxylamines during photostabilisation still generates controversy. In order to explain how alkyl hydroxyl-amines fit into the photostabilisation mechanism, a nitroxyl radical - 4 hydroxyl 2,2,6,6 tetramethyl piperidinyl-1-oxyl (4OHTMPNO.)* and its corresponding hydroxylamine, 4-hydroxyl, 2,2,6,6 tetramethyl piperidinyl -1-ol (4OHTMPNOH) - a nitroxyl precursor were examined as photostabilisers for Polypropylene.

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* Table of structure, code names and number of all compounds are on p. 36.

3.2 RESULTS

Both 4OHTMPNO$^\cdot$ and 4OHTMPNOH are effective melt stabilisers for PP during thermal procesing in a closed mixer of a torque rehometer (in restricted oxygen) as shown in Fig. 3.1 in which no change in torque was observed with processing time - giving no indication of chain scission or crosslinking. In excess oxygen however, (Fig. 3.2) a gradual but small drop in torque (in both cases) with increasing processing time, indicated the occurence of gradual chain scission.

Figs. 3.3 and 3.4 show the melt flow index (MFI) of PP samples containing both compounds processed in the closed and open mixers, respectively. There was almost no change in MFI in the closed-mixer-procesed samples in both cases until later stages of processing in which a slight increase was observed. In the open mixer however, both compounds show slight increases in MFI values until later stages of processing when MFI increases more noticeably, thus suggesting a decreased melt stabilising activity by both compounds under such severe processing operation (in excess oxygen for long processing times).

The build-up of hydroperoxides with processing time in PP processed with both compounds are shown in Fig. 3.5 for processing in closed mixer and Fig. 3.6 for open mixer processing. Although both compounds, to a reasonable extent, restricted extensive formation of hydroperoxides during processing (compared to the unstabilised control, in restricted oxygen (Fig. 3.5)), samples containing 4OHTMPNOH showed slightly higher hydroperoxide concentration than those processed with 4OHTMPNO$^\cdot$ in which almost no change in hydroperoxides concentration was observed until later stages of processing. In the presence of excess oxygen however

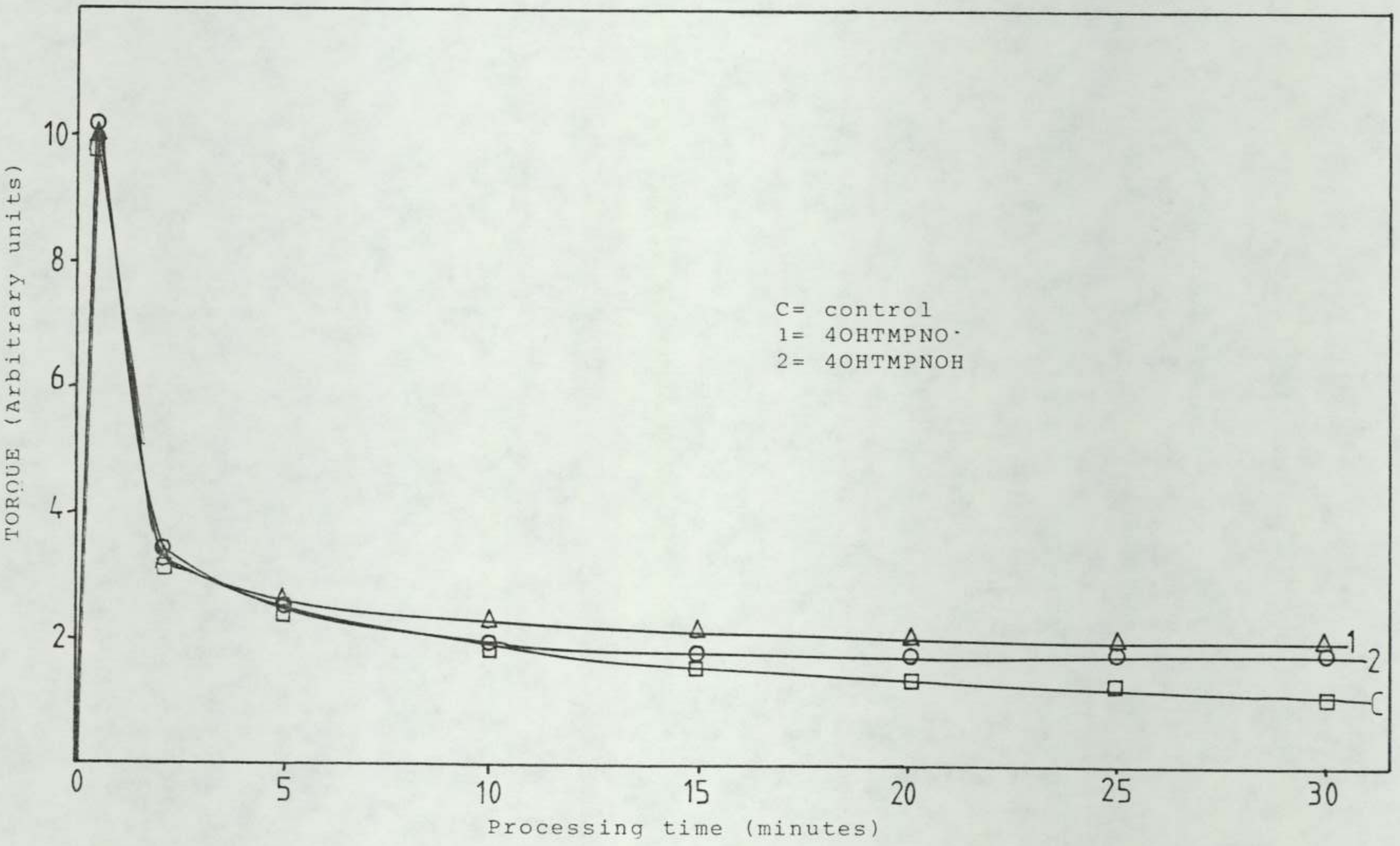


Fig. 3.1: Dependence of torque on processing time of PP containing 1.16x10^{-3}mol/100g of (1) 4OHTMPNO· (2) 4OHTMPNOH (C) control processed in a closed mixer at 180°C.

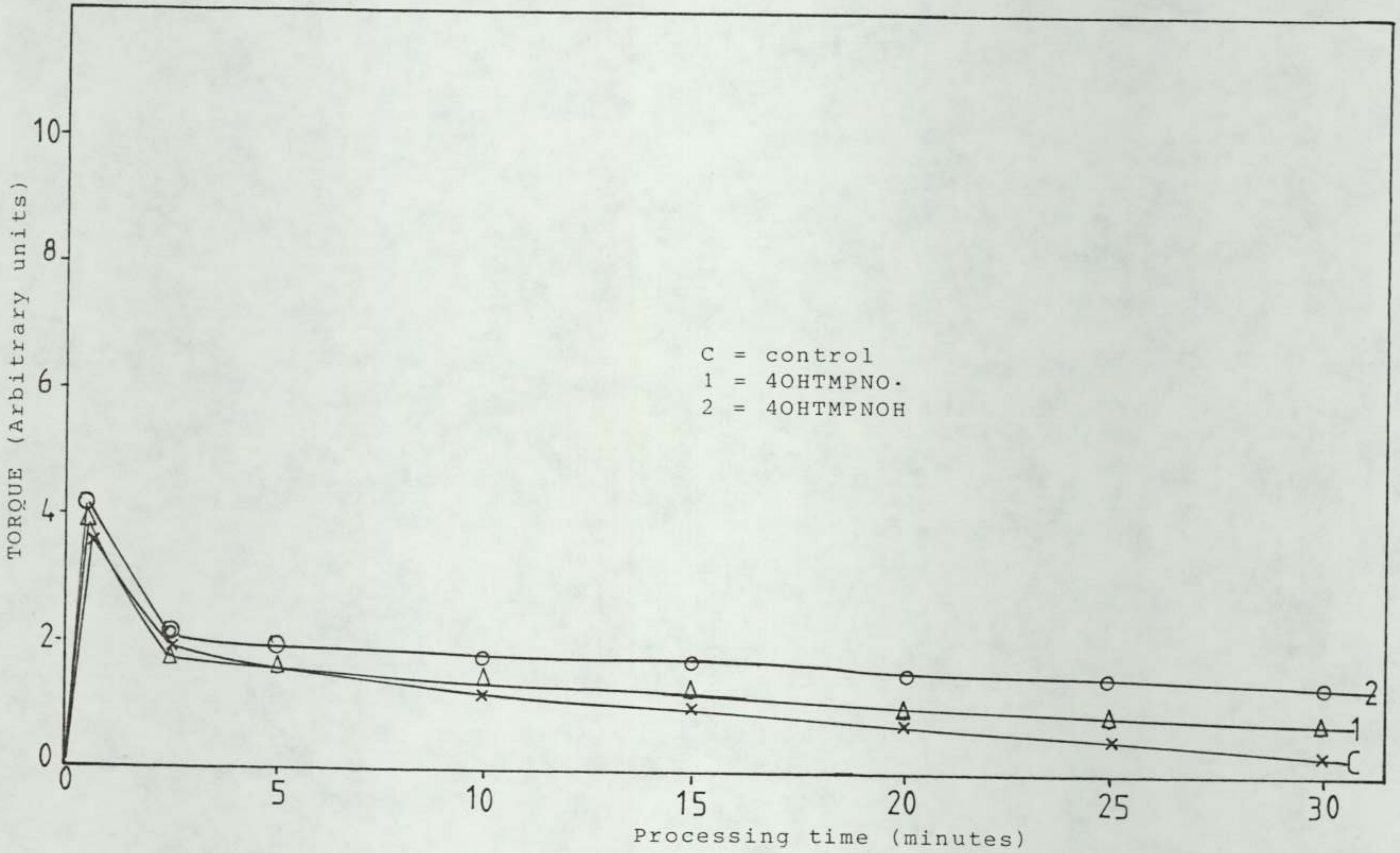


Fig. 3.2: Dependence of torque on processing time of PP containing 1.16x10^{-3}mol/100g of (1) 4OHTMPNO· (2)4OHTMPNOH (C) control processed in an open mixer at 180°C.

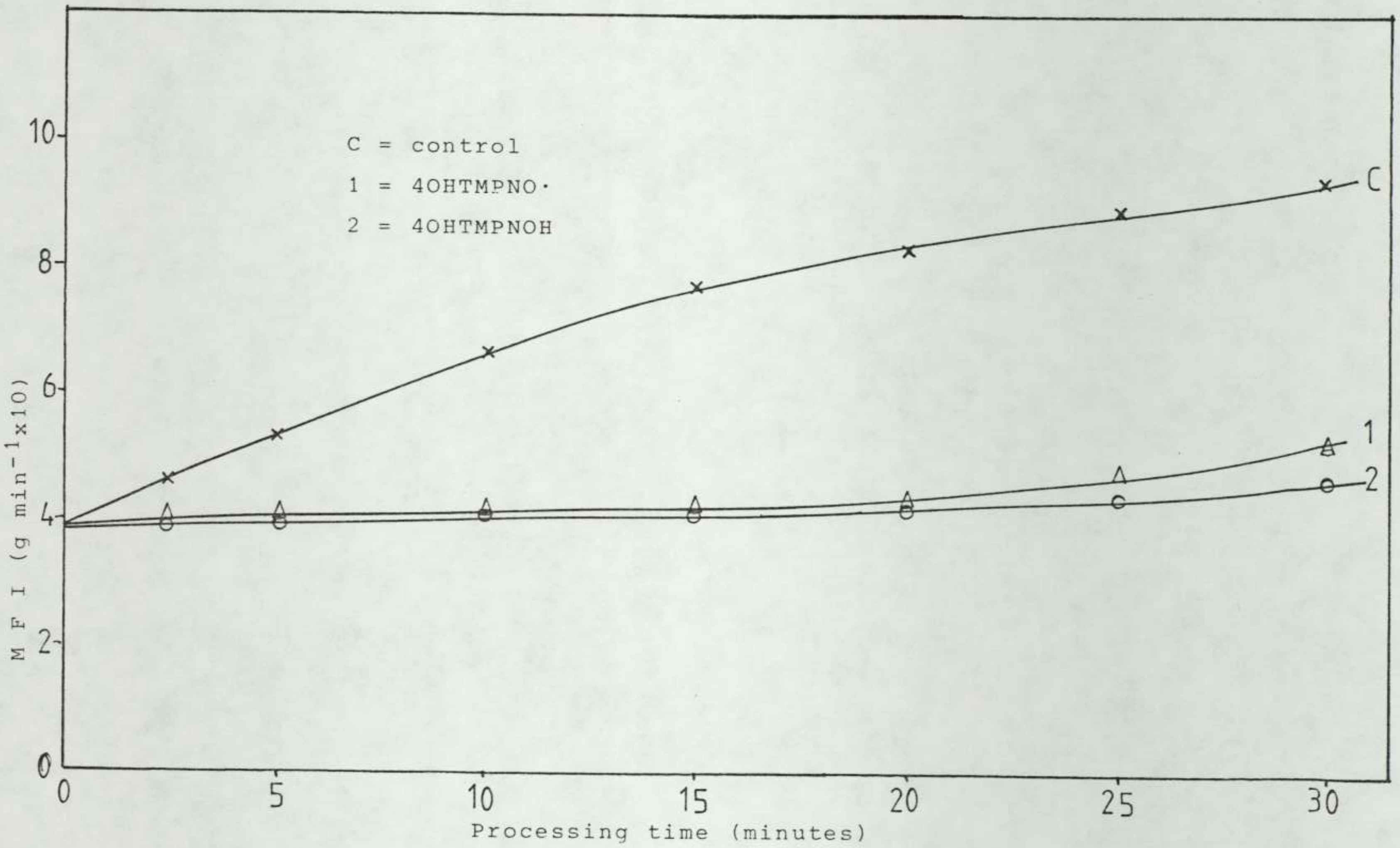


Fig. 3.3: Dependence of MFI(230°C, 2.16kg) on processing time of PP containing 1.16×10^{-3}mol/100g of (1)4OHTMPNO· and (2)4OHTMPNOH (C) control processed in a closed mixer at 180°C.

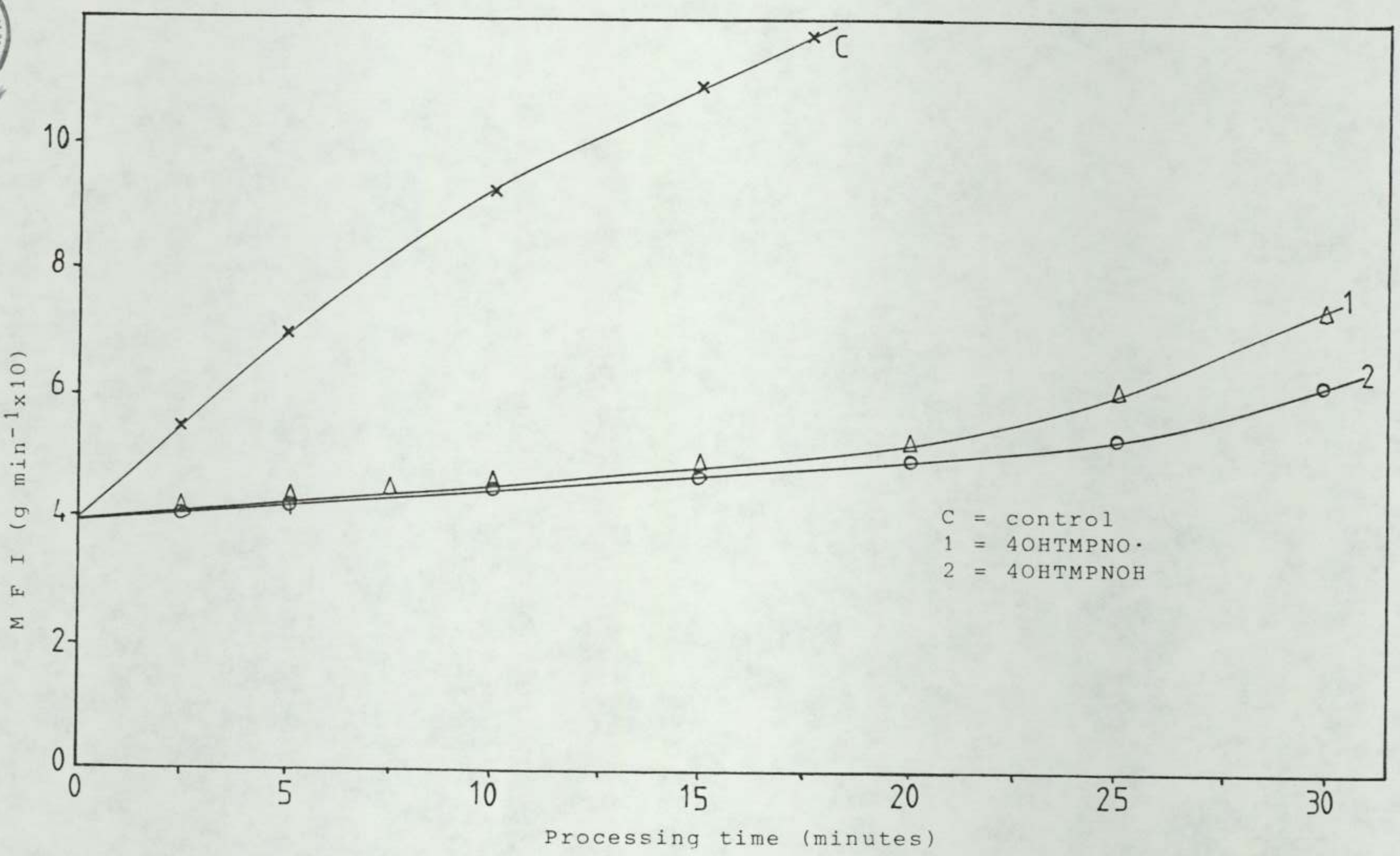


Fig. 3.4: Dependence of MFI(230°C, 2.16kg) on processing time of PP containing 1.16x10^{-3} mol/100g of (1)@OHTMPNO· (2)4OHTMPNOH (C) control processed in an open mixer at 180°C.

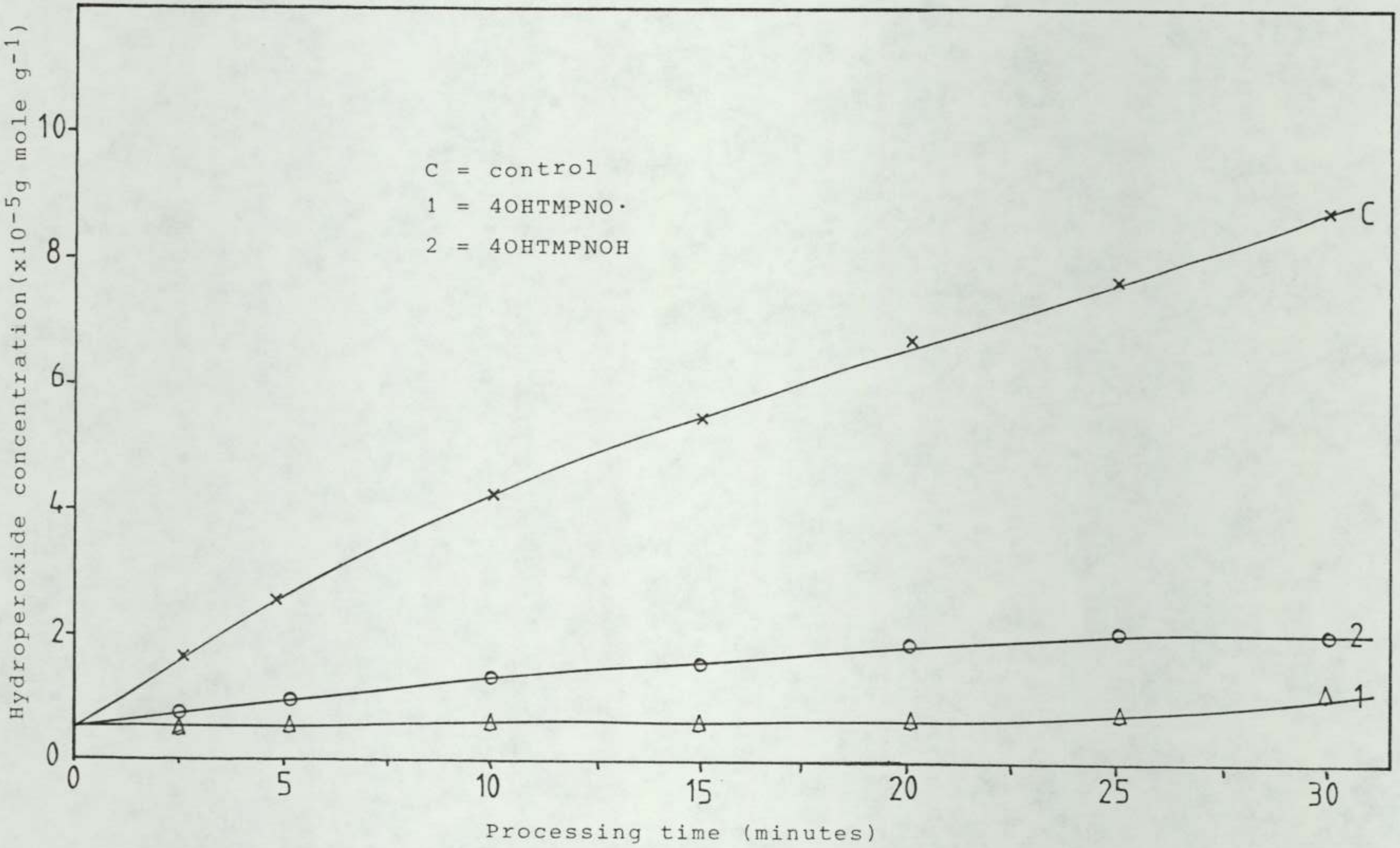


Fig. 3.5: Dependence of hydroperoxide concentration on processing time of PP containing 1.16×10^{-3} mol/100g of (1) 4OHTMPNO· and (2) 4OHTMPNOH (C) control processed in a closed mixer at 180°C

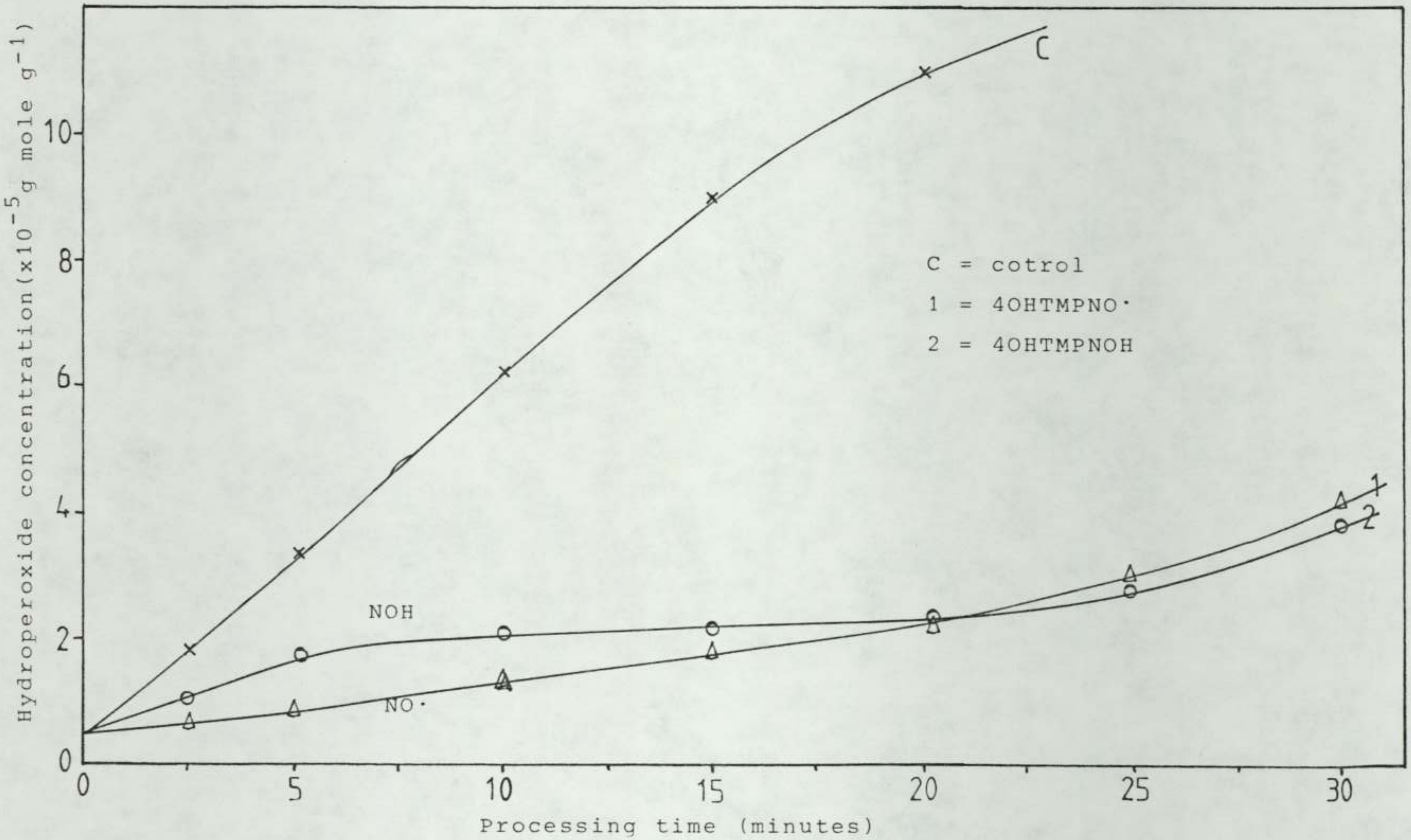


Fig 3.6: Dependence of hydroperoxide concentration on processing time of PP containing 1.16×10^{-3}mol/100g of (1)4OHTMPNO· and (2)4OHTMPNOH (C) control processed in an open mixer at 180°C.

(Fig. 3.6) there was an initial rapid hydroperoxide formation in the case of 4OHTMPNOH which later levels off, then there is a gradual increase with processing time. The same picture of a gradual increase with processing time was obtained in the case of 4OHTMPNO$^{\bullet}$. Thus the fact that both compounds prevent hydroperoxide formation reasonably well, particularly in restricted oxygen, suggest that they interfere with the radical chain propagation sequence in PP during processing, almost certainly by deactivating the alkyl and alkylperoxyl propagating radical species.

The subsequent photostability of PP films processed at different times with 1.16×10^{-3}mol/100g (~0.2%) of 4OHTMPNO$^{\bullet}$ in both closed and open mixers is shown in table 3.1 and summarised in Fig. 3.7.

Table 3.1 **u.v. EMT of PP + 1.16×10^{-3}mol/100g (~0.2%) of 4OHTMPNO$^{\bullet}$ processed at 180^{o}C**

Processing time (minutes)	u.v embrittlement time (hrs)	
	CM	OM
2.5*	1660	1570
5	1560	1470
7.5	1480	1380
10	1400	1265
12.5	1370	1170
15	1340	1090
17.5	1330	1000
20	1340	905
25	1400	670
30	1510	280

* Shearing rate was increased to 70 rpm for better mixing (all other samples were processed at the normal shear rate of 60 rpm.)

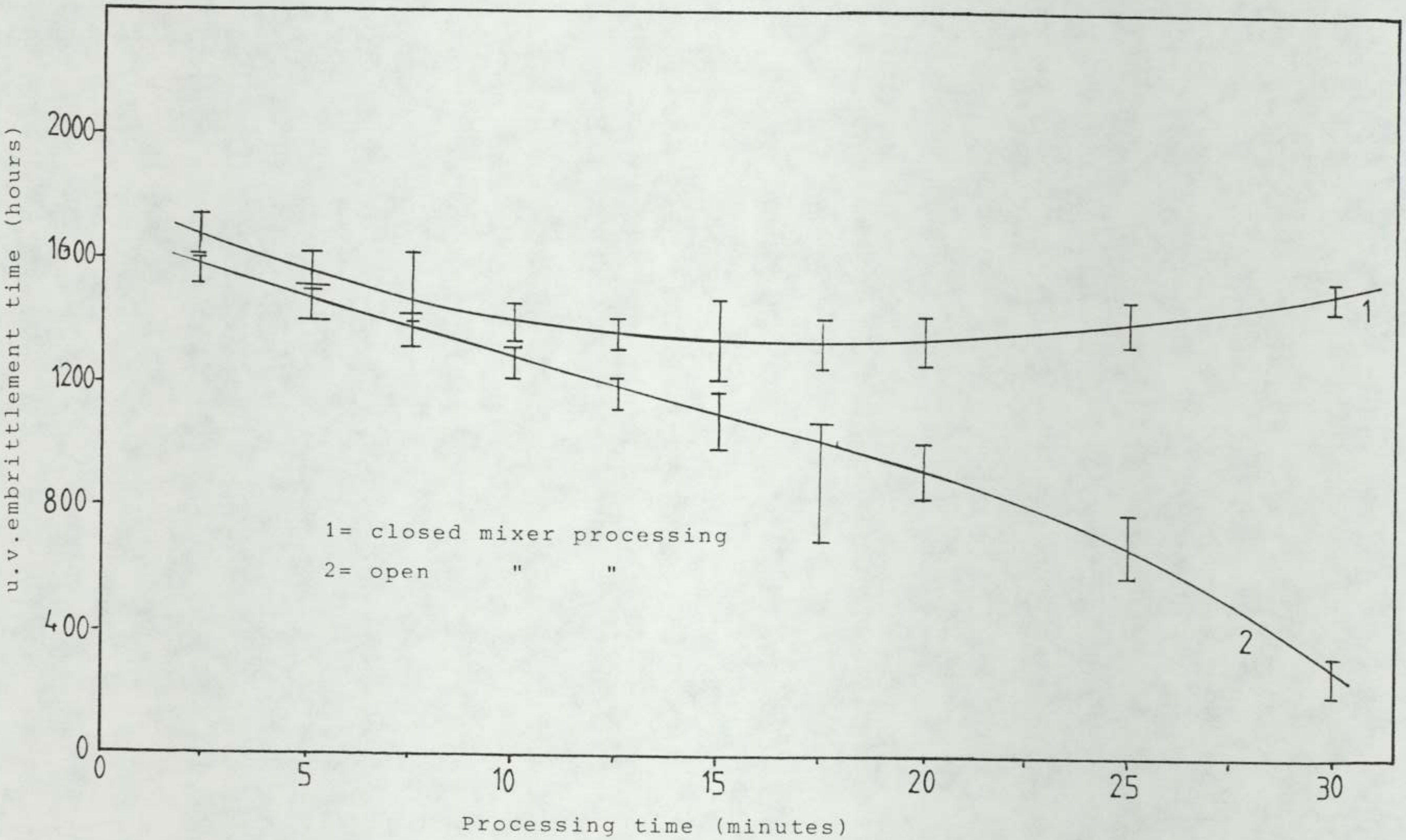


Fig. 3.7: Effect of processing time on u.v.embrittlement time of PP containing 1.16x10-3 mol/100g of 4OHTMPNO· processed in (1) a closed mixer (2) an open mixer at 180°C.

In the samples processed in the closed mixer Fig. 3.7 (curve 1) photostability slightly decreased with processing time up to about 15 minutes, followed by a gradual increase, while in the open mixer, a decrease in photostability with increasing processing time was observed. This and other results will be discussed in the next section.

Fig. 3.8 shows the effect of processing time on the carbonyl formation (with photo-irradiation) of PP containing 1.16 x 10^{-3}mol/100g processed in a closed mixer. All samples show no induction period and the rates of carbonyl formation with u.v. irradiation are identical in all cases, particularly at the initial stages of photo irradiation. For samples processed in an open mixer on the other hand (fig. 3.9) the longer the processing time, the faster the rate of carbonyl formation under the effect of u.v. light, thus the lower the stability; and when time to a constant level of carbonyl formation (e.g. 0.3 index) was examined for all samples, (with processing times) as shown in Fig. 3.10, a picture similar to the relationship between photostability and processing time (fig. 3.7) was obtained.

The photostability of PP containing 1.16 x 10^{-3}mol/100g of 4OHTMPNOH processed in both closed and open mixers are shown in table 3.2 and demonstrated in Fig. 3.11.

Unlike in the case of 4OHTMPNO$^{\bullet}$, 4OHTMPNOH effects a recurring pattern of an increase, followed by a decrease in photostability of PP with processing time in the closed mixer Fig. 3.11(curve 1) but generally, the magnitude of the increase, increases with processing time. In the open mixer however, a behaviour, similar to 4OHTMPNO. was

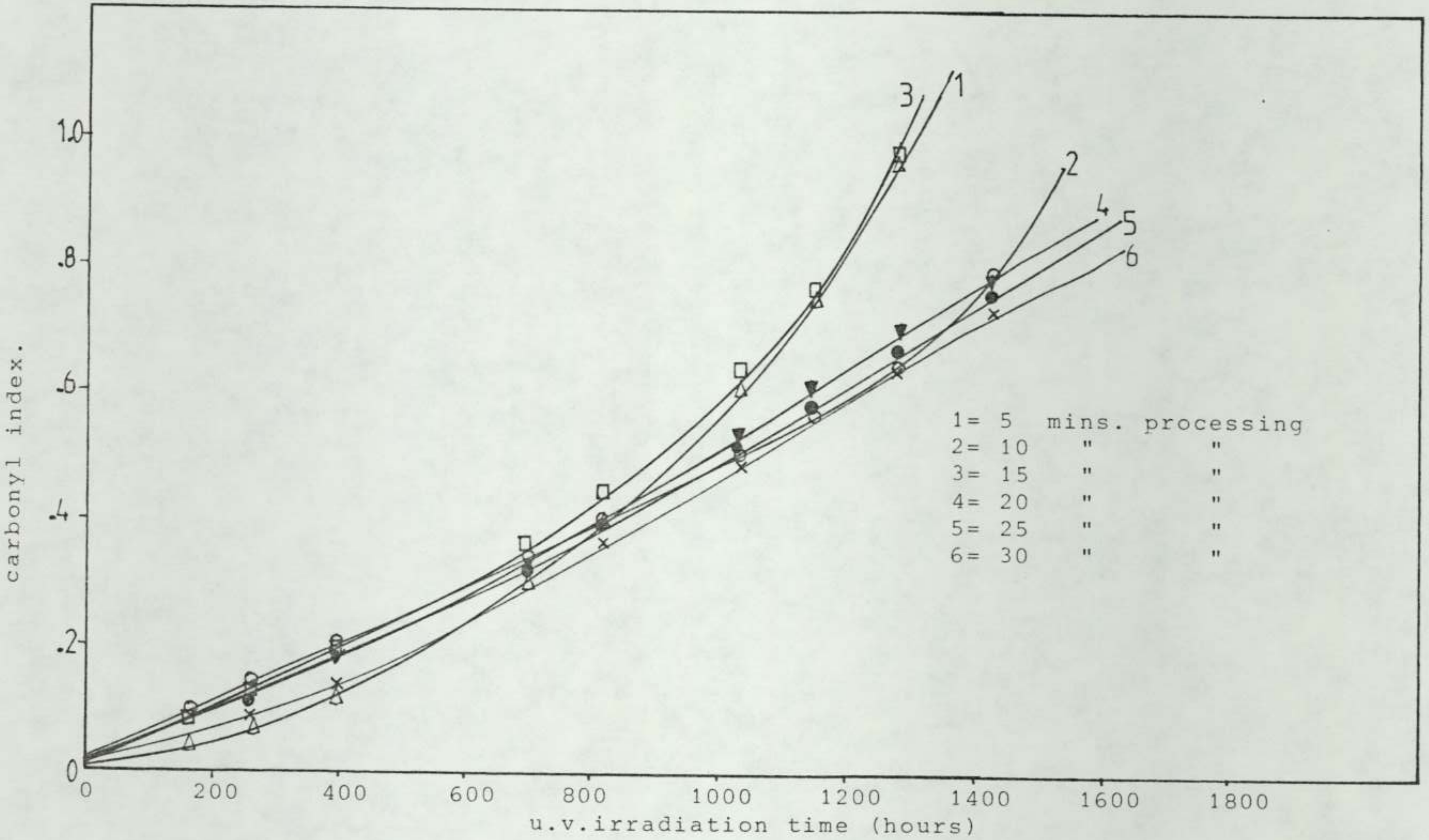


Fig. 3.8: Effect of processing time on carbonyl formation with u.v.irradiation of PP containing 1.16x10^{-3}mol/100g of 4OHTMPNO· processed in a closed mixer at 180°C.

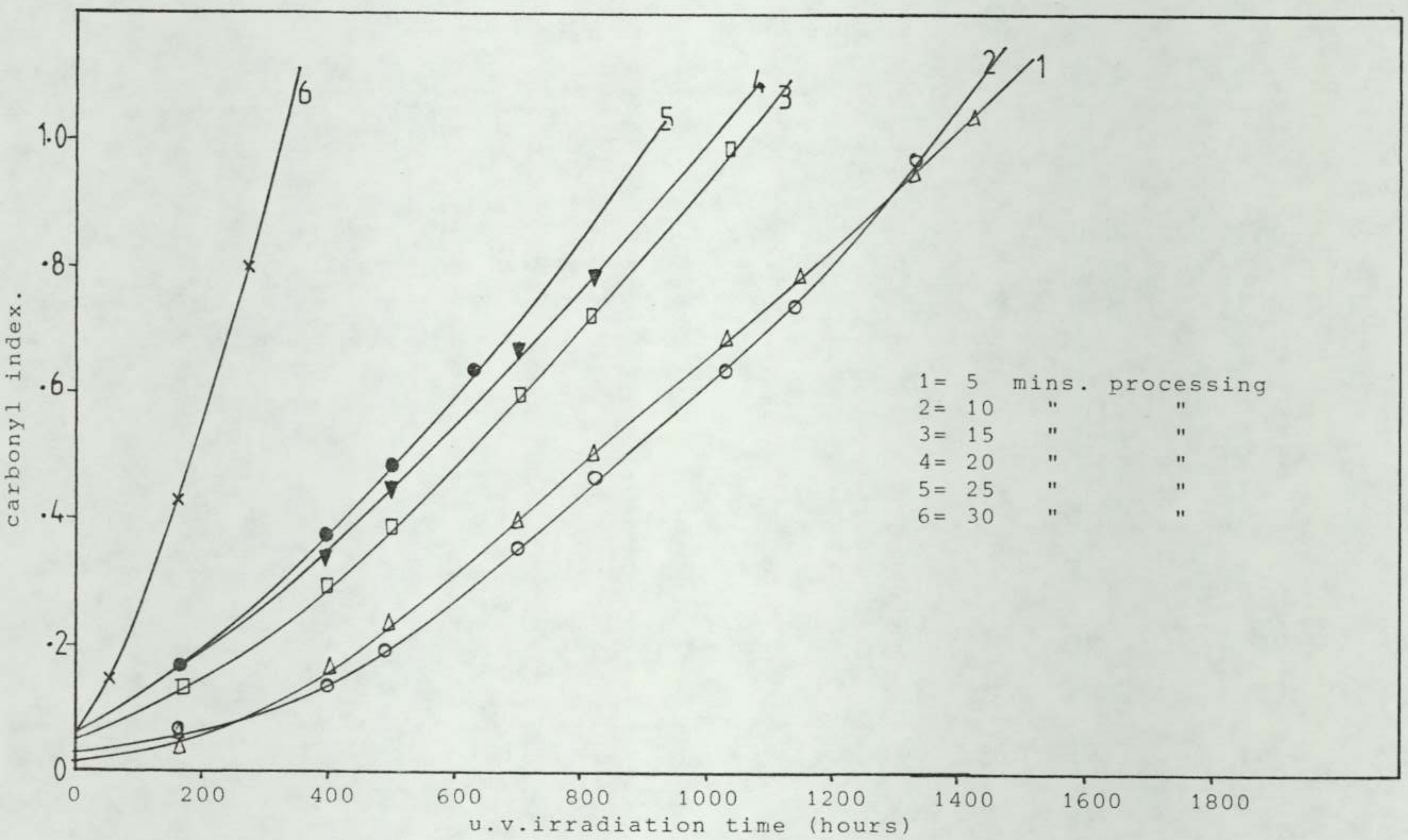


Fig. 3.9: Effect of processing time on carbonyl formation with u.v.irradiation of PP containing 1.16x10^{-3}mol/100g of 4OHTMPNO· processed in an open mixer at 180°C.

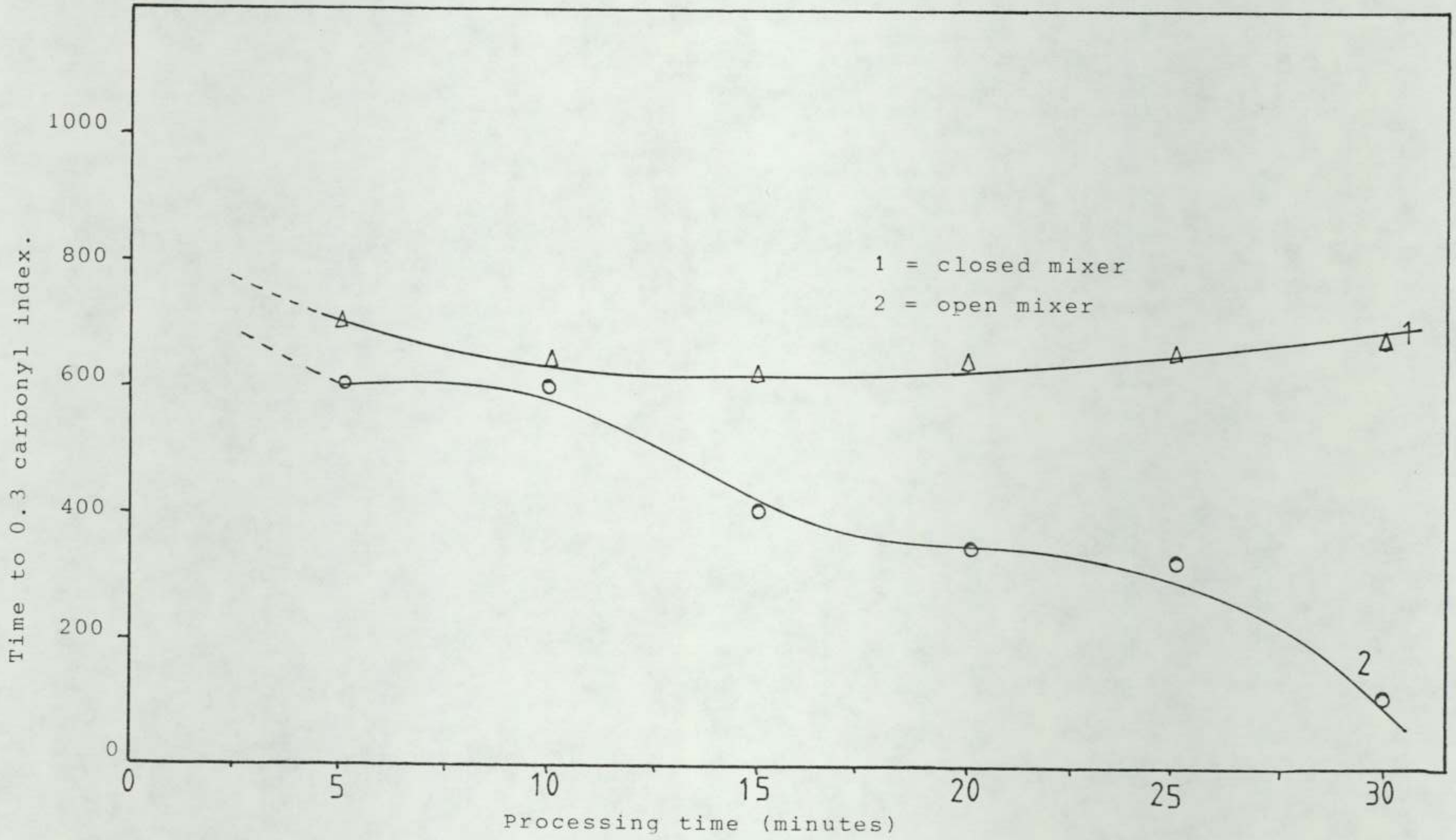


Fig. 3.10: Effect of processing time on time to a constant (0.3) carbonyl index in PP containing 1.16x10^{-3}mol/100g of 4OHTMPNO· processed in (1)a closed mixer (2) an open mixer at 180^{o}C

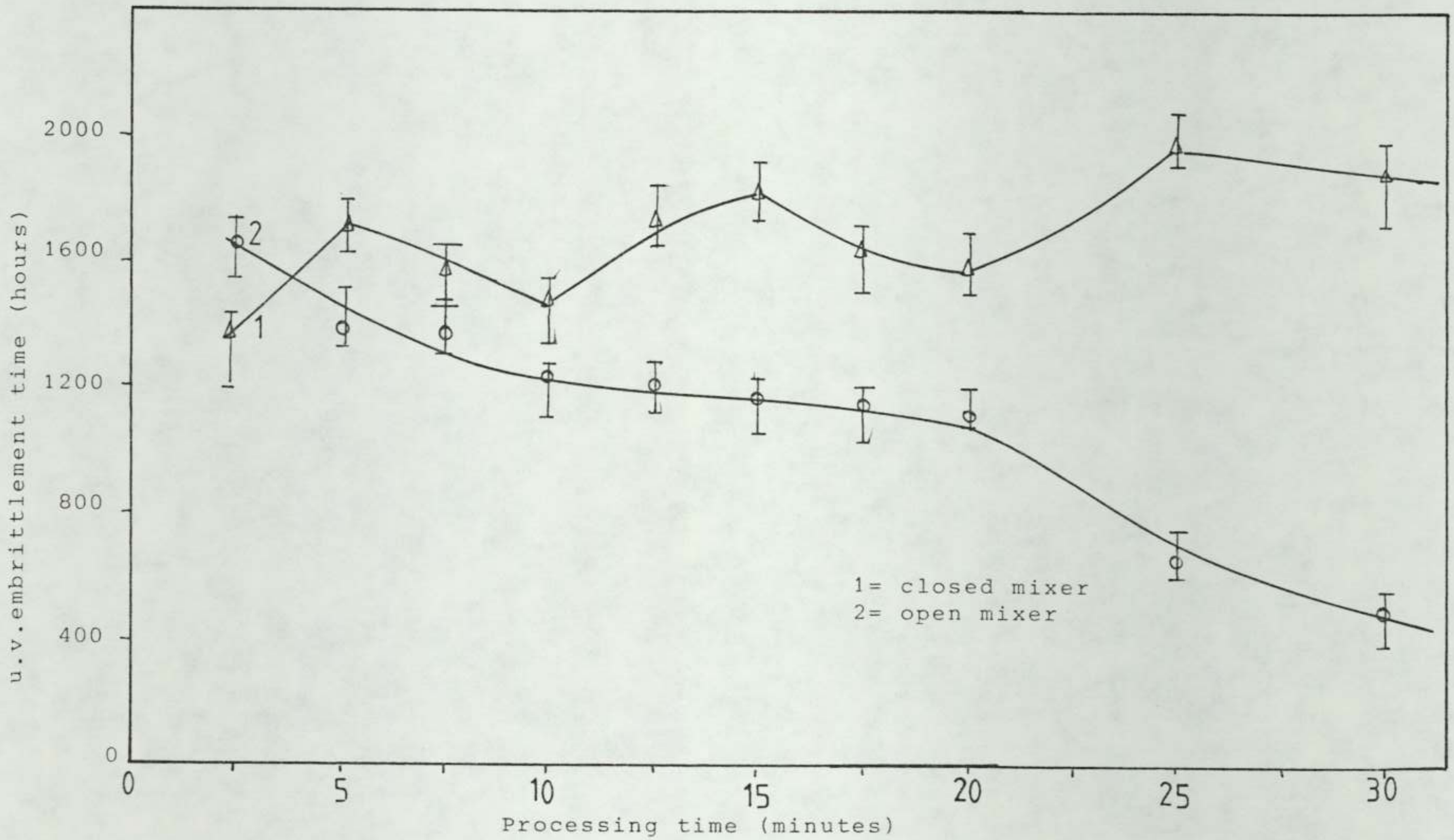


Fig. 3.11: Effect of processing time on u.v.embrittlement time of PP containing 1.16×10^{-3}mol/100g of 4OHTMPNOH processed in (1)a closed mixer (2) an open mixer at 180°C

Table 3:2 **U.V. EMT of PP + 1.16x10^{-3}mol/100g (~ 0.2%) of 4OHTMPNOH. processed at 180°C.**

Processing time (minutes)	U.V EMT (hours)	
	CM	OM
2.5*	1370	1660
5	1710	1370
7.5	1580	1370
10	1480	1220
12.5	1730	1210
15	1820	1170
17.5	1645	1145
20	1580	1145
25	1980	650
30	1885	510

* shearing rate was increased to 70 rpm for better mixing.

obtained (Fig. 3.7) in which photostability decreased with increasing processing time. But, at initial stages of processing (e.g. 2.5 minutes) photostability in the samples processed in excess oxygen were better than in samples processed under restricted oxygen conditions but as processing time increases the embrittlement time starts to decrease gradually (see Fig. 3.11).

Figs. 3.12 and 3.13 show the effect of processing time on carbonyl formation (under the effect of u.v. light) of PP containing 1.16 x 10^{-3}mol/100g (0.2%) of 4OHTMPNOH processed in closed and open mixers respectively. In the closed mixer (Fig. 3.12) all films showed an induction period before the eventual build-up of the carbonyl. The induction period was relatively long in samples processed for long periods (e.g. 25 & 30 minutes). In the open mixer however, (Fig. 3.13) the longer the processing time, the faster the rate of carbonyl formation and thus, the lower the photostability. A similar pattern of relationship between photostability and processing time (Fig. 3.11) was obtained when time to a constant level of carbonyl formation(e.g. 0.3) was examined against processing time as shown in Fig. 3.14.

Having examined the effect of the prior thermal processing of 4OHTMPNO˙ and 4OHTMPNOH on the subsequent photostability of PP, effect of additive concentration on the subsequent photostability was also investigated. Table 3.3 shows the effect of concentration of both 4OHTMPNO. and 4OHTMPHNOH and the effect of different processing conditions on the photostability of PP. This is summarised in Fig. 3.15 for 4OHTMPNO. and Fig. 3.16 for 4OHTMPHNOH.

In both additives a positive concentration effect was observed, i.e. photostability increased with increasing concentration. However, samples processed in the closed mixer show better photostability than those processed in the open mixer which in turn, show better photostability than those processed under a blanket of argon. However, when all these samples were solvent extracted (with dichloromethane for

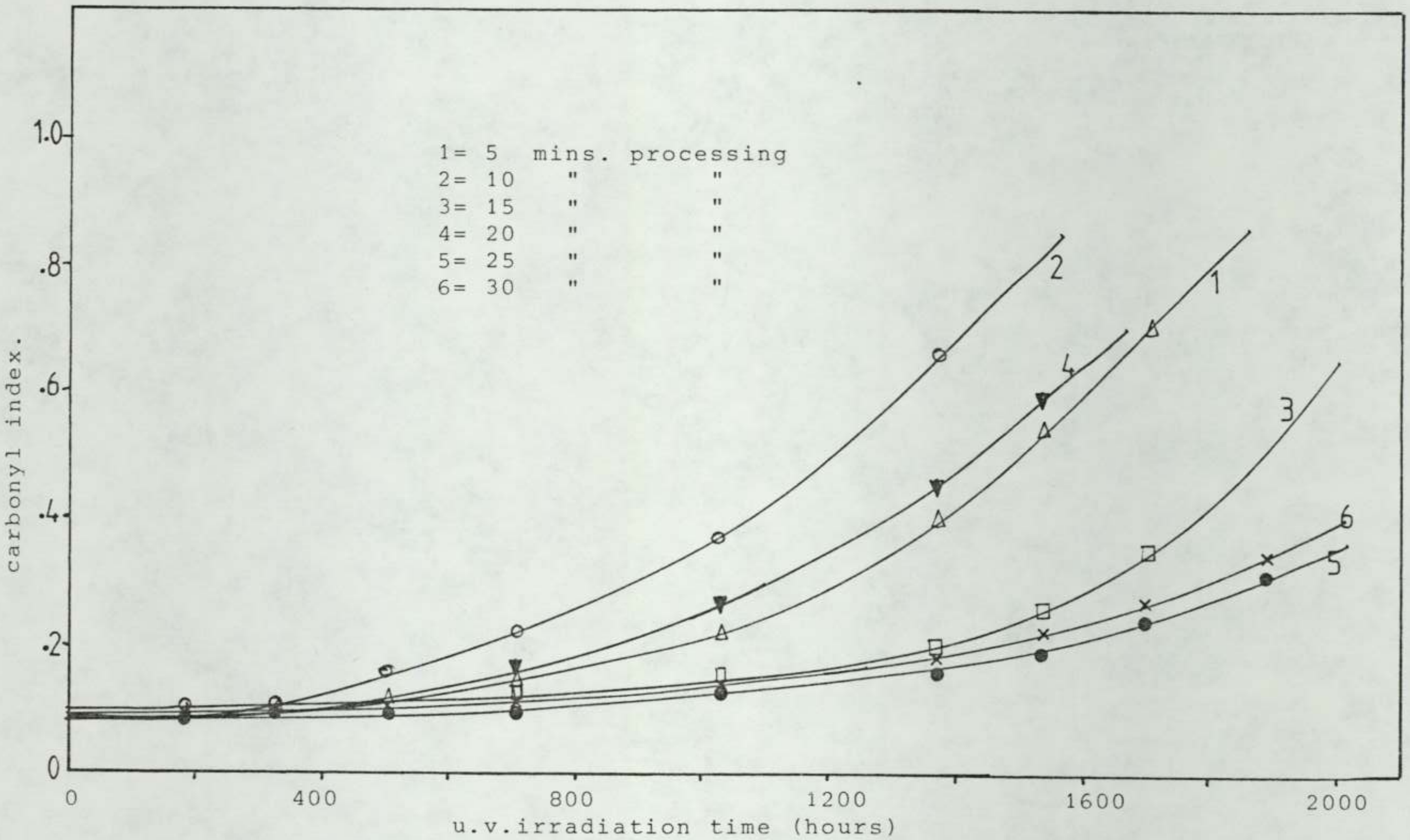


Fig. 3.12: Effect of processing time on carbonyl formation with u.v.irradiation of PP containing 1.16x10^{-3}mol/100g of 4OHTMPNOH processed in a closed mixer at 180°C.

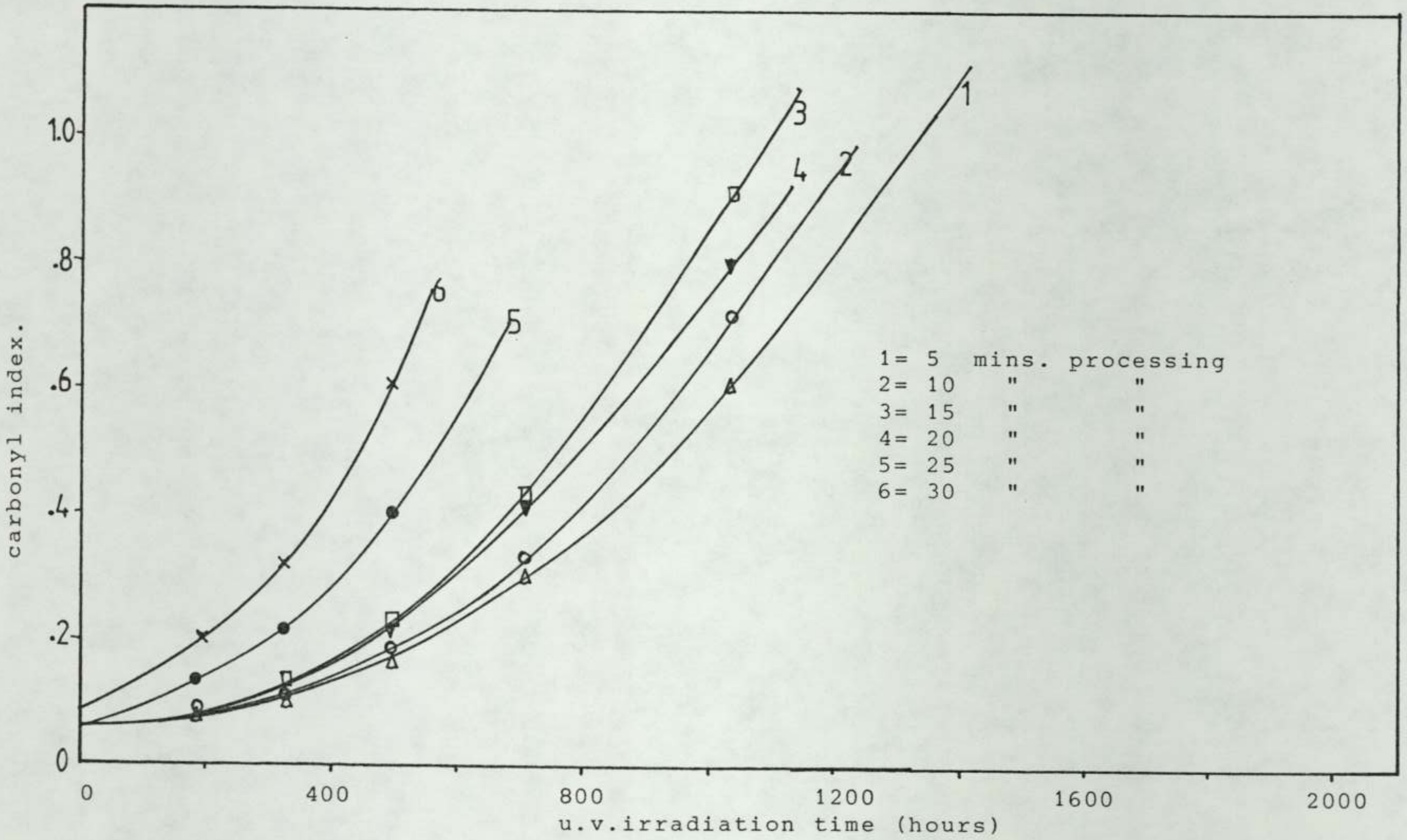


Fig. 3.13: Effect of processing time on carbonyl formation(during irradiation)of PP containing 1.16x10^{-3}mol/100g of 4OHTMPNOH processed in an open mixer at 180°C.

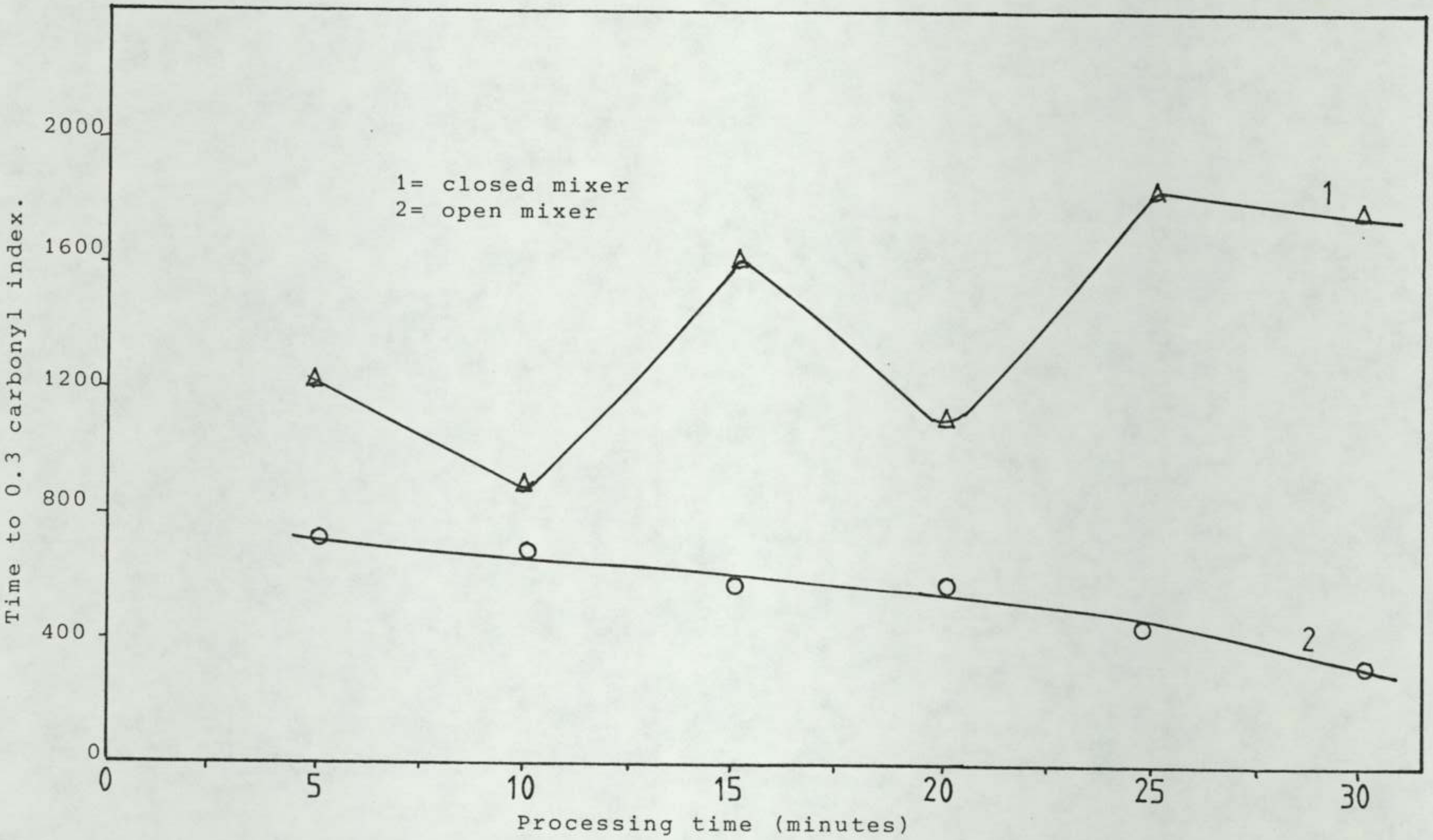


Fig. 3.14: Effect of processing time on time to a constant(0.3) carbonyl index of PP containing 1.16x10^{-3}mol/100g of 4OHTMPNOH processed in (1)a closed mixer (2)an open mixer at 180°C.

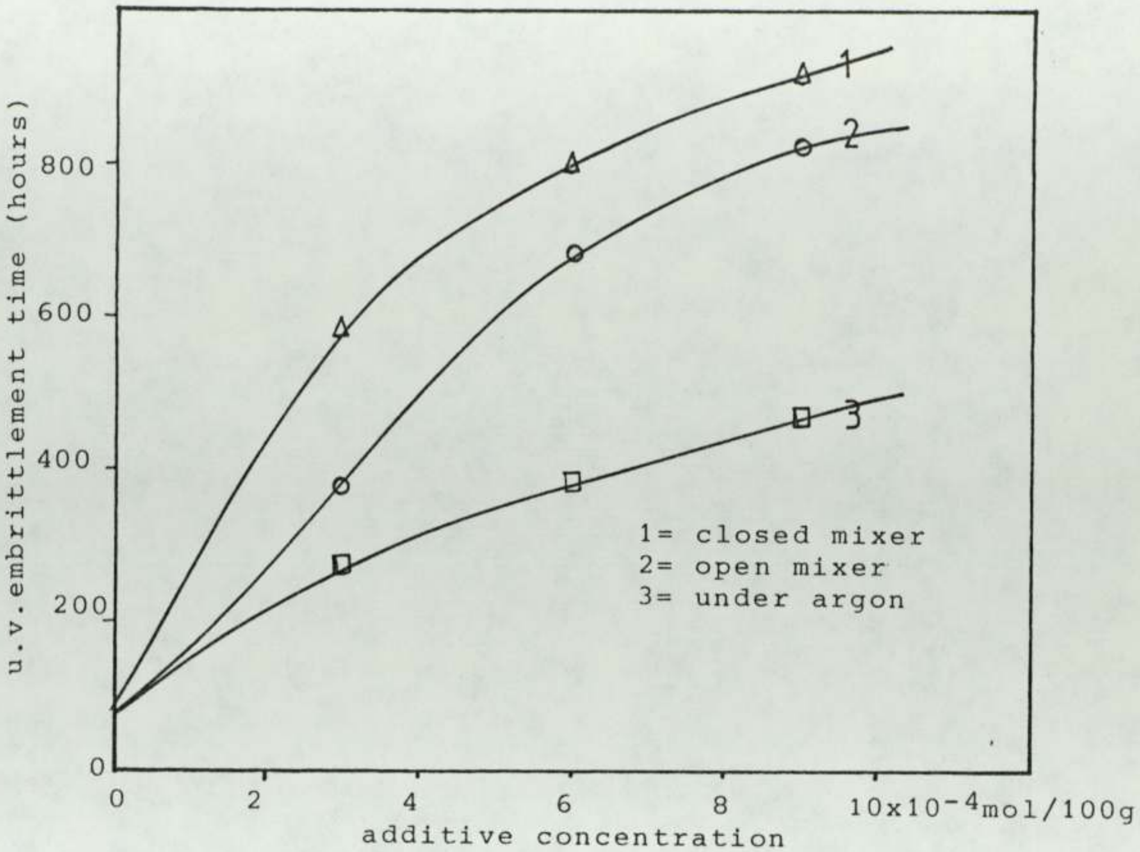


Fig. 3.15: Effect of additive conc. and processing condition on u.v.embrittlement time of PP processed with 4OHTMPNO· in (1) a closed mixer (2) open mixer (3) under argon for 10 mins. at 180°C.

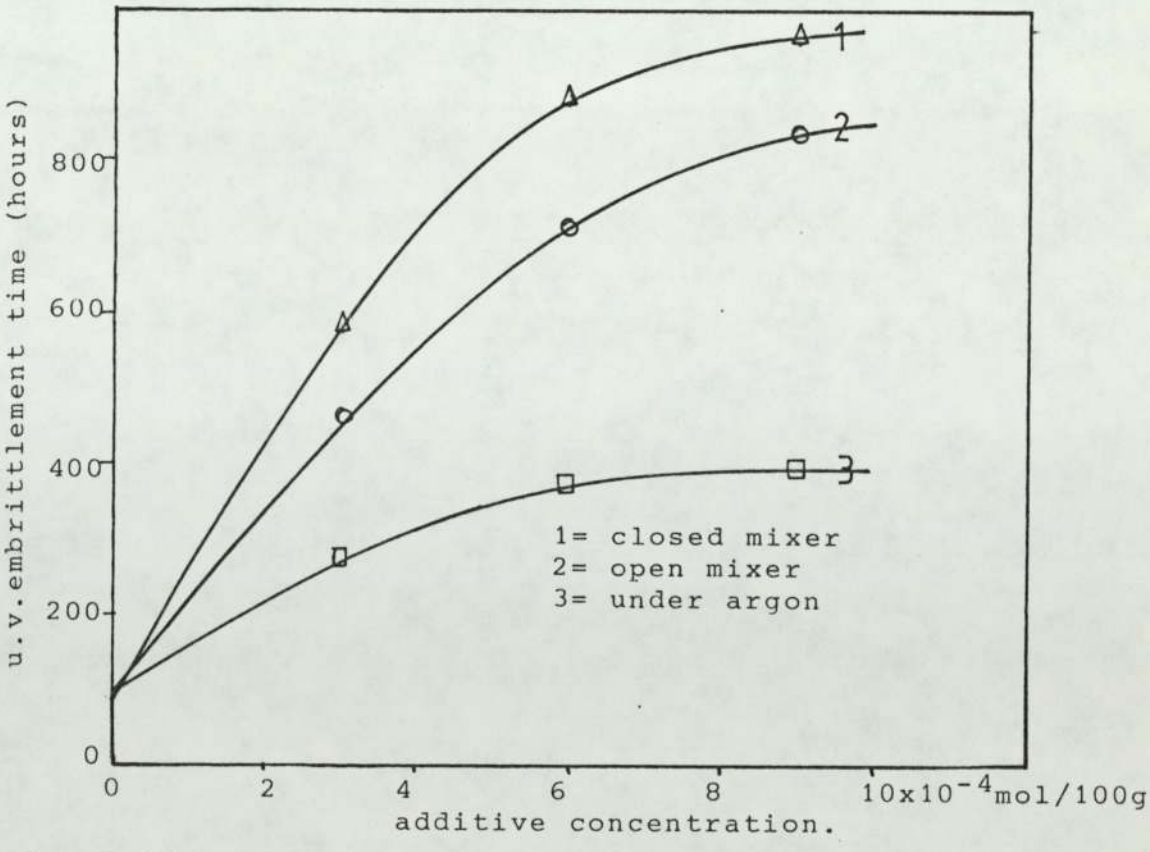


Fig. 3.16: Effect of additive conc. and processing condition on u.v.embrittlement time of PP processed with 4OHTMPNOH in (1) closed mixer (2) open mixer (3) under argon for 10 mins. at 180°C.

Table 3.3 Effect of concentration & processing conditions on u.v. EMT of PP + $>N-O^{\bullet}$ & $>NOH$

Processing* condition	Concentration ($\times 10^{-3}$ mol/100g)	u.v. embrittlement time (hours)	
		4OHTMPNO$^{\bullet}$	4OHTMPNOH
Closed Mixer	3	585	585
	6	800	890
	9	920	970
Open Mixer	3	370	465
	6	690	715
	9	820	840
Argon	3	275	275
	6	370	370
	9	465	395

* Procesing temperature = 180°C.

18 hours at 35°C under nitrogen) see Chapter 2, Section 2.3.3. photostability in all samples was greatly reduced and almost to the same level irrespective of additive concentration, processing conditions or indeed whether the additive was 4OHTMPNO. or 4OHTMPNOH as shown in table 3.4 and Figs. 3.17 and 3.18 (for 4OHTMPNO. and 4OHTMPNOH respectively.

Figs. 3.19 and 3.20 show the effect of additive concentration and solvent extraction on carbonyl formation of PP containing 4OHTMPNO. and 4OHTMPNOH processed in a closed mixer for 10 minutes. In all cases, there is little or no induction period, although in the unextracted samples, the higher the concentration the slower the rate of carbonyl formation, hence the higher the photostability. In the extracted

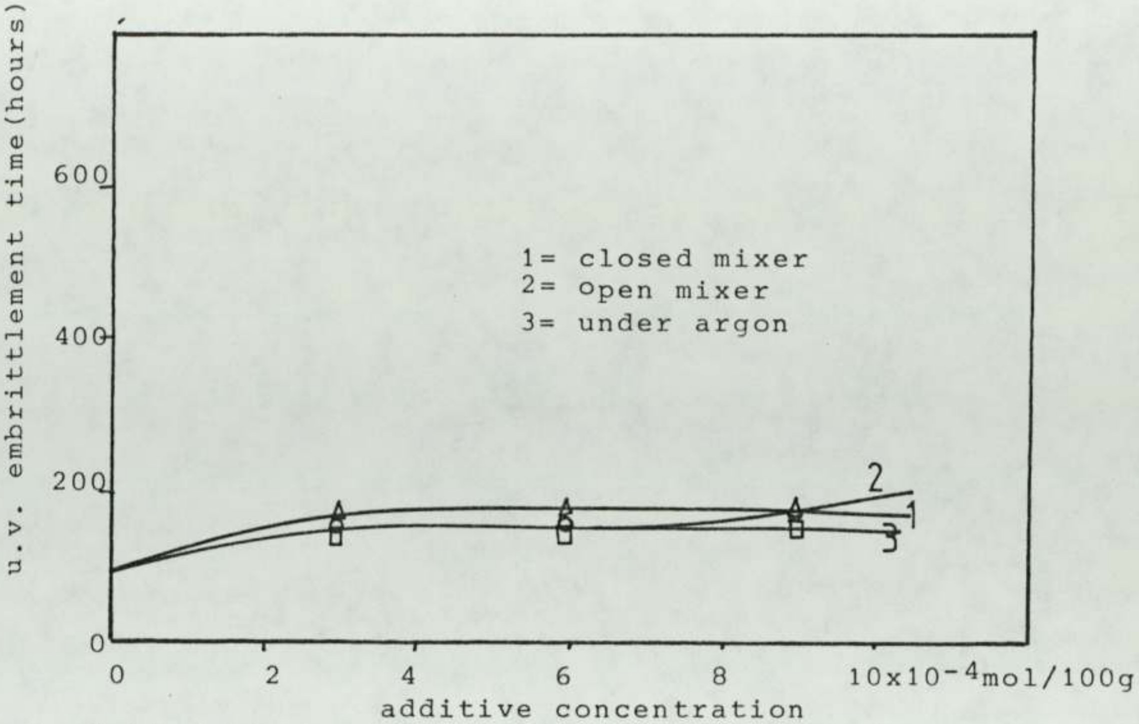


Fig 3.17: Effect of extraction on u.v. EMT of PP processed with different conc. of 4OHTMPNO· in (1)closed mixer (2)open mixer (3)under argon for 10 mins. at 180°C.

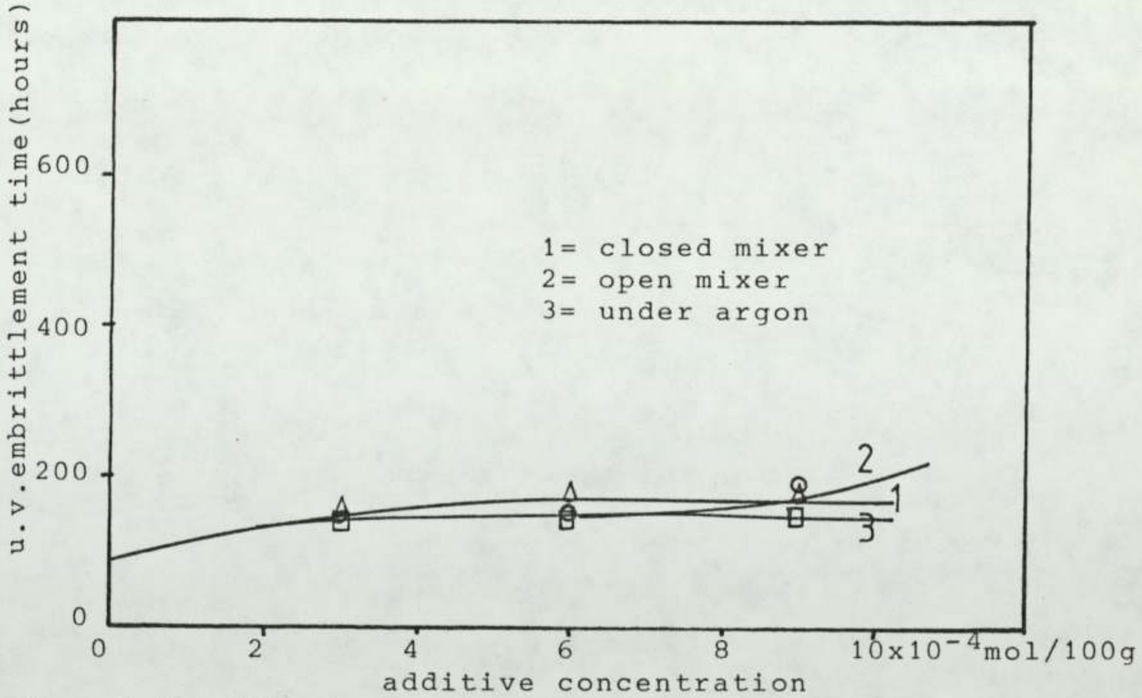


Fig. 3.18: Effect of extraction on u.v.EMT of PP processed with different conc. of 4OHTMPNOH in (1)closed mixer (2)open mixer (3)under argon for 10 mins. at 180°C.

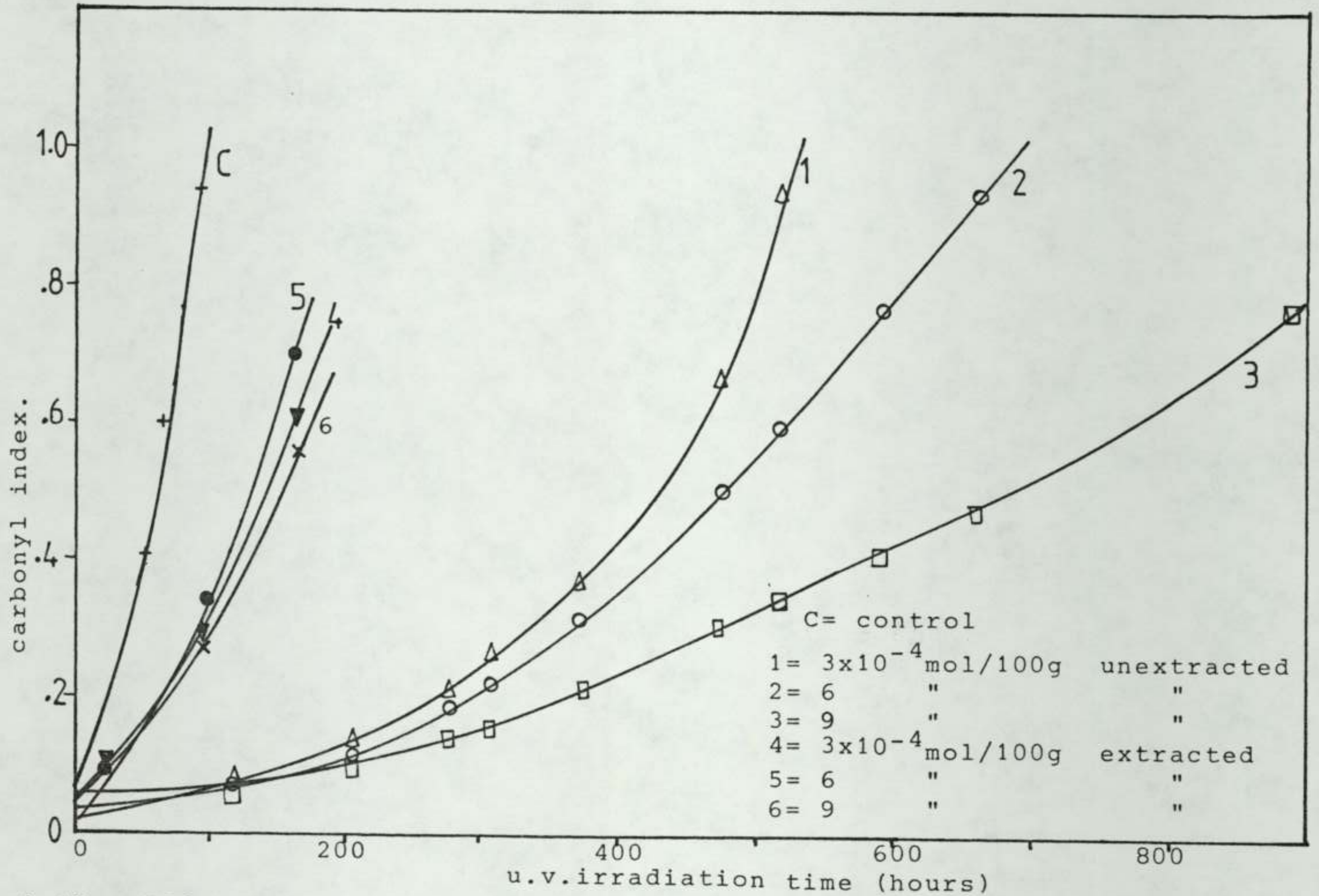


Fig 3.19: Effect of additive conc. and extraction on carbonyl formation in PP processed with 4OHTMPNO· in a closed mixer for 10 mins. at 180°C.

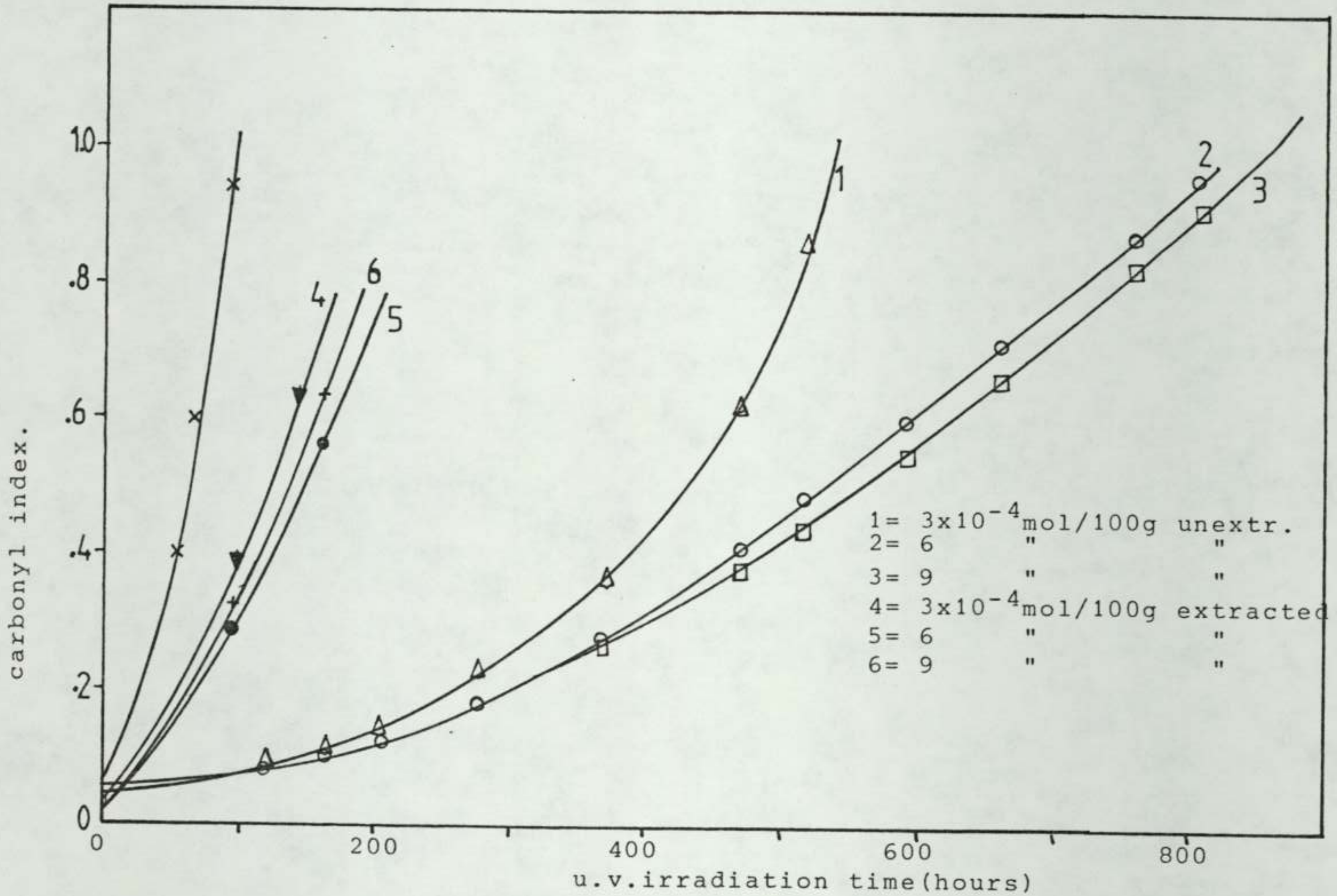


Fig. 3.20: Effect of additive conc.and extraction on carbonyl formation of PP processed with 4OHTMPNOH in a closed mixer for 10 mins. at 180°C.

Table 3.4 Effect of solvent extraction on u.v. embrittlement time of PP + NO. and NOH

Processing* condition	Concentration (x10^{-3}mol/100g)	u.v. embrittlement time (hours)	
		4OHTMPNO.	4OHTMPNOH
Closed Mixer	3	170	150
	6	170	170
	9	170	170
Open Mixer	3	150	150
	6	150	150
	9	170	170
Argon	3	↑	↑
	6	150	150
	9	↓	↓

* Procesing temperature = 180°C; processing time - 10 minutes.

samples however, the carbonyl formation was identical irrespective of concentration. The same is ture of samples processed in the open mixer with 4OHTMPNO. and 4OHTMPNOH (figs. 3.21 and 3.22 respectively) as well as those processed under argon as shown in Figs. 3.23 and 3.24 for 4OHTMPNO. and 4OHTMPNOH respectively.

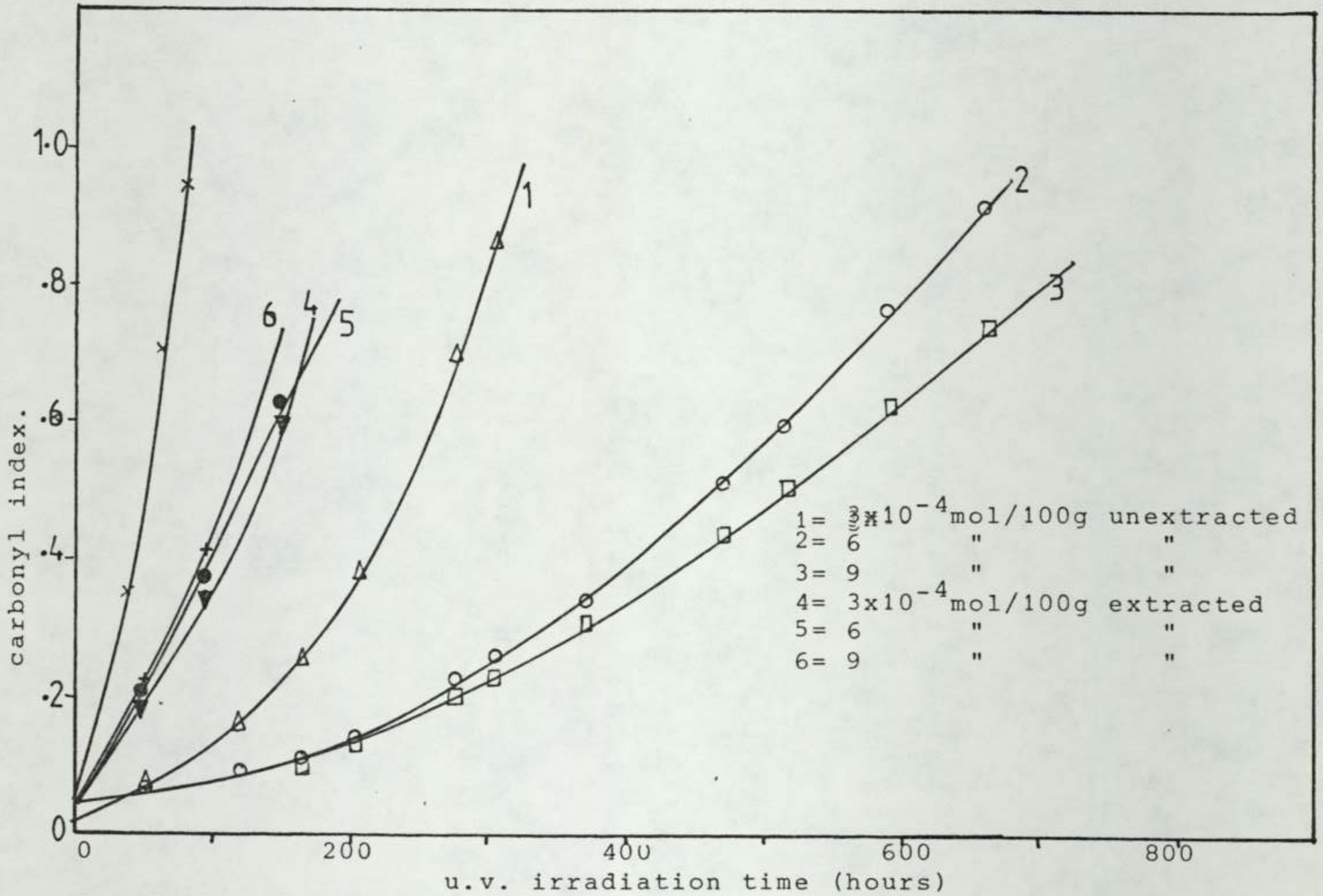


Fig. 3.21: Effect of additive conc. and extraction on carbonyl formation of PP processed with 4OHTMPNO· in an open mixer for 10 mins. at 180°C.

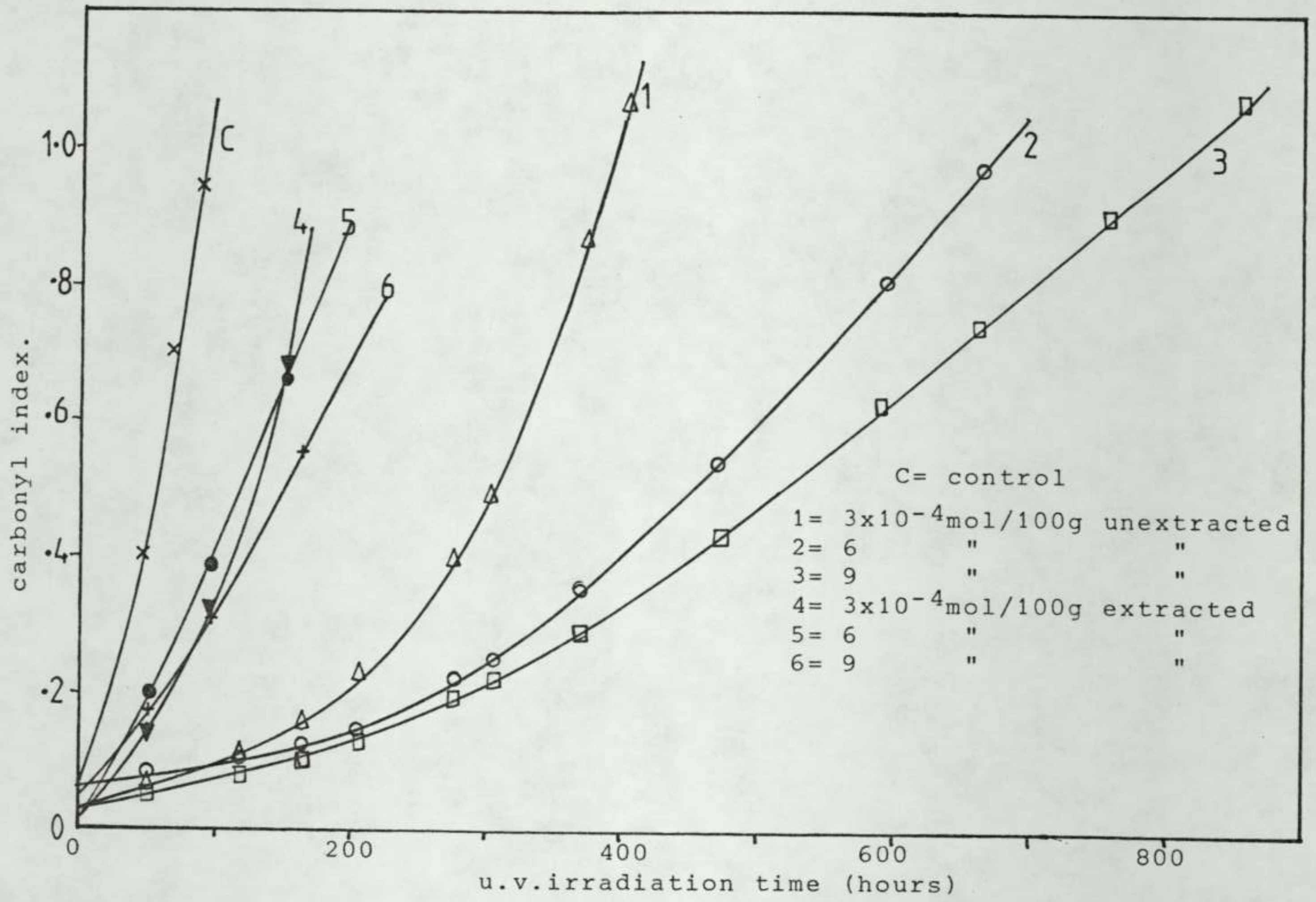


Fig. 3.22: Effect of additive conc. and extraction on carbonyl formation in PP processed with 4OHTMPNOH in an open mixer for 10 mins. at 180°C.

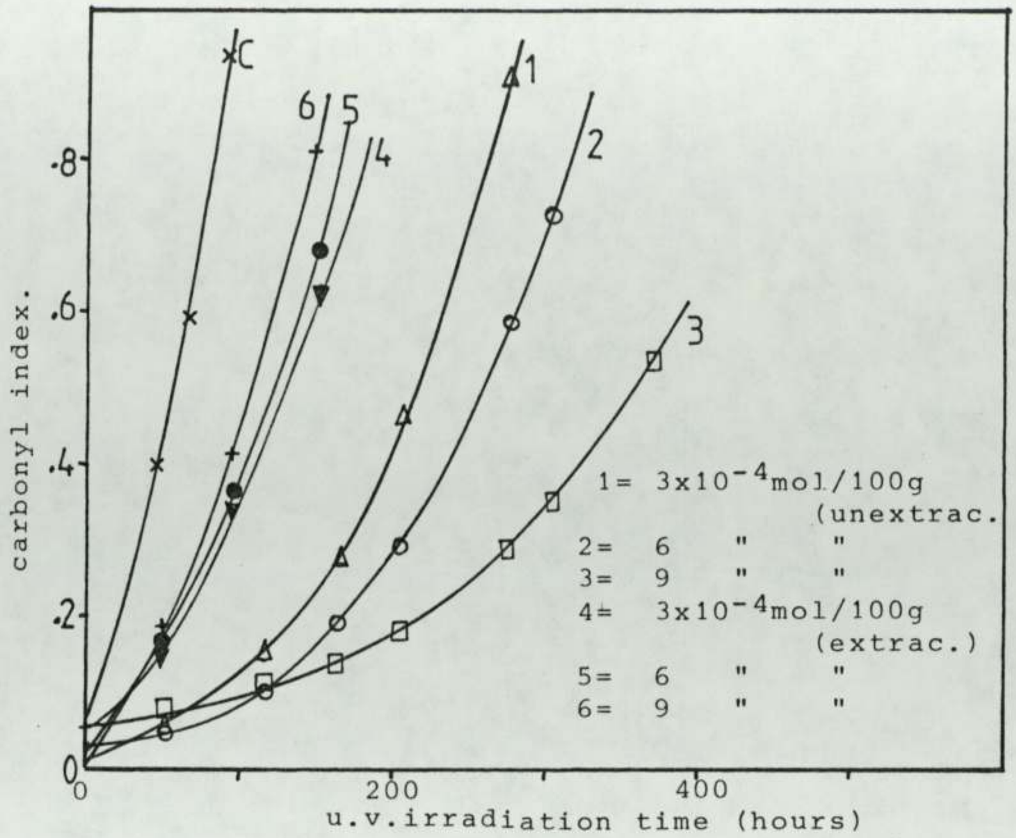


Fig. 3.23: Effect of additive conc. and extraction on carbonyl formation in PP processed with 4OHTMPNO· under argon for 10 mins. at 180°C.

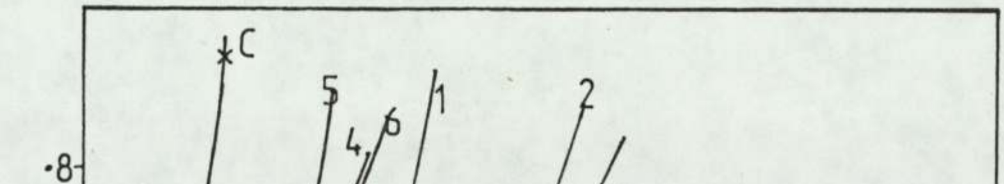


Fig. 3.24: Effect of additive conc. and extraction on carbonyl formation in PP processed with 4OHTMPNOH under argon for 10 mins. at 180°C.

3.3 DISCUSSION

The melt stability of PP by 4OHTMPNO. (processed in a closed mixer) as evidenced by the torque values, melt flow index and hydroperoxide formation with processing time (Figs. 3.1, 3.3 and 3.5 respectively) suggest that 4OHTMPNO. interferes with the chain propagation of PP during processing. Literature suggest(92,143) that nitroxyl radicals react with macro-alkyl radicals, thus deactivating the radicals before they could go into oxidative chain reactions but the mode of this reaction is still being investigated.

Electron spin resonance (e.s.r) examinations of PP films processed with 4OHTMPNO. in both closed and open mixers (fig. 3.25) show that there is a flunctuating concentration of nitroxyl radicals in the PP films with processing time in samples processed in the closed mixer while in the open-mixer-processed films, after the first 5 minutes, there is a gradual decrease in nitroxyl radical concentration until it depletes completely after 17.5 minutes and no more radical could be observed. Nitroxyl radical consumption and regeneration must be taking place, though the magnitude of the regeneration process decreases with increasing processing time. Reactions 1-4 may explain this regeneration process. However, the resultant alkyl hydroxylamines in reaction 1 are known to be thermally unstable(112,145) and may dissociate at temperatures as high as 180°C during the procesing operation.

Fig. 3.26 shows that during the processing operation, olefinic unsaturation forms progressively with increasing processing time in the closed mixer processed samples, indicating that reaction 3 was probably in operation and that the corresponding free hydroxylamine was being formed from the thermal mechano-chemical reaction of the nitroxyl radicals with the polymer radical. It has been suggests(109) that hydroxylamines are relatively labile compunds and rapidly decompose to give nitroxyl radicals during even the shortest practicable extraction step(146) hence could not be isolated or estimated. (Indeed, they have a half-life of 3 hours at 21°C in the presence of even traces of peroxides(146). However, during the initial stages of extraction of PP films containing 4OHTMPNO. (procesed in a closed mixer at 180°) a solution test on the extract as described previously (Chapter 2, Section 2.3.9) showed the presence of the free hydroxylamine(139). Upon complete extraction of these films (soxhlet extraction for 12 hours in dichloromethane) and upon oxidation of the extract with m-chloroperbenzoic acid to achieve complete conversion of the hydroxylamine to the corresponding nitroxyl radicals (see Chapter 2, Section 2.3.13), e.s.r. examinations of the oxidised extracts show that the total nitroxyl radical concentration stayed fairly constant with processing time (in the closed mixer-processed samples) as shown in Fig. 3.27. The hydroxylamine concentration was therefore estimated by the difference between total nitroxyl radical concentration (in the oxidised extract) and the nitroxyl radical concentration in the film, as shown in Fig. 3.28. It is very clear that variation of hydroxylamine concentration with processing time is a mirror image of the nitroxyl radical variation. This confirms the reversibility of the redox reaction of nitroxyl radicals and hydroxylamines. Furthermore when 0.5% of 4OHTMPNO. (w/w) in PP was processed in a closed mixer and the Fourier Transform infra-red (FTIR) spectrum of the unstabilised film was substracted from the spectrum of the stabilised film (both spectra were

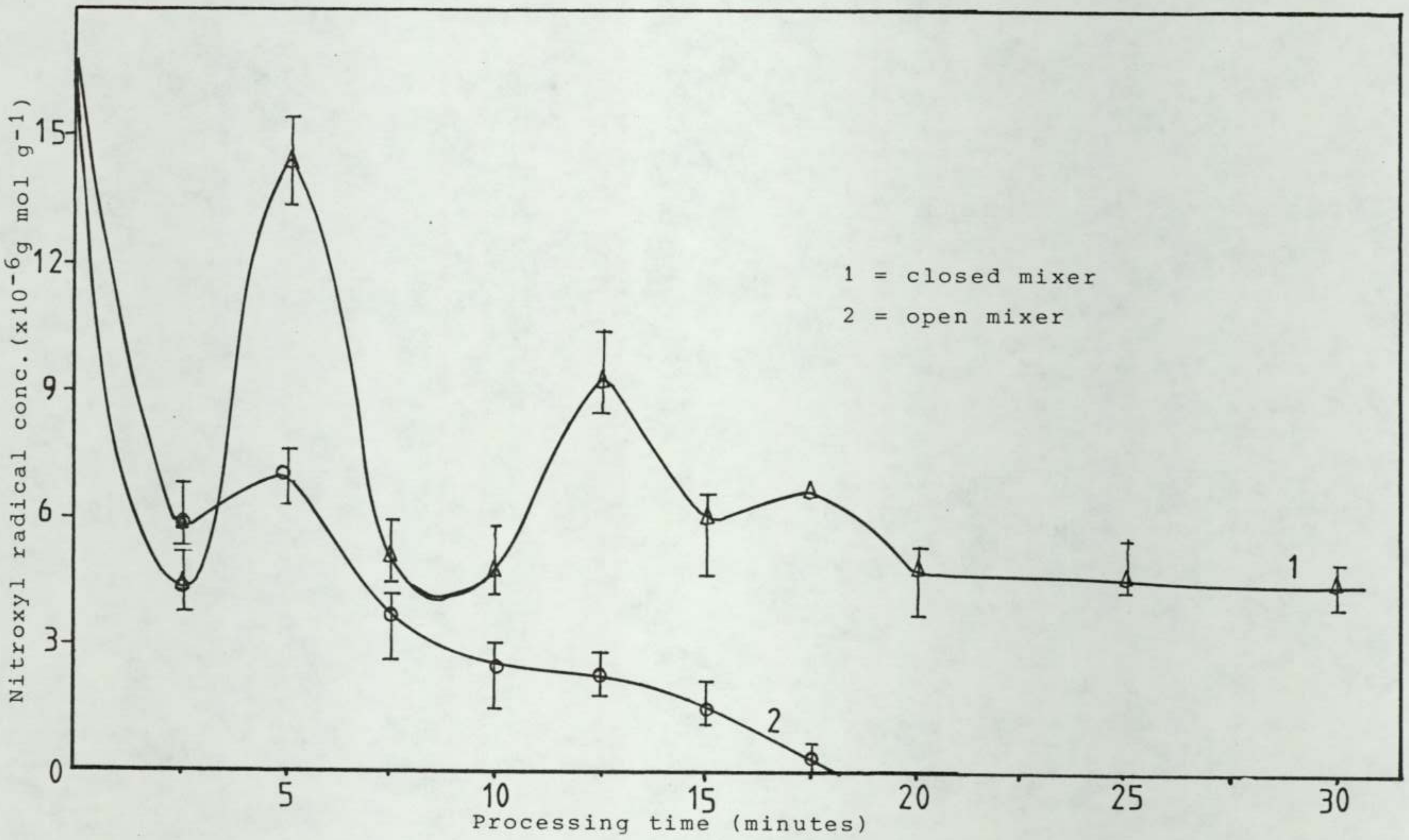


Fig. 3.25: Dependence of nitroxyl radical conc. on processing time of PP processed with 1.16×10^{-3} mol/100g of 4OHTMPNO· in (1)a closed mixer (2) open mixer at 180°C.

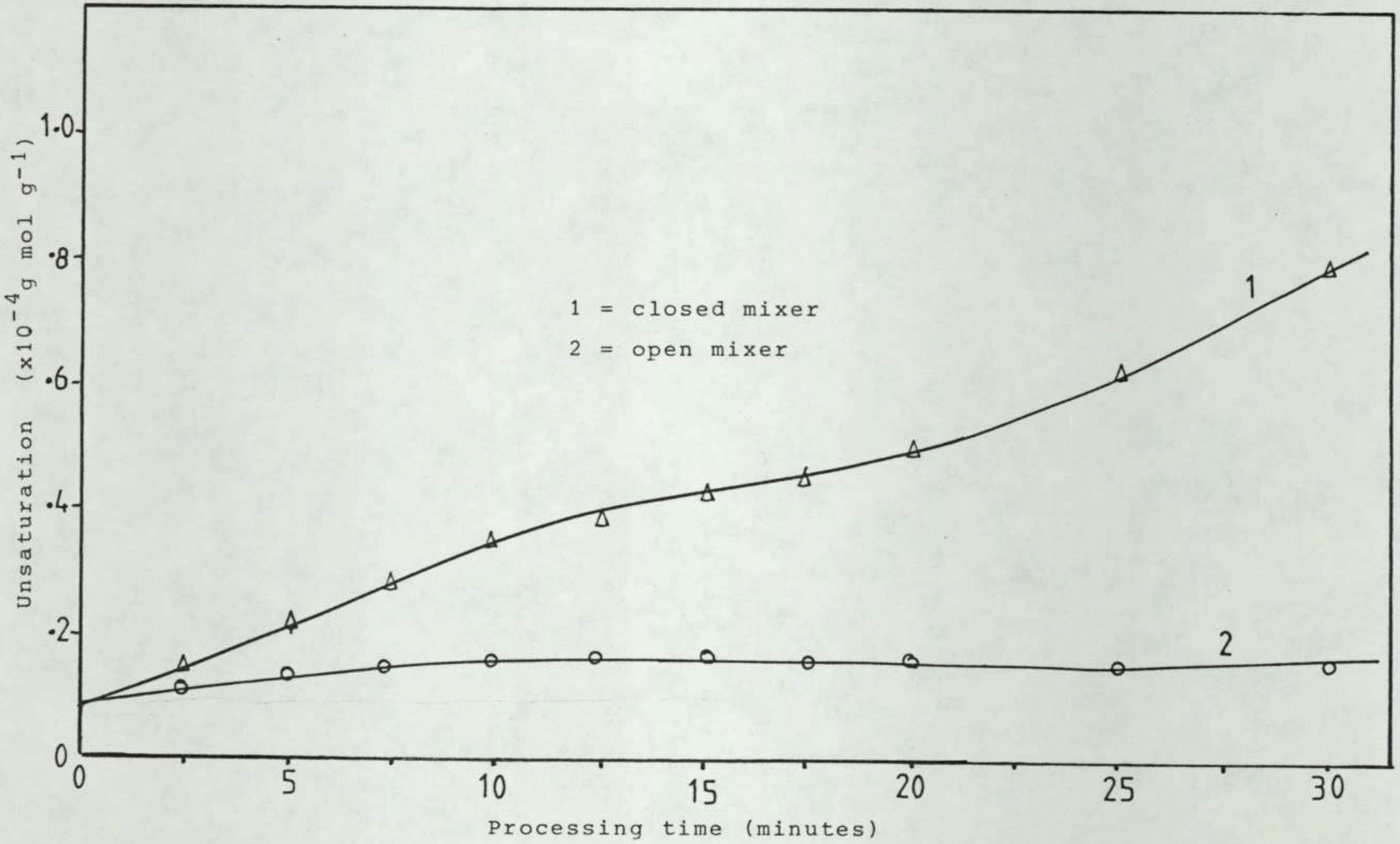


Fig. 3.26: Dependence of unsaturation on processing time of PP processed with 1.16x10^{-3} mol/100g of 4OHTMPNO· in (1)a closed mixer (2) open mixer at 180°C

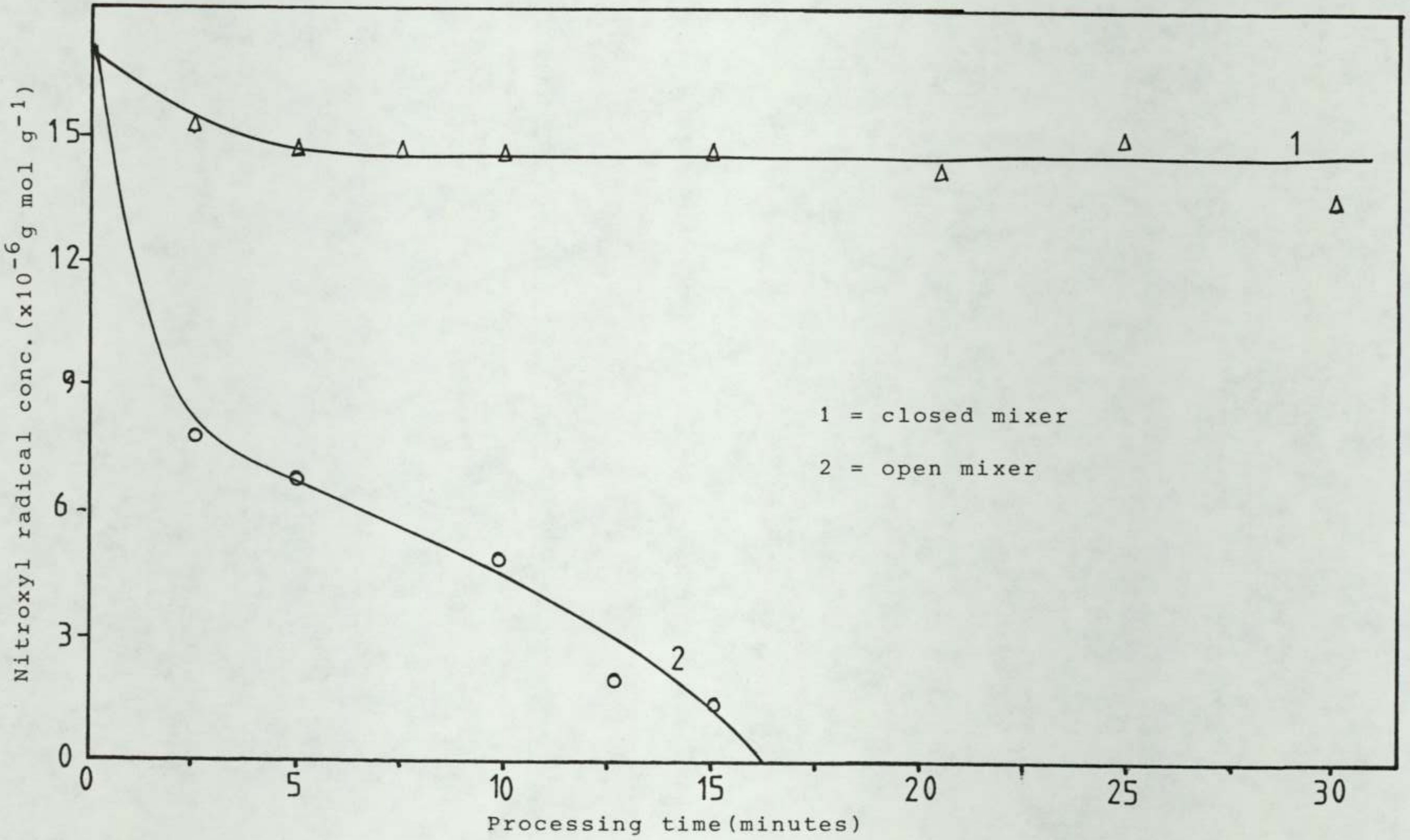


Fig 3.27: Effect of processing time on total nitroxyl radical conc.(upon extraction,oxidation) of PP processed with 4OHTMPNO· in (1) a closed mixer (2) open mixer at 180°C.

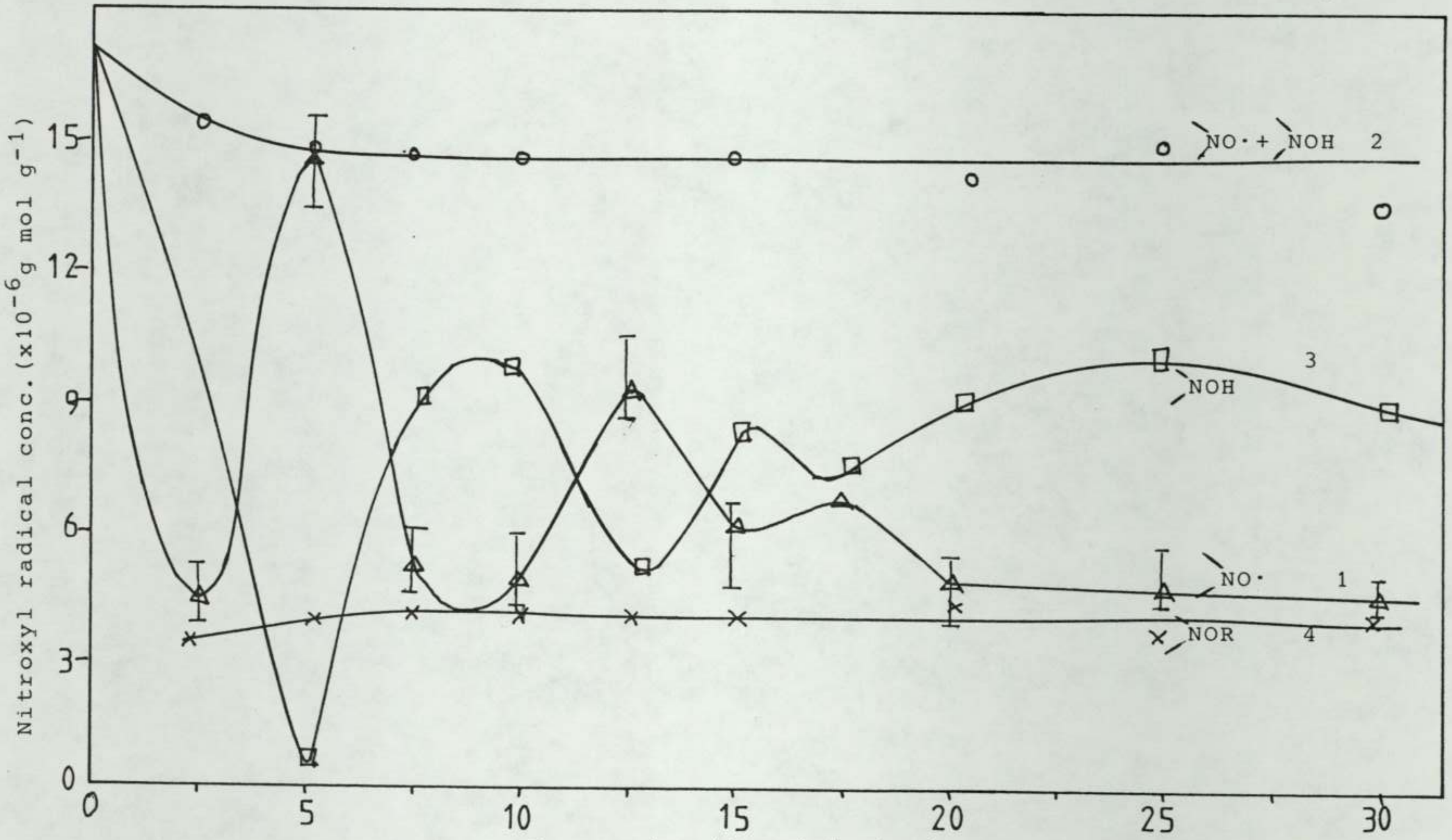


Fig. 3.28: Effect of processing time on (1) NO· conc. (2) total radical conc.-upon extraction and oxidation (3) NOH conc. (deduced) (4) NOR conc. (deduced) in PP processed with 1.16×10^{-3}mol/100g of 4OHTMPNO· in a closed mixer at 180°C.

recorded on a Perkin-Elmer FTIR 1500 spectrometer) an absorption at 3420 cm^{-1} was obtained (Fig. 3.29) corresponding to the hydroxylamine absorption(147).

The total nitroxyl radical concentration in the oxidised extracts (NO. and that due to NOH) is slighty less than the originally added concentration. The difference is shown in Fig. 3.28 (curve 4) and may be due to the formation of alkyl hydroxylamines and other unextractable products, though the contribution is a very small part of the total.

From these results, it could therefore be deduced that during thermal processing of PP with 4OHTMPNO., the predominant melt stabilisation reaction involves the formation of the corresponding hydroxylamine as evidenced by the corresponding increase in olefinic unsaturation and the general decreasing trend in nitroxyl radical concentration in the processed polymer film as shown in Fig. 3.30. Nitroxyl radical regeneration in the system must therefore involve free hydroxylamines as previously proposed(117). Additionally, in model (solution) systems, no evidence was found(145) for the reaction of alkylperoxyl (ROO.) radicals with alkylhydroxylamines to give nitroxyl radicals (N-O.) and ROOR.

In the open mixer however, as shown in Fig. 3.31 there is generally a decrease in total nitroxyl radical concentration (in the oxidised extract) with processing time suggesting that the nitroxyl radical was being consumed more rapidly in the presence of oxygen and regeneration of the nitroxyl radical is not favoured under this condition. Similarly, as in the closed mixer processed samples, the estimated concentration of hydroxylamine by difference is a mirror image of the nitroxyl radical concentration in the processed film.

Electron spin resonance (e.s.r) examination of PP films processed with 4OHTMPNOH in both closed and open mixers show that there is an alternating increase and decrease in nitroxyl radical concentration under both processing conditions but the trend is generally towards an increase in nitroxyl concentration in the closed mixer processed samples while it is decreasing in the open mixer samples, as shown in Fig. 3.32. The increasing trend in the closed mixer samples is accompanied by a gradual increase in hydroperoxide concentration in the PP samples (Fig. 3.5) which suggest that hydroxylamine was being converted to the nitroxyl radical in a process which involves the formation of hydroperoxides.

$$\rangle NOH \xrightarrow{ROO.} \rangle N - O\cdot + ROOH \qquad - (4)$$

In the open mixer samples however, it appears that the conversion of the hydroxylamine to nitroxyl radicals occurred within the first few minutes as the concentration of nitroxyl radical formed from the hydroxylamine in the open mixer is much higher than the closed mixer processed samples in the first 5 minutes, after which the concentration of the NO. in the closed mixer increases while in the open mixer decreases (fig. 3.32). Additionally hydroperoxide concentration (in open mixer samples) increased significantly before levelling off. (Fig. 3.6)

However, the generation of nitroxyl radicals (in the closed mixer samples) was not accompanied by a substantial formation of unsaturation (Fig. 3.33) as was the case in PP containing 4OHMPNO. suggesting that regeneration of hydroxylamine is not favoured under this condition.

The total nitroxyl radical concentration upon extraction and oxidation with m-chloroperbenzoic acid as in the case of PP containing 4OHTMPNO. is shown in Fig. 3.34 for PP containing 4OHTMPNOH processed in both open and closed mixers. The hydroxylamine concentration in the films was again estimated by the difference between the total nitroxyl radical concentrations (Fig. 3.34) and the nitroxyl radical concentration in the processed films before extractions. (Fig. 3.32). These are shown in Figs. 4.35 and 4.36 for closed mixer and open mixer samples respectively. The relative concentrations of nitroxyl radicals and hydroxylamines will depend on the relative concentrations of alkyl and alkylperoxyl radicals present in the system at any given time and this is affected by both the applied torque acting on the polymer and the oxygen concentration present in the mixing chamber at any given time. Thus, the nitroxyl radicals formed (in situ) probably enter into reactions (under this processing condition of restricted oxygen) which do not involve formation of hydroxylamines and/or olefinic unsaturation. It could therefore be deduced that during thermal processing of PP in a closed mixer with 4OHTMPNOH, the nitroxyl radical concentration at initial processing times is low Fig. (3.32 curve 1) but increases with increasing processing time and that at the initially low nitroxyl concentration reactions which exclude the formation of olefinic unsaturation are predominant (- probably alkyl radical scavenging). An indirect evidence to support the possible alkyl radical scavenging is shown in Fig. 3.37. A significant absorption in FTIR in PP processed with 0.5% (w/w) 4OHTMPNOH at 1100-1140 cm^{-1} corresponding to the N-O-C absorption(148) was observed.

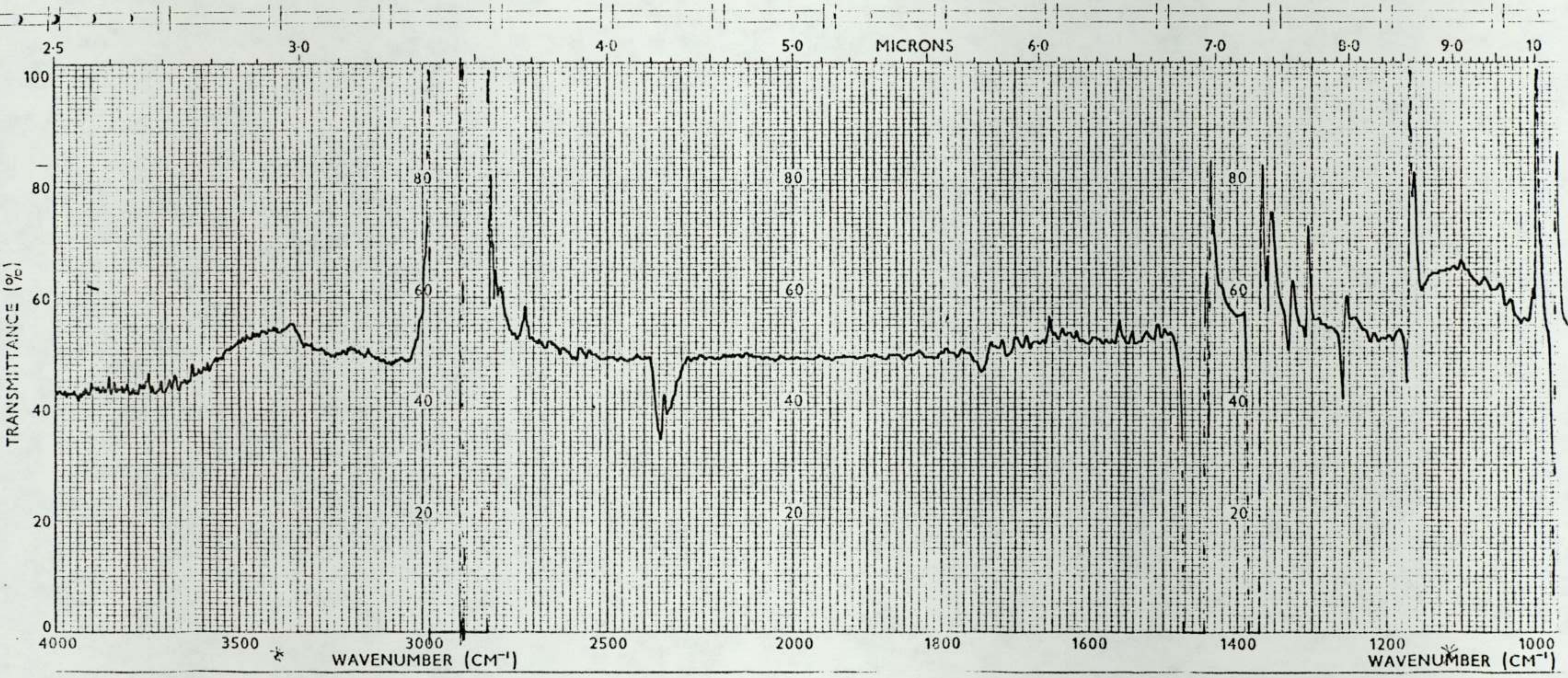


Fig. 3.29 : FTIR spectrum of PP processed with 0.5% (w/w) of 4OHTMPNO· in a closed mixer at 180^{O}C.

(after substraction of unstabilised PP spectrum.)

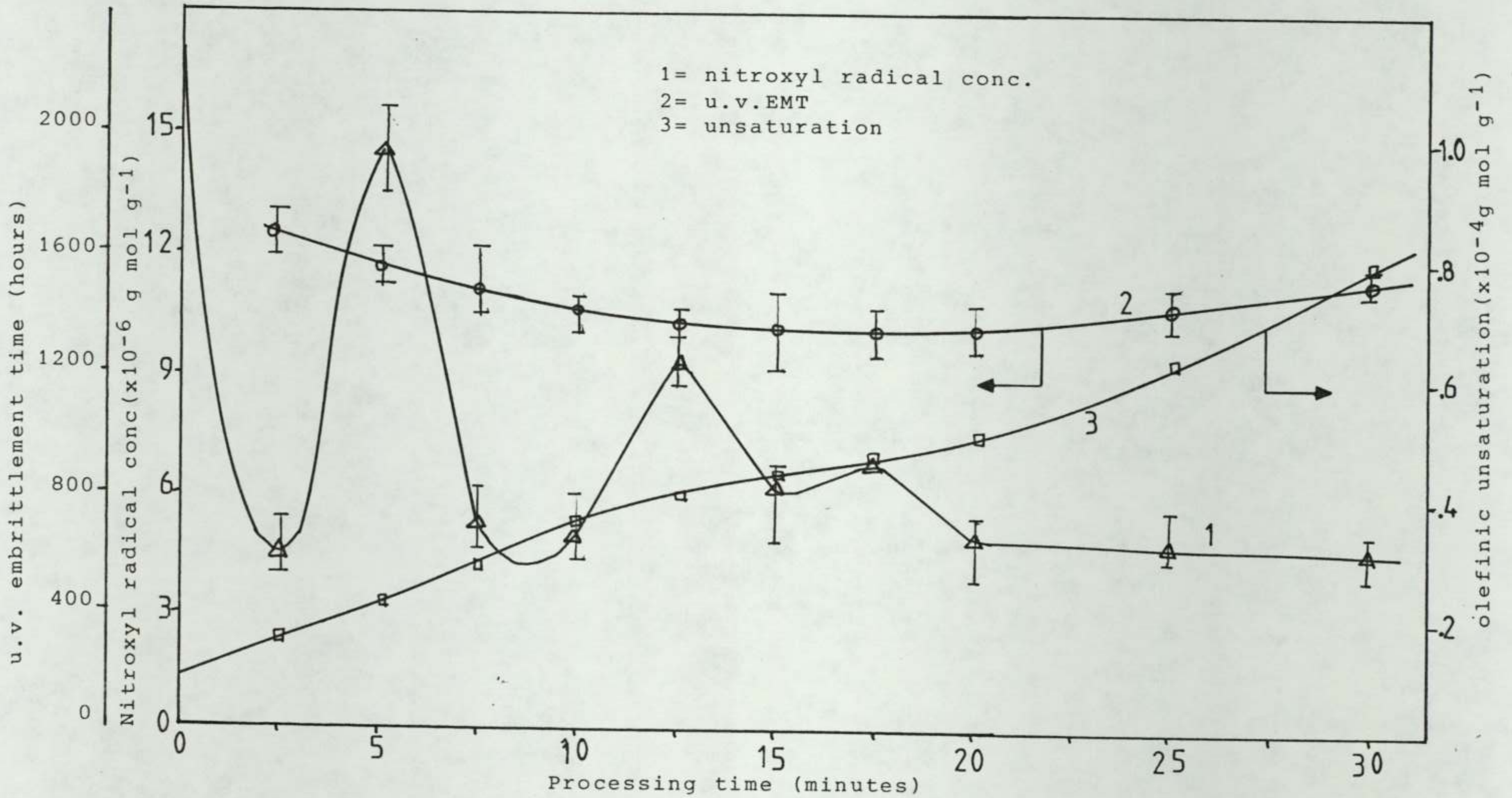


Fig. 3.30: Effect of processing time on (1) NO· conc. (2)u.v EMT (3) unsaturation in PP processed with 1.16×10^{-3}mol/100g of 4OHTMPNO· in a closed mixer at 180°C.

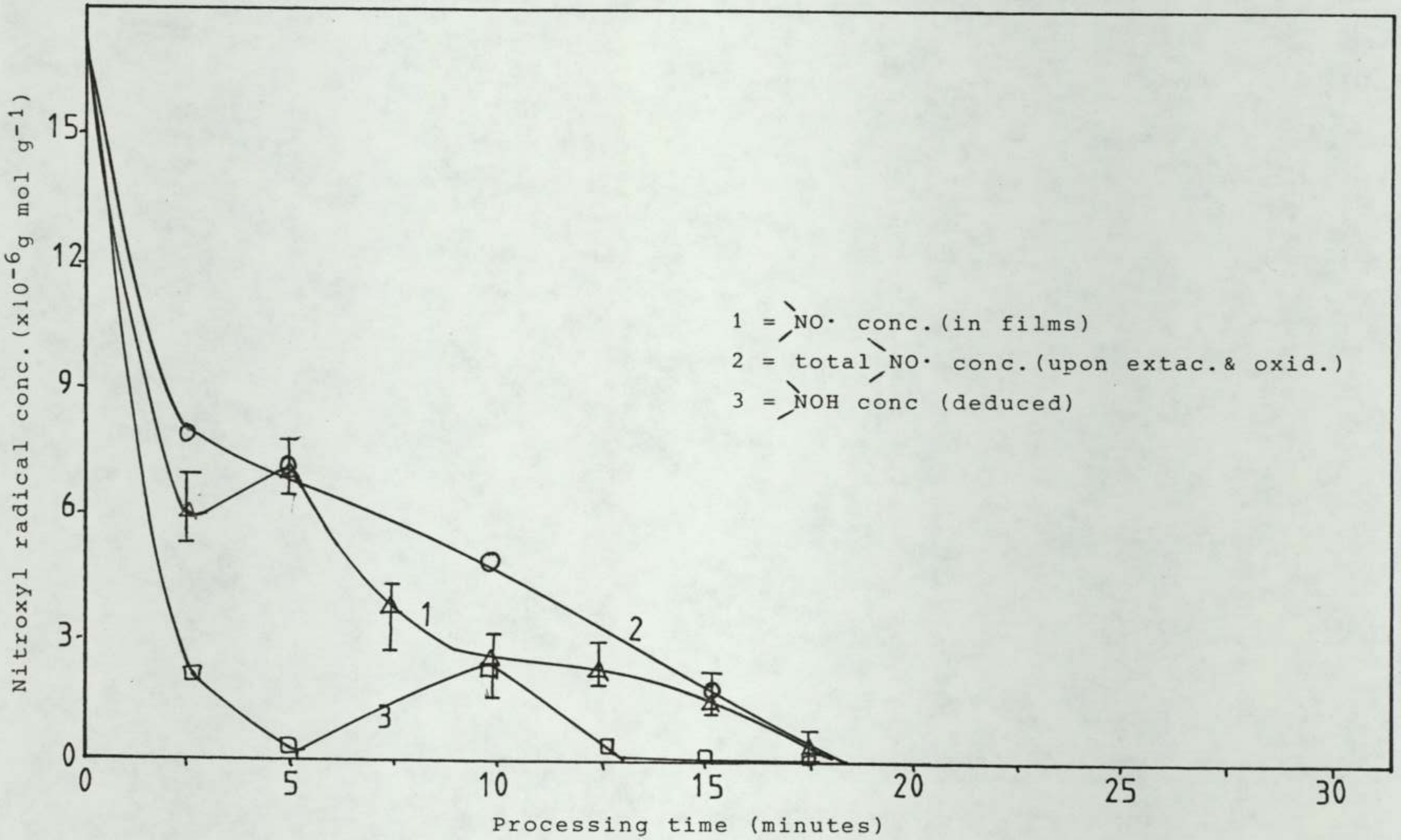


Fig 3.31: Effect of processing time on (1) NO· conc. (2) total NO conc.(3) NOH conc. in PP processed with 1.16x10^{-3}mol/100g of 4OHTMPNO· in an open mixer at 180°C.

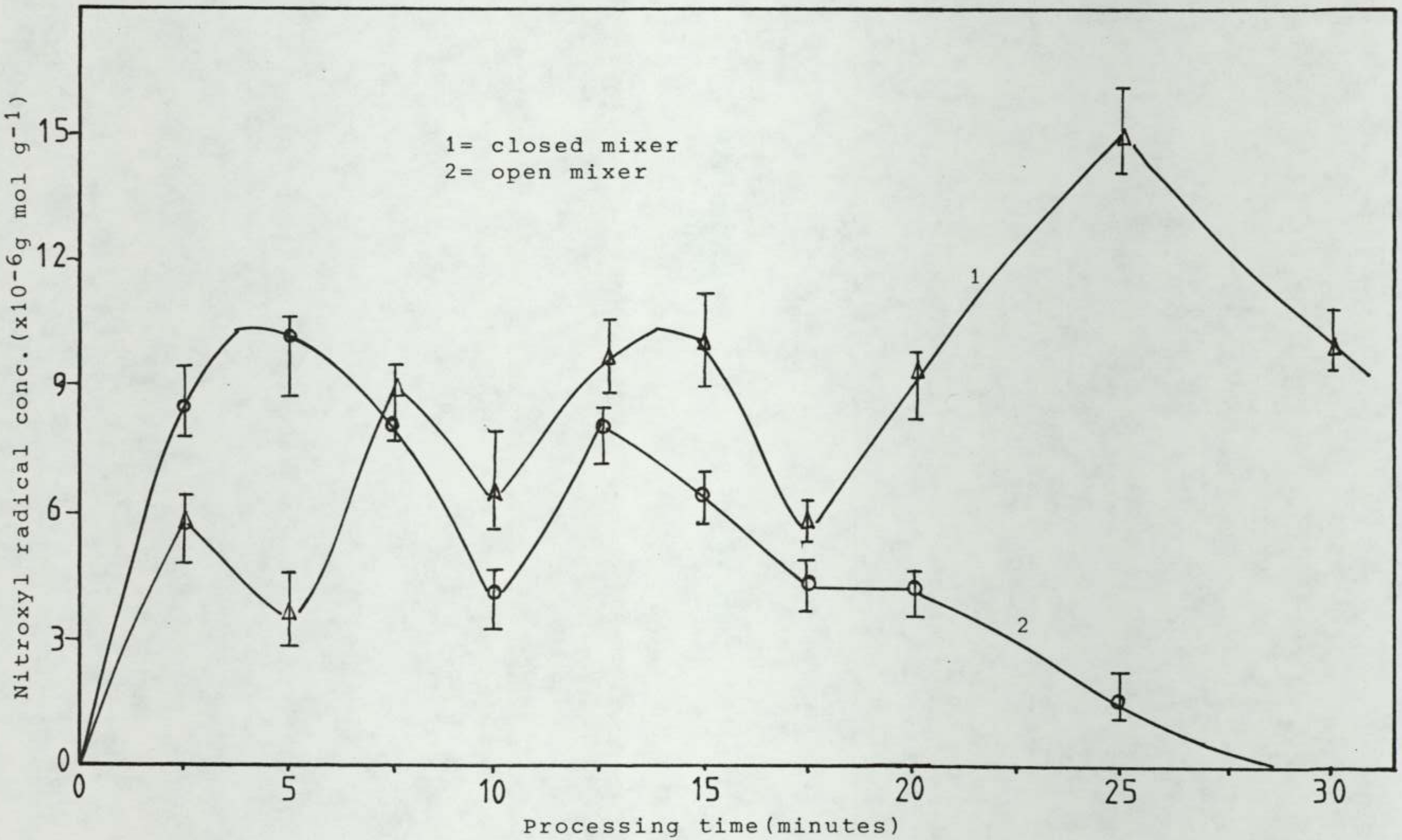


Fig 3.32: Dependence of (derived) nitroxyl radical conc. on processing time of PP processed with 1.16x10^{-3}mol/100g of 4OHTMPNOH in (1) a closed mixer (2) open mixer at 180°C.

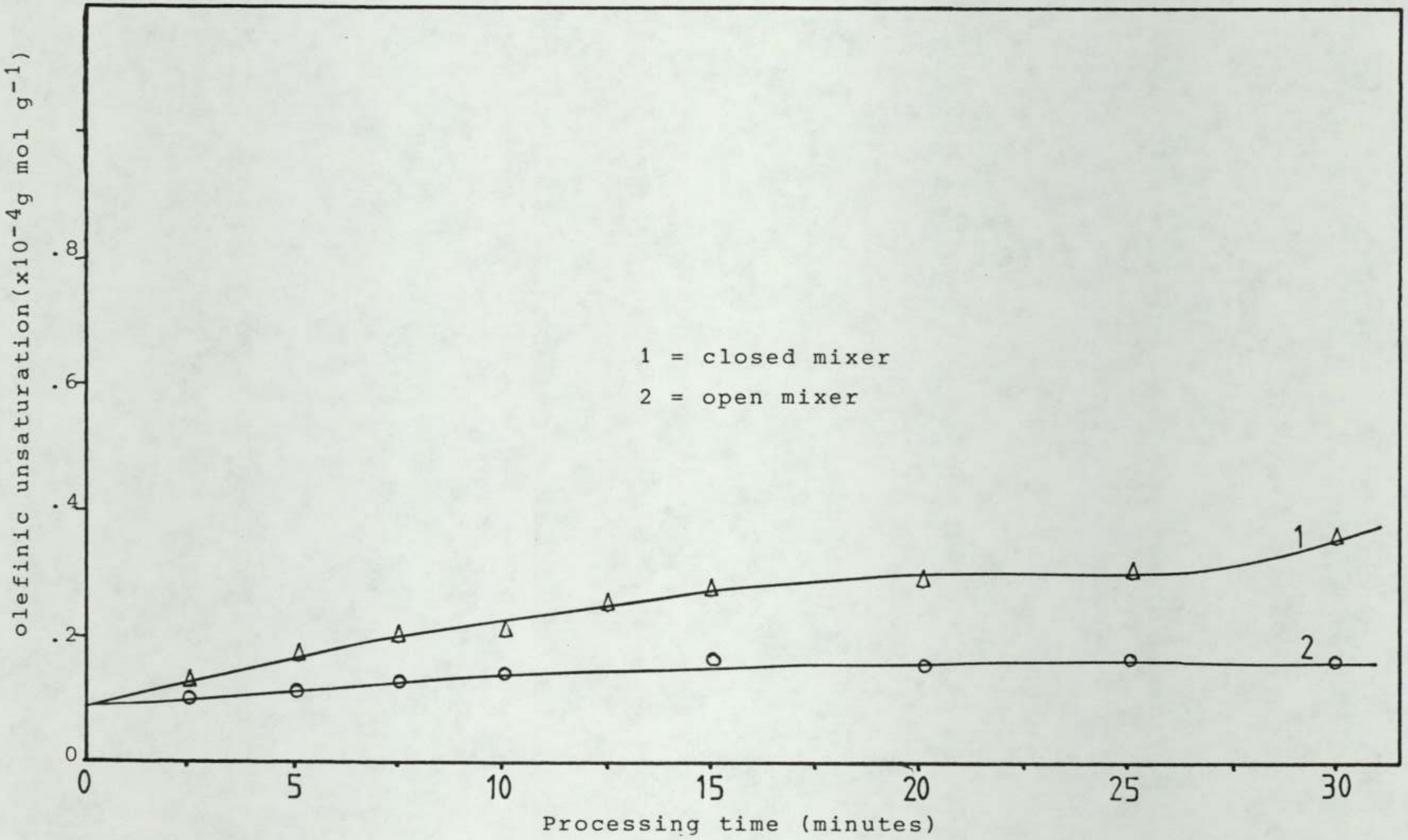


Fig 3.33: Dependence of unsaturation on processing time of PP processed with 1.16x10^{-3}mol/100g of 4OHTMPNOH in (1) closed mixer (2) open mixer at 180°C.

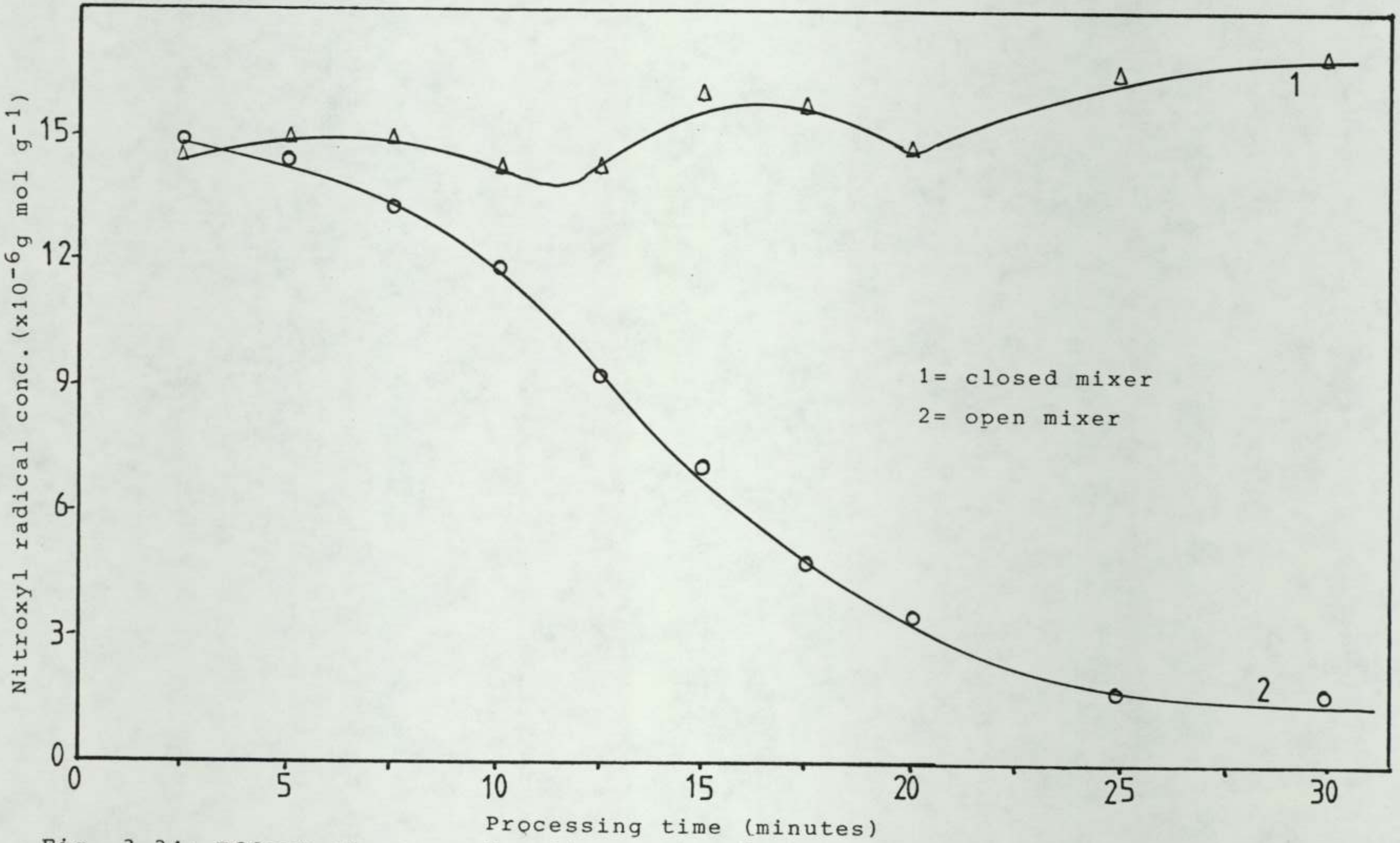


Fig. 3.34: Effect of processing time on total nitroxyl radical conc. (upon extr. & oxid.) of PP processed with 4OHTMPNOH in (1) a closed mixer (2) an open mixer at 180°C.

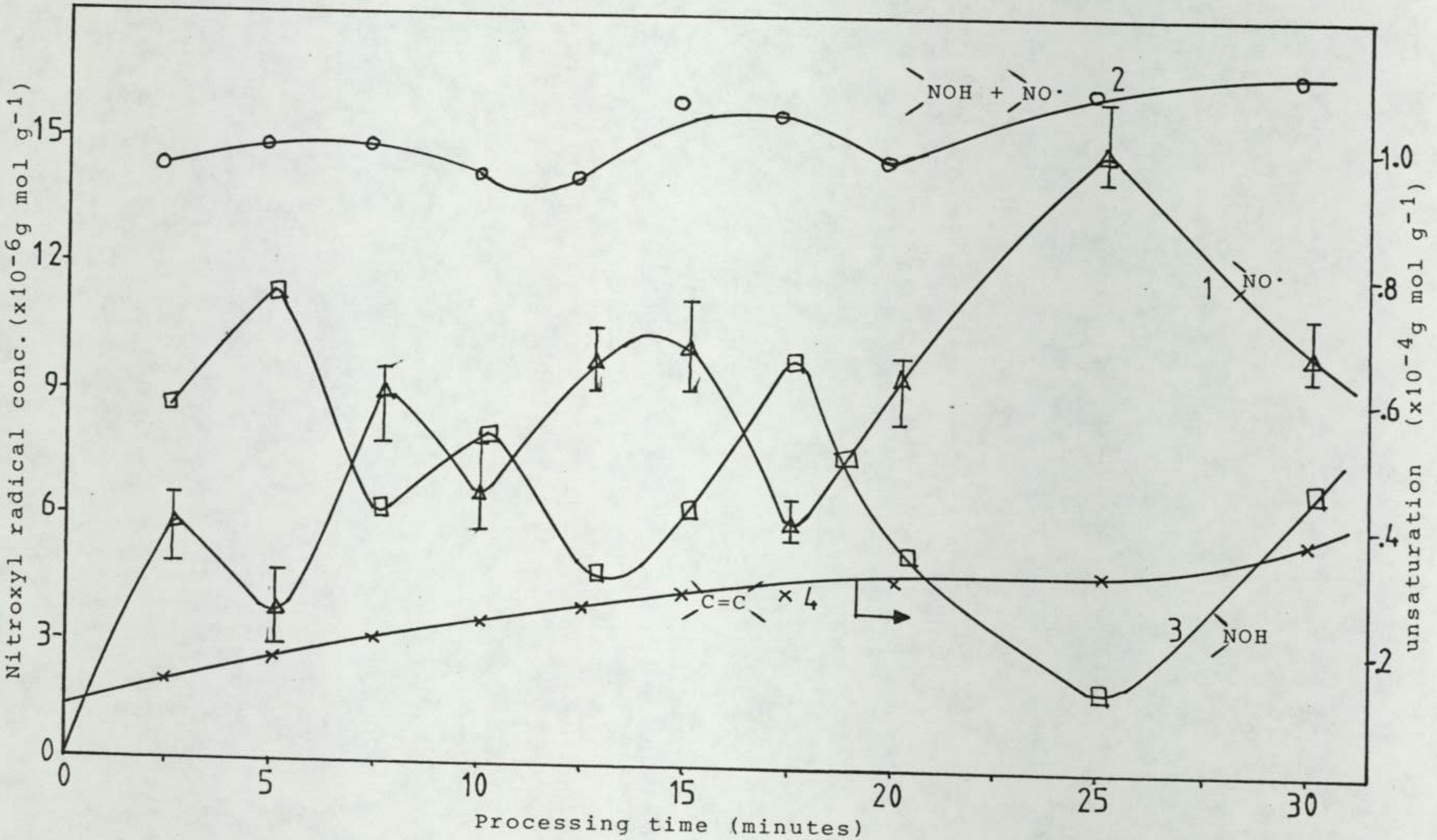


Fig. 3.35: Effect of processing time on (1) NO· conc. (2) total(NO· + NOH) radical conc. (3) NOH conc. (4) olefinic unsaturation conc. in PP processed with 1.16x10^{-3}mol/100g of 4OHTMPNOH in a closed mixer at 180^{o}C.

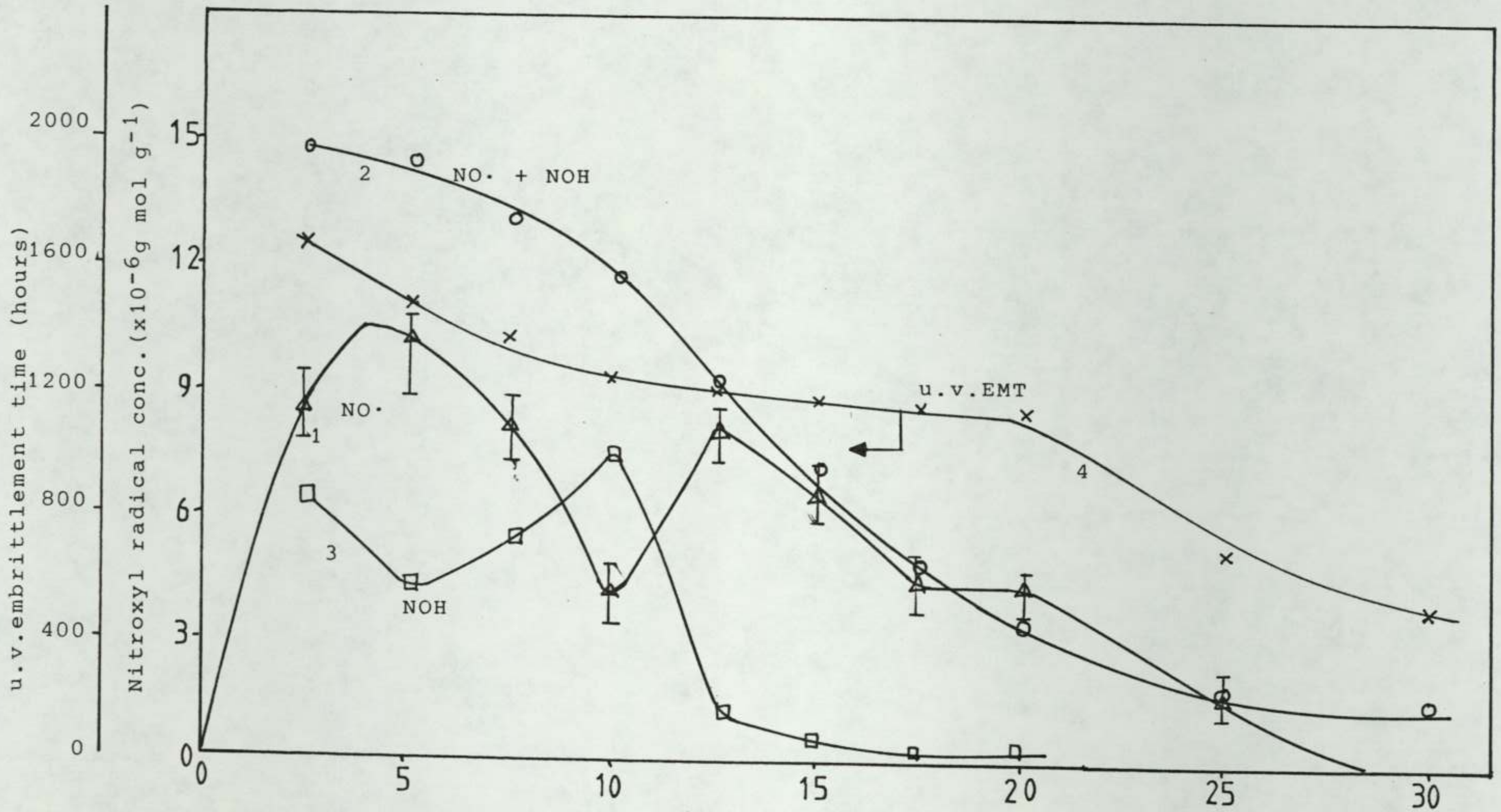


Fig. 3.36: Effect of processing time on (1) NO· conc.(2) total(NO· + NOH) conc.(3) NOH (4) u.v.EMT of PP processed with 1.16×10^{-3}mol/100g of 4OHTMPNOH in an open mixer at 180°C.

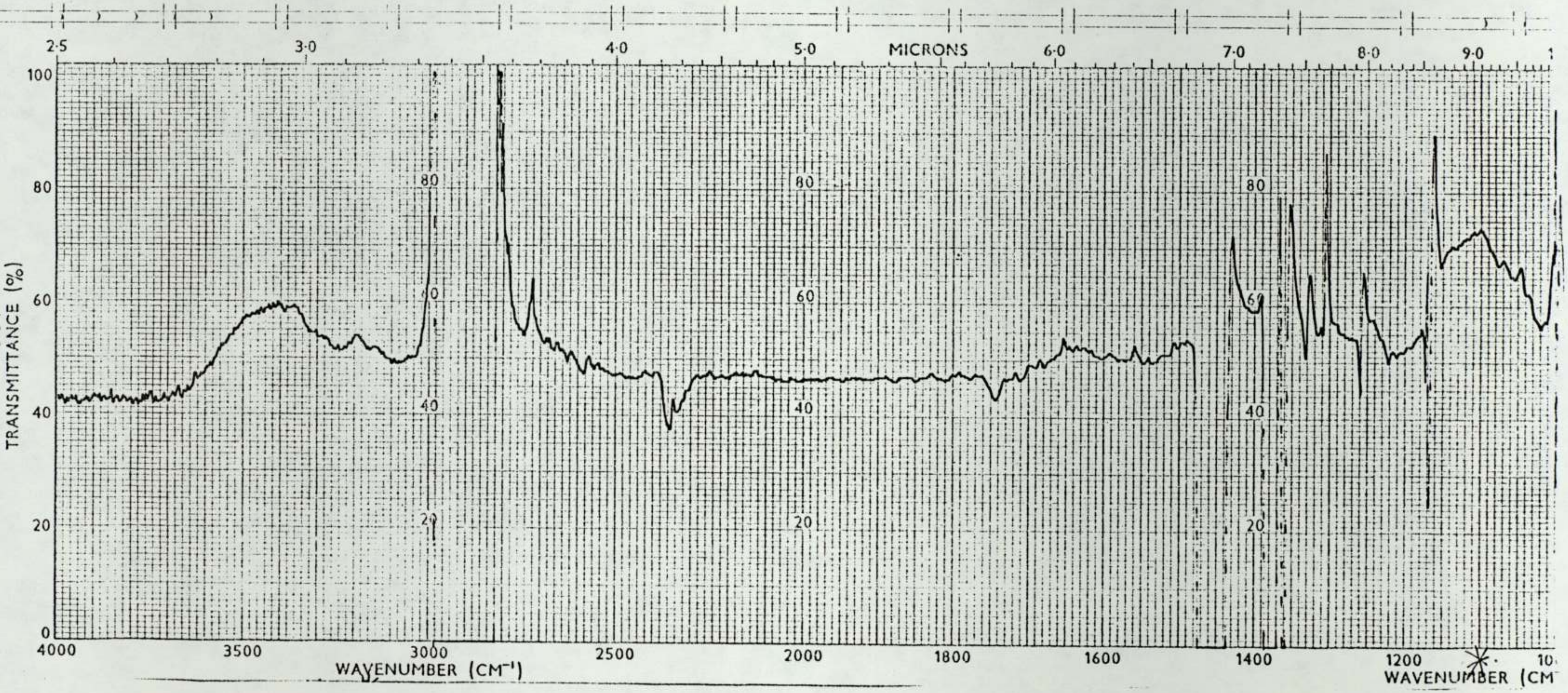


Fig. 3.37 : FTIR spectrum of PP processed with 0.5% (w/w) of 4OHTMPNOH in a closed mixer for 10 minutes at 180°C. (after substraction of unstabilised PP spectrum.)

Figs. 3.38 and 3.39 compares the nitroxyl radical concentrations and the subsequent u.v. embrittlement times of films containing 1.16 x 10^{-3}mol/100g 4OHTMPNO. and 4OHTMPNOH processed in the closed and open mixers. In the closed mixer, nitroxyl radical was being formed from 4OHTMPNOH increasingly with processing time while the trend in the case of 4OHTMPNO·was a decrease in nitroxyl radical concentration with processing time (Fig. 3.38). The magnitude of this difference however is not manifest in the u.v. embrittlement times of the samples. In the open mixer samples, both 4OHTMPNO. and 4OHTMPNOH show the same general trend of a decrease in nitroxyl radical concentration with processing time (Fig. 3.39) with 4OHTMPNOH having higher concentrations of nitroxyl radicals than 4OHTMPNO. The magnitude of differences in concentration of nitroxyl radicals is again not shown in embrittlement times though the tread of a decrease with processing time is observed.

Fif. 3.40a shows a typical e.s.r. spectrum of nitroxyl radicals in PP. By broadening the reasonance, the features of a triplet was obtained (Fig. 3.40b) with a splitting factor (aN) of 15.7G which is not inconsistent with a nitroxyl radical,(65) while Fig. 3.40c shows a typical spectrum of the nitroxyl radical in solution (dichloromethane) upon extraction and oxidation.

During the subsequent photo-oxidation of films containing 4OHTMPNO. it is generally accepted that photostabilisation mechanism is almost certainly due to the "trapping" or deactivation of macro-alkyl radicals formed under the effect of u.v. light. It is also accepted that the trapping theory cannot explain the effectiveness of nitroxyl radicals as photostabilisers, and as is the case in melt stabilisation, two

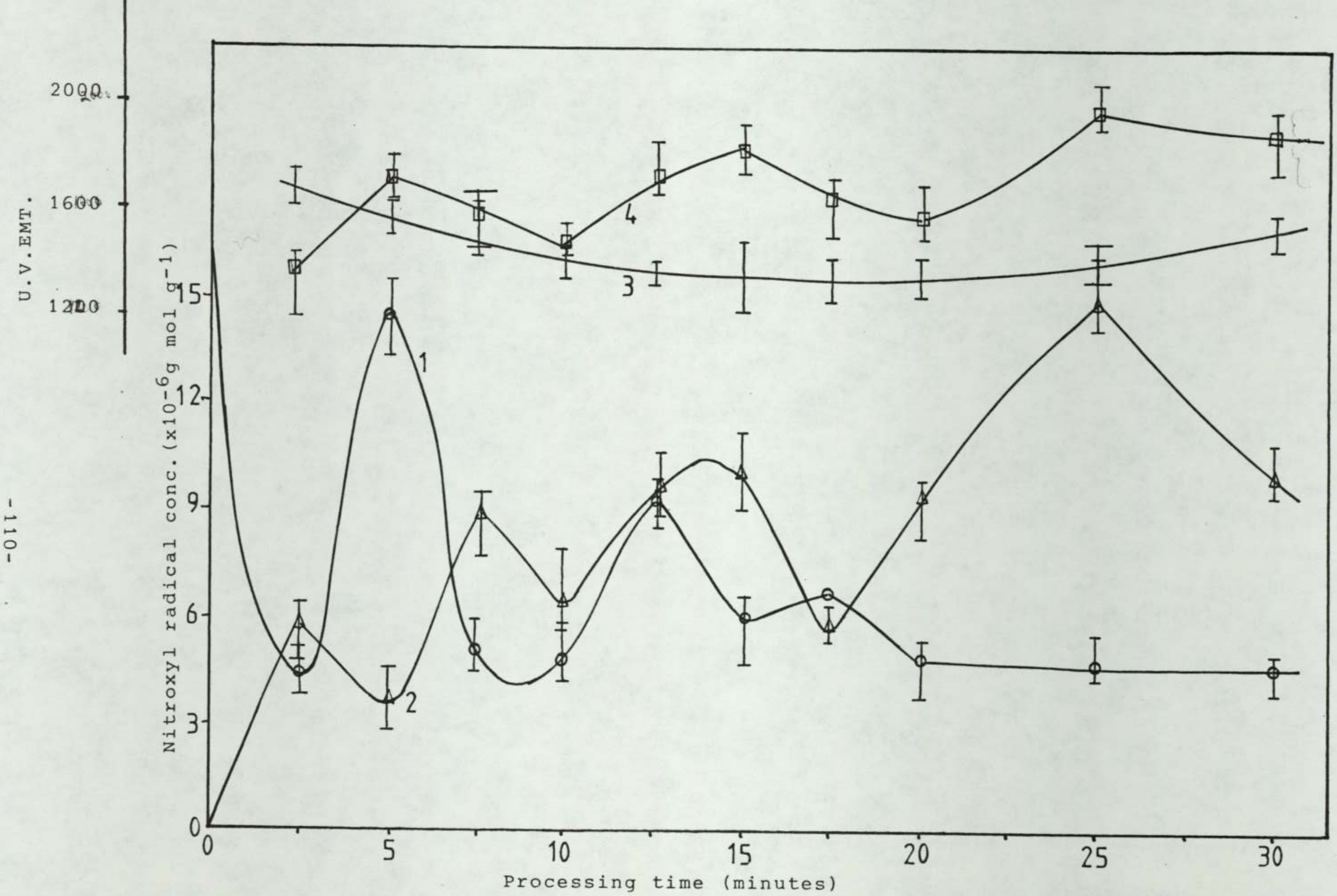


Fig. 3.38: Effect of processing time on NO· conc. in PP processed with (1) 4OHTMPNO· (2) 4OHTMPNOH (conc.= 1.16x10^{-3}mol/100g) and their u.v. EMT (3) 4OHTMPNO· (4) 4OHTMPNOH. All samples processed in a closed mixer at 180°C.

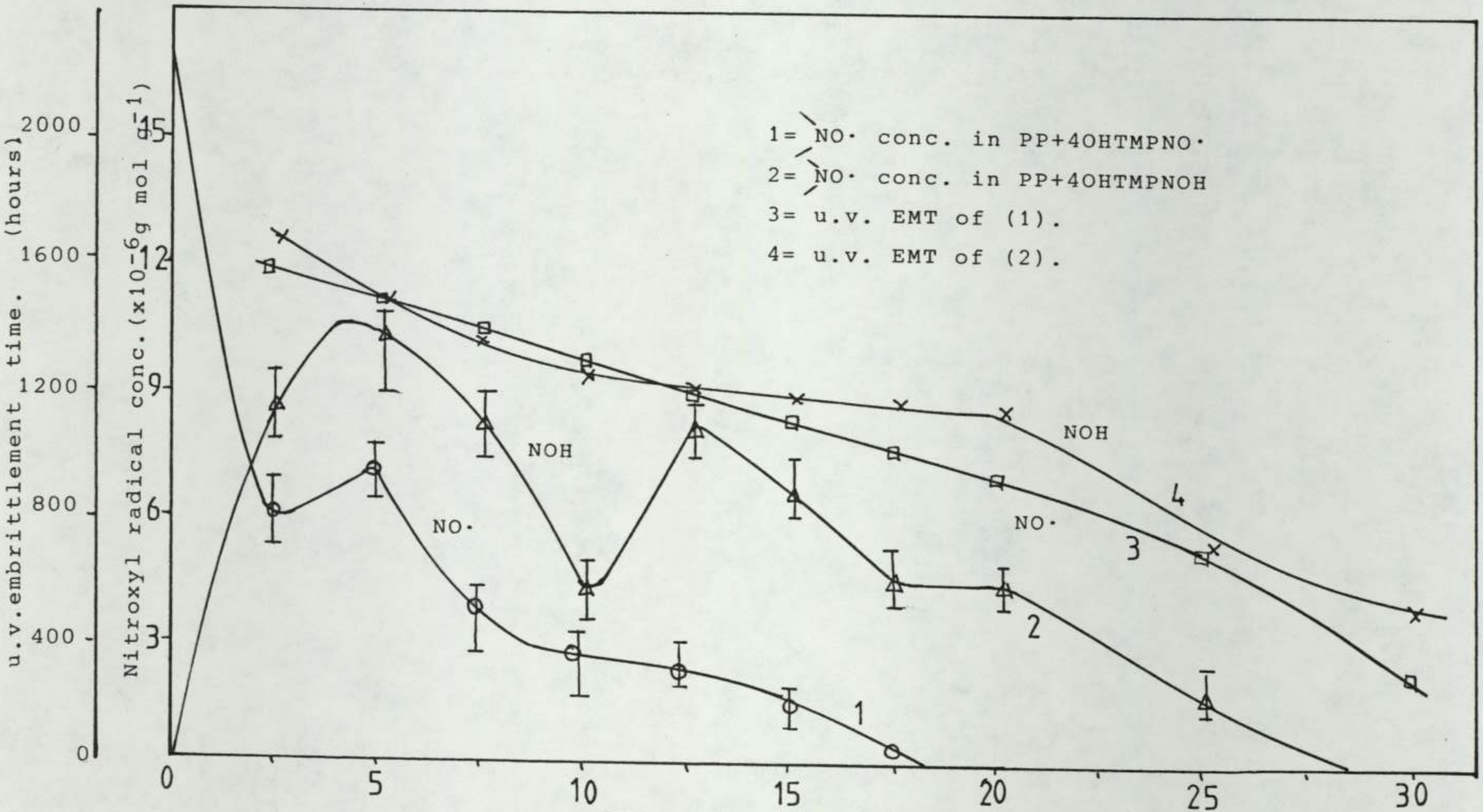


Fig. 3.39: Effect of processing time on radical conc, and u.v.EMT of PP processed with 4OHTMPNO· and 4OHTMPNOH .(conc.= 1.16x10^{-3} mol/100g)

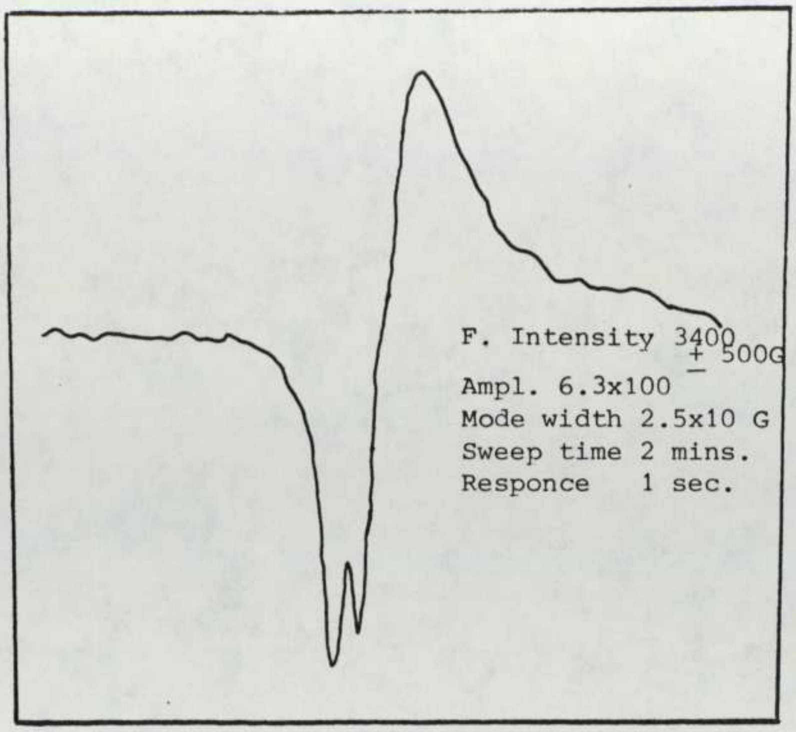


Fig 3.40(a): A typical e.s.r. spectrum of nitroxyl radical in PP (conc. = $6x10^{-4}$mol/100g.)

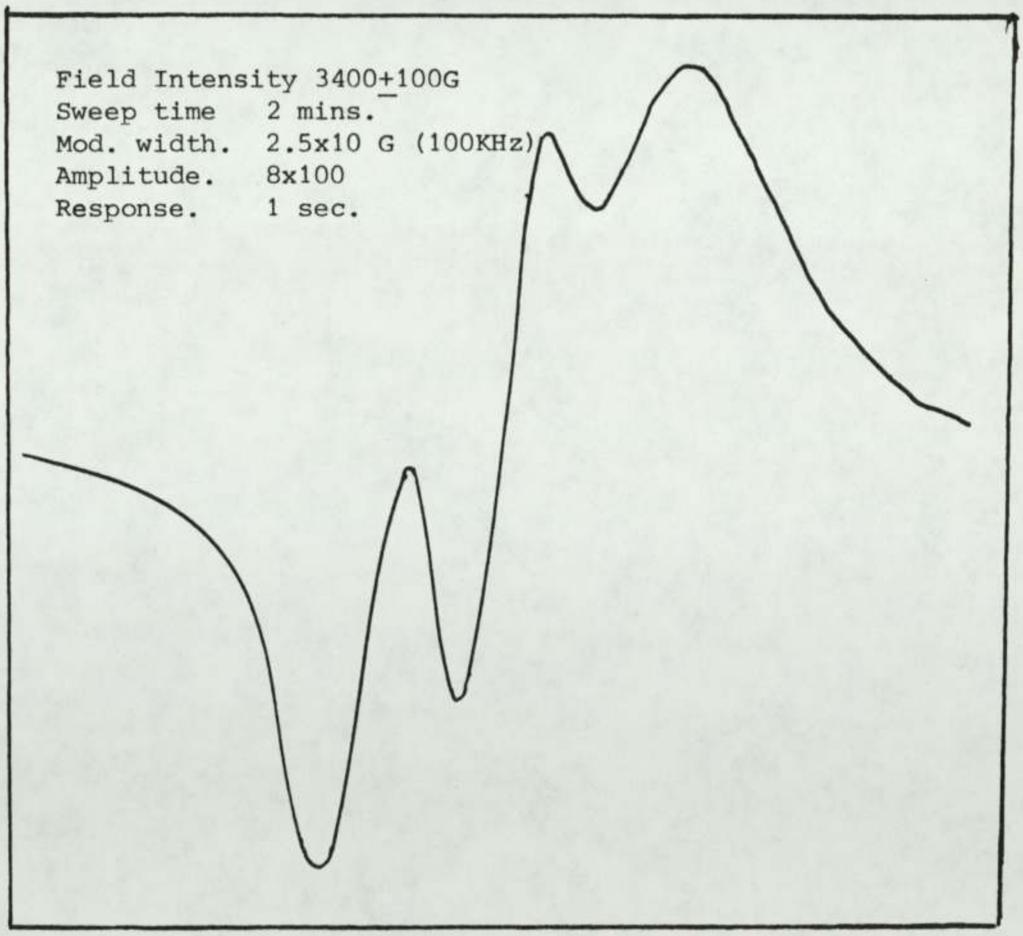


Fig. 3.40(b) :Broadened resonance of nitroxyl radical in PP (conc. $6x10^{-4}$mol/100g) a_N= 15.7G

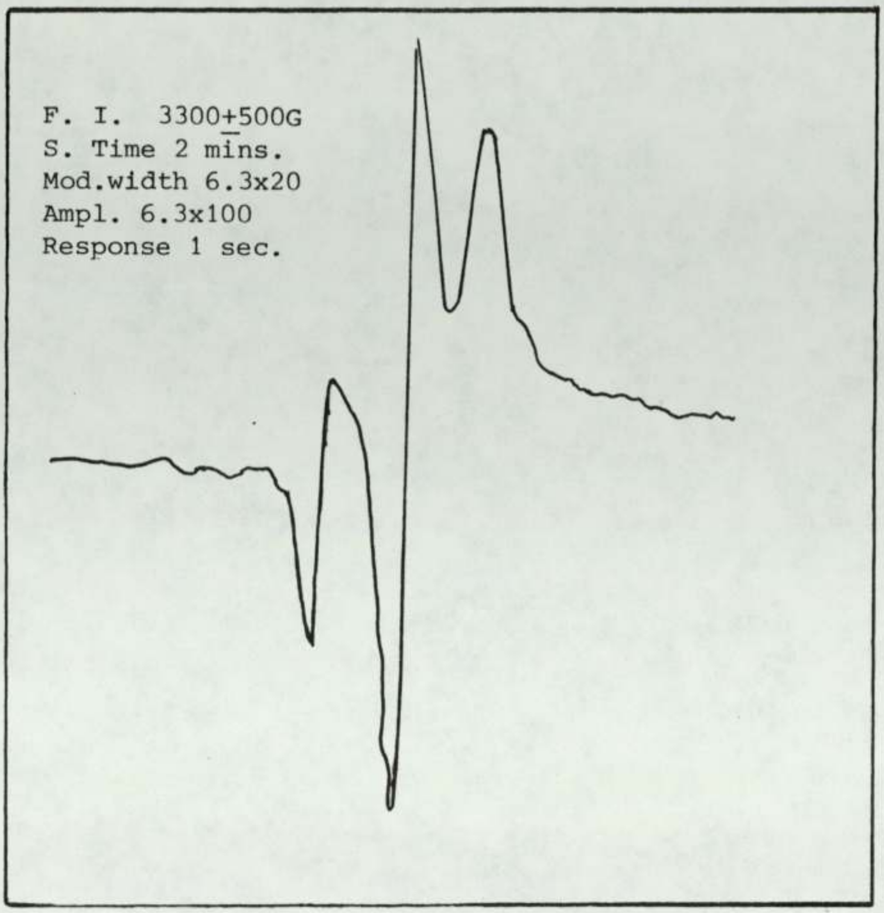


Fig. 3.40(c): A typical spectrum of nitroxyl in dichloromethane upon extraction (and oxidation)

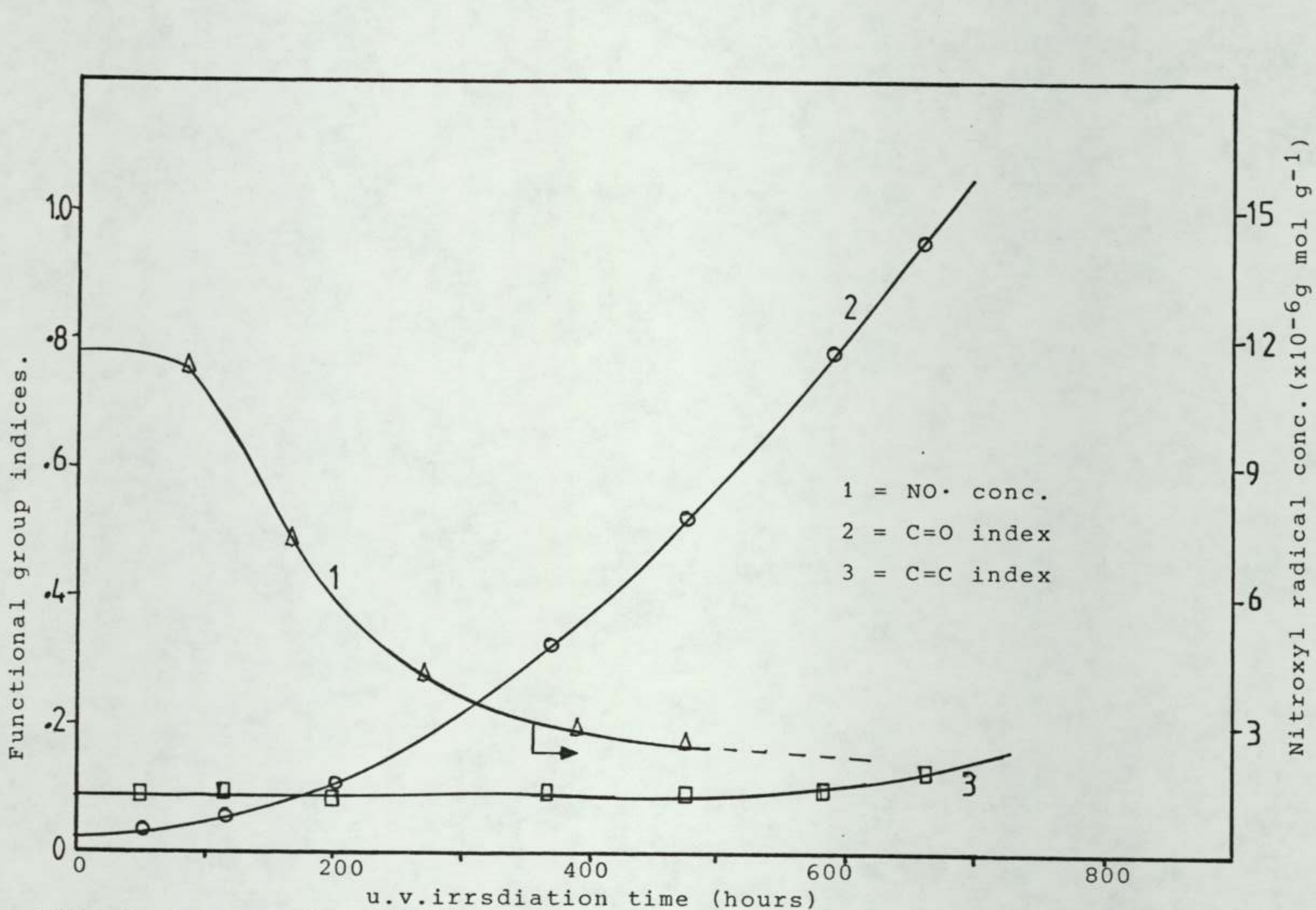
mechanism have been proposed to account for nitroxyl radical regeneration (see reactions 1, 2 and 3).

Although the mechanism of free hydroxylamine and olefinic unsaturation formation(39) from the reaction of nitroxyl radical and alkyl radical could be deduced to be in operation during the thermal processing in the closed mixer, no evidence in this work suggests that this is the case under photo oxidative conditions. Figs. 3.41 and 3.42 show the dependence of unsaturation index in infra-red (1645 cm^{-1}) with irradiation time for PP containing 4OHTMPNO. and 4OHTMPNOH respectively. (concentration = 6×10^{-4} m/100g). The unsaturation indices remained almost constant throughout the photo-irradiation time. Thus it seems the regeneration of nitroxyl radicals would be by a reaction not involving olefinic unsaturation, and that the stabilisation mechanism will be by alkyl radical seavenging and therefore will depend on the nitroxyl radical concentration in the system at anytime. Although Dagonneau and his co-workers(140) suggest that the alkyl hydroxylamines formed from alkyl radical scavenging by nitroxyl radicals can break reversibly and that the newly formed radicals disproportionate to give olefin and hyroxylamine as in reactions (5) and (6) no evidence was provided to support this assertion and none, was found in this work.

$$\rangle NO^{\bullet} + R^{\bullet} \rightleftharpoons \rangle NOR \qquad -(5)$$

$$\rangle NO^{\bullet} + R^{\bullet} \longrightarrow \rangle N - OH + \rangle C = C\langle \qquad -(6)$$

Thus it would seem that the regeneration mechanism during photo oxidation involves mainly the reaction of alkylperoxyl radicals with alkyl hydroxylamines (reaction 2) although doubts still exist as to the rate of the reaction.



<u>Fig. 3.41:</u> Dependence of (1) NO· conc. (2) C=O index (3) C=C index on u.v irradiation of PP processed with 6×10^{-4}mol/100g of 4OHTMPNO· in a closed mixer for 10 mins. at 180^{o}C.

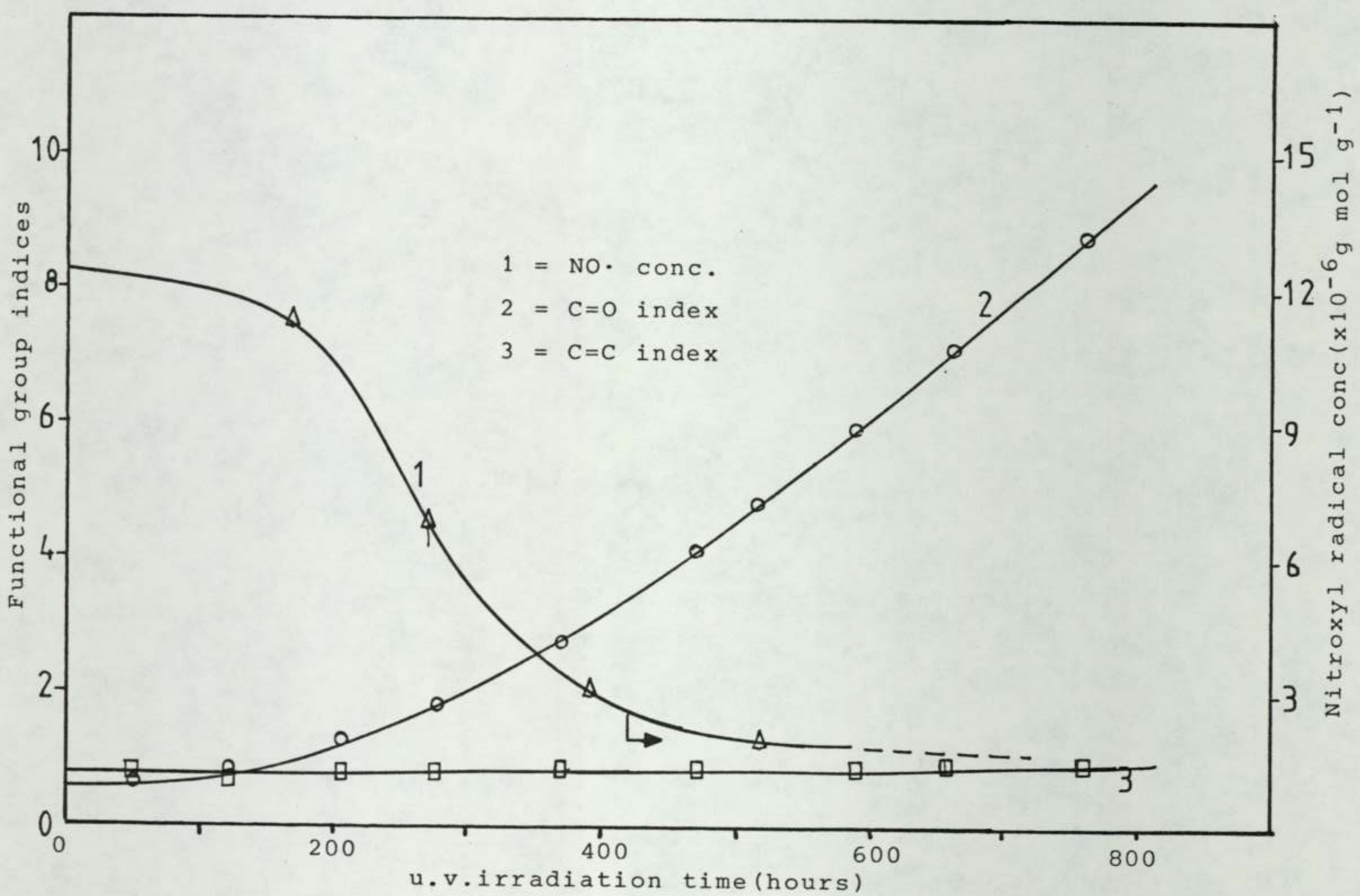


Fig. 3.42: Dependence of (1) NO· conc. (2) C=O index (3) C=C index on u.v. irradiation of PP processed with 6×10^{-4} mol/100g of 4OHTMPNOH in a closed mixer for 10 minutes at 180°C

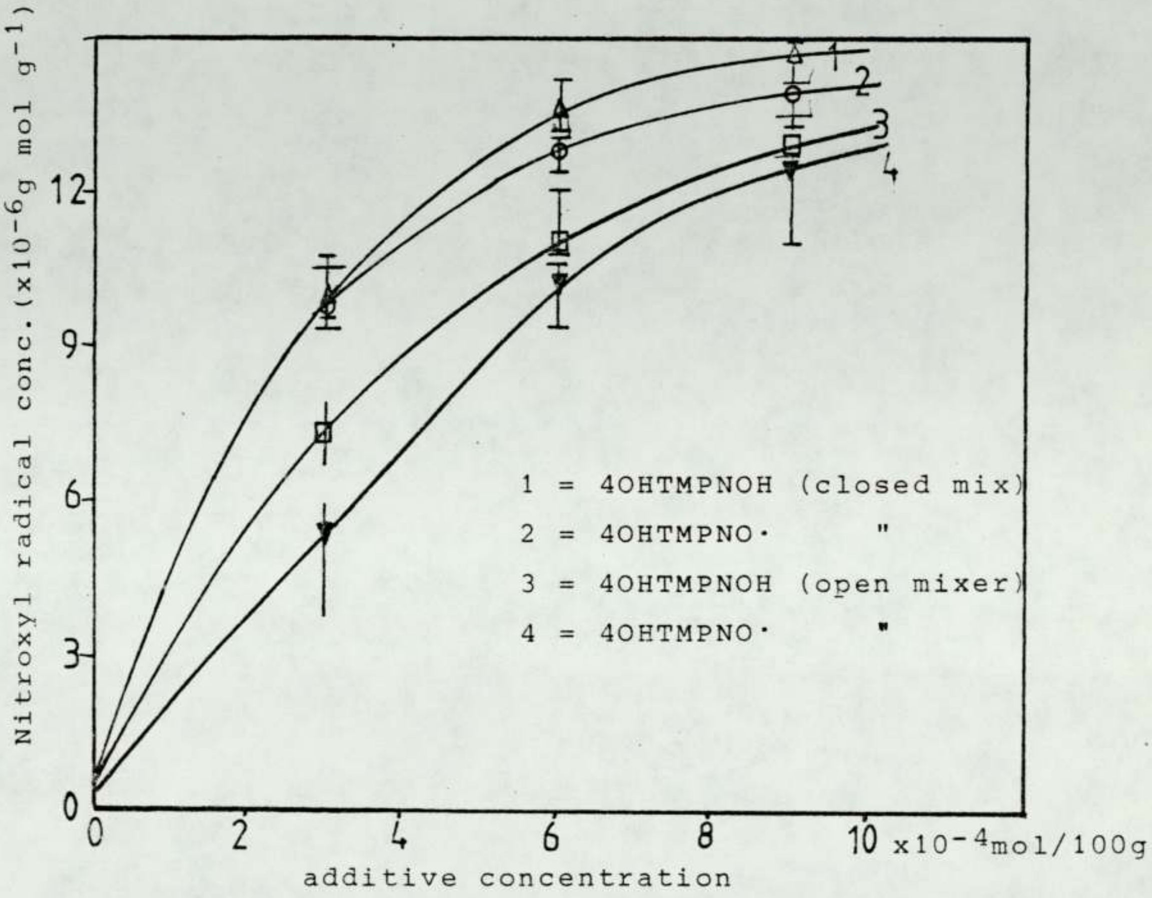


Fig. 3.43: Effect of additive concentration on NO· conc. of PP processed with 4OHTMPNO· and 4OHTMPNOH in both open and closed mixers for 10 mins. at 180°C.

The increase in photostability of PP with increasing concentration of both 4OHTMPNO. and 4OHTMPNOH (figs. 3.15 and 3.16 respectively) in both the closed and open mixers is almost certainly due to the corresponding increase in nitroxyl radical concentration as shown in Fig. 3.43. The photostabilising activity of 4OHTMPNOH on PP is very comparable (even in closed-mixer-processed samples) to that of 4OHTMPNO. This must however depend on the concentration of alkyl and alkyl peroxyl radicals present during the processing operation which may also depend on a number of other factors. The significantly reduced photostability activity of both compounds when processed with PP under argon atmosphere must be due to rapid consumption of the nitroxyl radical under argon(108) due to the absence of the regeneration of nitroxyl radicals.

The fact that upon extraction of films containing 4OHTMPNO. and 4OHTMPNOH processed under argon in the open and closed mixers, photostabilisation of the films were reduced greatly but not to zero level (see Fig 3.28) suggest that alkyl hydroxylamines (unextractable) must play a part, however small, in the overall photostabilition mechanism.

3.4 Synergism with commercial stabilisers and antioxidants

The behaviour of 4OHTMPNO. in the presence of commercial antioxidants and stabilisers was evaluated. Two components synergistic combinations of 4OHTMPNO. with HOBP and Tinuvin 770 were examined.

The u.v. embrittlement times of the different synergistic combinations with calculated synergism (%) are shown in tables 3.5 and 3.6 and summarised in Fig. 3.44.

Table 3.5

4OHTMPNO. $\times 10^{-4}$mol/ 100g	HOBP $\times 10^{-4}$mol/ 100g	UV EMT (hrs)	% * synergism.
10 (0.172)	0 -	1100	-
8 (0.136)	2 (0.065)	2270	175
6 (0.103)	4 (0.13)	2900	148.6
5 (0.086)	5 (0.16)	3150	165.9
4 (0.069)	6 (0.2)	3200	163.6
2 (0.034)	8 (0.26)	3340	221.8
0 -	10 (0.33)	800	-

Table 3.6

4OHTMPNO. $\times 10^{-4}$mol/ 100g	Tin 770 $\times 10^{-4}$mol/ 100g	u.v. EMT Hours	% * synergism
10 (0.172)	0 -	1100	
8 (0.138)	2 (0.1)	2510	
6 (0.103)	4 (0.19)	3150	
5 (0.086)	5 (0.24)	3310	25.54
4 (0.069)	6 (0.29)	3400	
2 (0.034)	8 (0.38)	3570	
0 -	10 (0.48)	3600	

Figures in brackets are weight percentages

$$* \text{ Synergism } \%^{(95)} = \frac{(Es - Ec) - [(E_1 - Ec) + (E_2 - Ec)]}{(E_1 - Ec) + (E_2 - Ec)} \times 100$$

Es = embrittlement time of synergist

Ec = embrittlement time of control

E_1 = embrittlement time of component 1

Ec = embrittlement time of component 2

In table 3.5 (and Fig. 3.44) it is shown that 4OHTMPNO. synergises well with HOBP, usually yielding percentage improvement of over 100, under u.v. irradiations with the optimum combination towards more of HOPB in the system than there is 4OHTMPNO. (See Fig. 3.45)

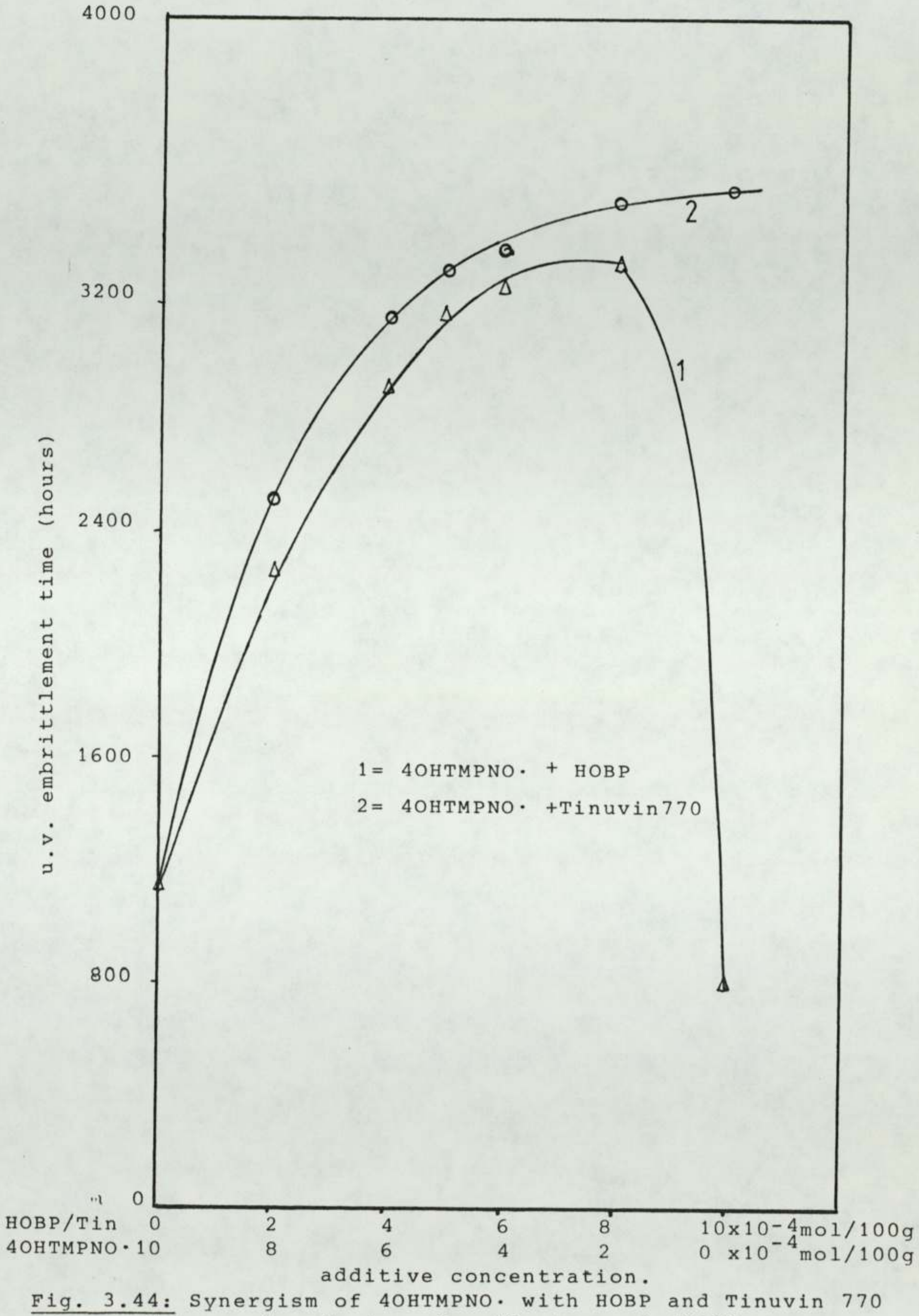


Fig. 3.44: Synergism of 4OHTMPNO· with HOBP and Tinuvin 770 processed in a closed mixer for 10 mins. at 180°C.

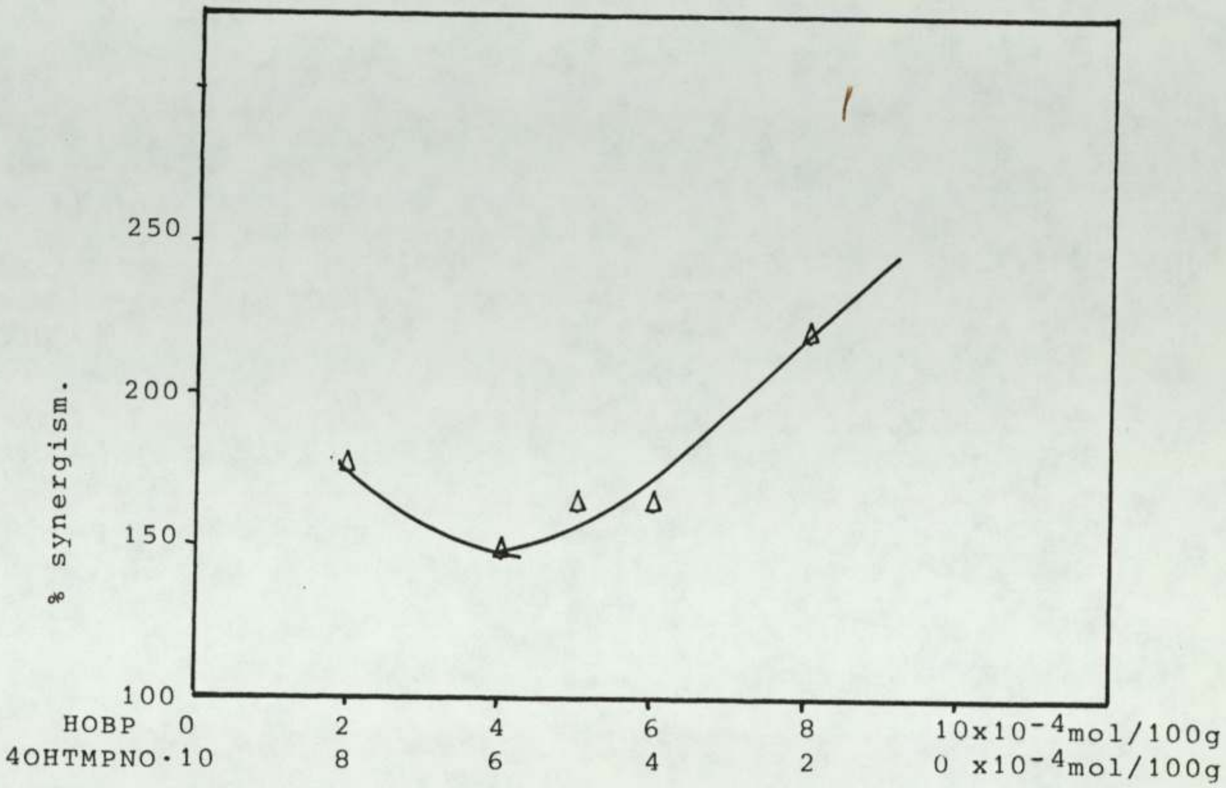


Fig. 3.45: Effect of additive combinations on the synergism (% improvement) in PP of 4OHTMPNO· and HOBP.

HOBP is a known u.v stabiliser whose activity though, is greatly reduced in the presence of peroxides.(150) It therefore goes to reason that compounds that prrevent the formation of peroxides or decompose then may synergise with HOBP. 4OHTMPNO. is an alkyl radical scavenger and as results show (Fig. 3.5) it effectively prohibits the formation of hydroperoxides. Thus, synergism between HOBP and 4OHTMPNO. may be due to mutual activities of alkyl radical scavenging and u.v. absorbing/screening mechanism by both components in the system. Additionally, the presence of 4OHTMPNO. may increase the solubility of HOBP in the system or vice-versa, thus increasing their effectiveness.

In the case of Tinuvin 770/4OHTMPNO. systems, no combination offers better photostability than Tinuvin 770 alone, as shown in Fig. 3.44 and as the concentration of Tinuvin 770 increases in the system, photostability increases. Thus, there is no significant advantage of synergism over Tinuvin 770 itself. Tinuvin 770 is known to stabilise PP under u.v. light by its transformational product - its corresponding nitroxyl. Thus, the little or no synergistic effect observed between it and 4OHTMPNO. may be due to either of the components deactivating the other, or that both compounds form complexes which are not very effective in photostabilisation of PP. There also may be cross termination reactions between radicals of the inhibitors.

$$A. + A. \longrightarrow A\text{———}A' \qquad -(7)$$

CHAPTER FOUR

NITROGEN- CONTAINING COMPOUNDS AS NITROXYL RADICAL PRECURSORS FOR PHOTOSTABILISATION OF POLYPROPYLENE

4.1 INTRODUCTION

A nitroso-alkane (tBuNO,III)*, a nitro-alkane ($tBuNO_2$,IV), an amino-alcohol (TAm, XII) a nitro-alcohol (TN, XIII) and a nitroso-amine (NDPA, XIV) were investigated as nitroxyl radical precursors for photostabilisation of Polypropylene.

tBuNO (III) has been used extensively as an alkyl-radical trap(119,152-154) (through a nitroxyl radical formation mechanism), for the identification of free radicals and their intermediates in model compounds, but its effectiveness as photostabilisers in polymer systems have not been fully studied. $tBuNO_2$(IV) is not a known radical trap. Although a recent study(155) suggested that its photostabilising activity in PP was via a radical trapping mechanism, through the formation of its corresponding nitroso compound and the subsequent formation of the corresponding nitroxyl radical, no evidence was produced to support this view.

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* Tables of structures, code names and numbers of all compounds used are on page s 36 and 37.

Photostabilising activity of TAm (XII) and TN (XIII) have not been investigated, although TAm has been found to be an excellent modifier for alkyd resins,(156) resulting in improvements of acid-resistance, salt-spray resistance, and gloss retention, while TN has been successfully employed as a cross-linking agent in an acrylic ester polymer or an acrylic ester vinyl polymer(157). Additionally, TN has been found to be good plasticisers for such synthetic rubbers as nitrile, chloroprene and acrylonitrile-chloroprene copolymers(158) and its solutions are effective preservatives and embalming fluids.(159)

NDPA (XIV) had been used for many years as a retarder of vulcanisation(160,161) in rubber and since the mechanism of retardation is thought to involve radical chain reactions(161,162) it may also have some photostabilising activity.

4.2 **RESULTS**

Figure 4.1 shows the dependence of torque on processing time of PP containing 5 x 10^{-3}mol/100g of the additives processed at 180°C in a closed mixer of a torque rheometer to restrict oxygen acess. tBuNO showed a good melt stabilising activity. TAm is the only additive that showed a slight decrease in torque suggesting chain- scission. However the torque after 2 minutes of processing for all samples stays at a higher level than that of the control throughout the processing operation, indicating an overall stabilising effect. In the open mixer (Fig. 4.2) a similar behaviour is observed. All additives seem to stabilise the polymer when compared to the control processed in the open mixer, with TAm having the worst activity, and do not offer any melt stabilisation when compared to a midly processed control. Melt flow index

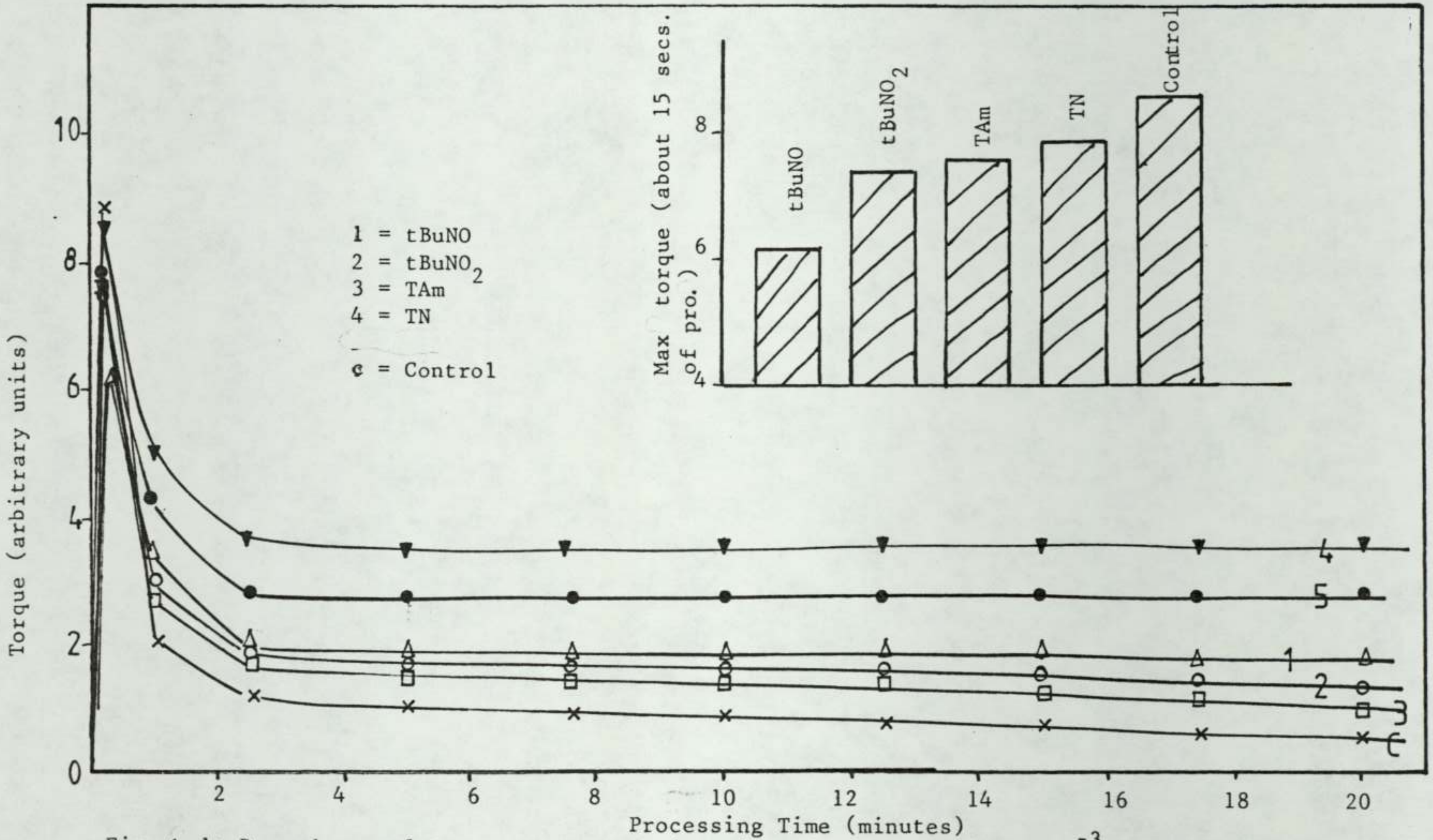


Fig. 4.1: Dependence of torque on processing time of PP containing 5×10^{-3} m/100g of (1) tBuNO, (2) $tBuNO_2$ (3) Tam, (4) TN (C) Control, no additive processed at 180°C in the closed mixer.

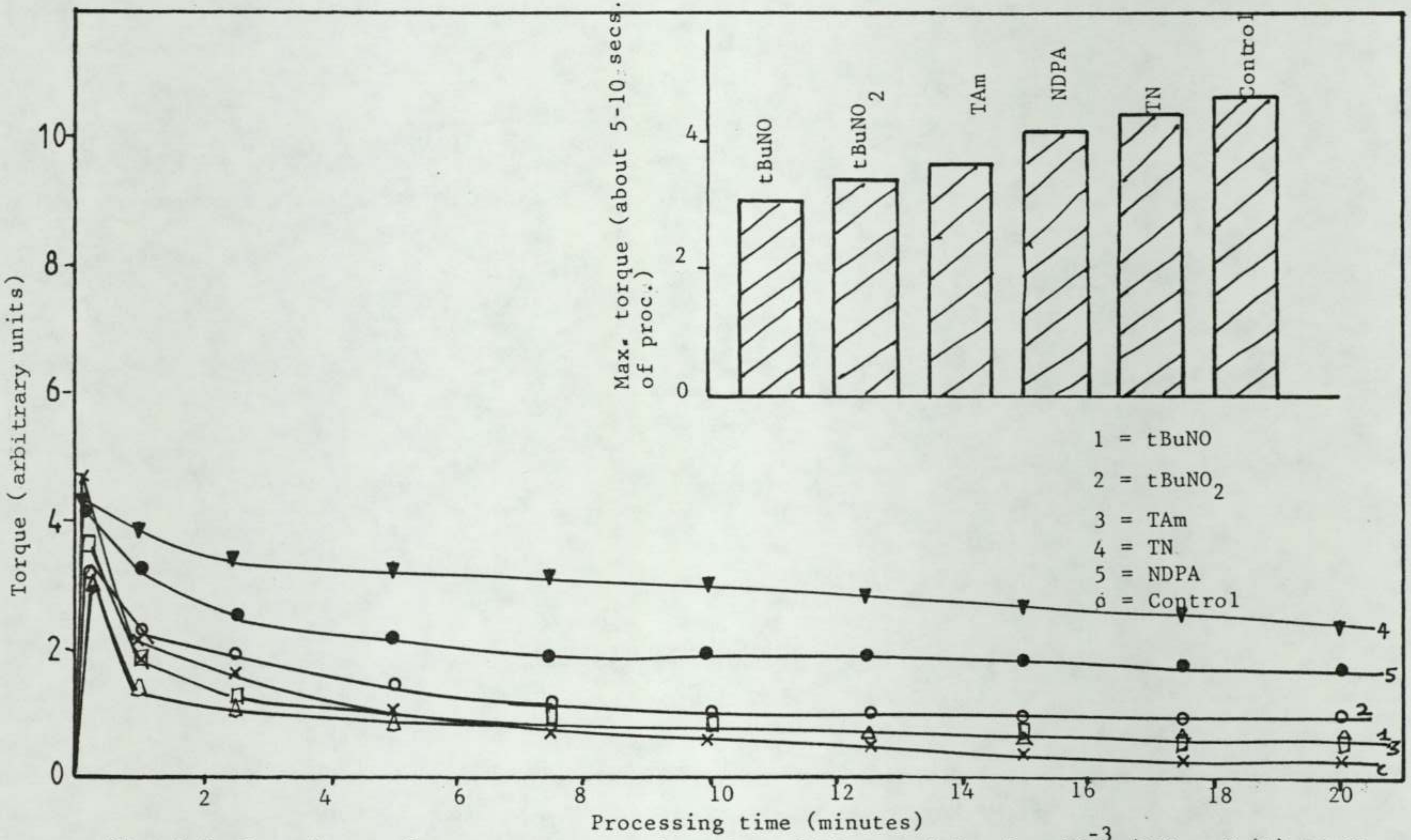


Fig. 4.2: Dependence of torque on processing time of PP containing 5 x 10^{-3} m/100g of (1) tBuNO (2) tBuNO$_2$ (3) TAm (4) TN (5) NDPA and (c) Control - no additive processed at 180°C in an open mixer

(MFI) of these samples (Fig. 4.4) confirm this (compared with control in Fig. 4.3).

Figures 4.3 and 4.4 show the effect of processing time on the melt flow index of PP containing 5 x 10^{-3}mol/100g of these additives processed in closed and open mixers respectively. In a closed mixer, all the additives studied here showed good melt stabilising effectiveness except TAm which offers only very little melt-stabilising activity to PP as shown by the sharp increase in MFI with processing time.

Figures 4.5 and 4.6 show the formation of hydroperoxides with processing time in a closed and open mixer respectively. In the closed mixer, tBuNO and NDPA prevented to a reasonable extent the build-up of hydroperoxides until later stages of processing while $tBuNO_2$, TAm and TN (curves 2,3,4) did not, although they reduced the level to below that of the unstabilised control. In the open mixer however, all the additives could not prevent hydroperoxide build-up with processing time. Hydroperoxide concentration in samples processed in the open mixer in the presence of all additives was more than that in samples processed in a closed mixer (in restricted oxygen).

The effect of processing time on the u.v. embrittlement times of PP containing the same molar concentration (5x10^{-3}mol/100g) of additives processed in a closed mixer at 180°C is demonstrated in figure 4.7 and table 4.1.

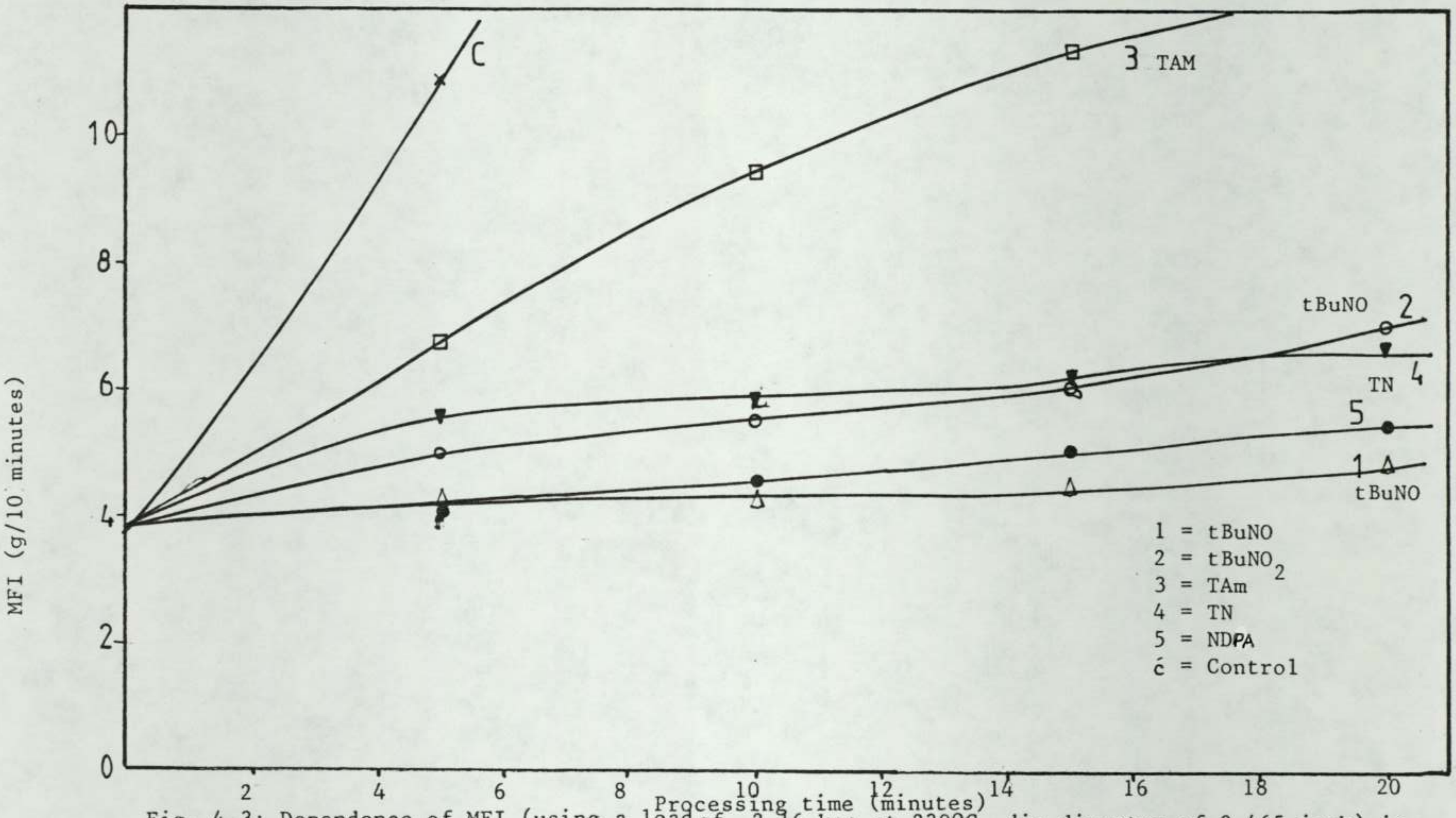


Fig. 4.3: Dependence of MFI (using a load of 2.16 kg: at 230°C, die diameter of 0.465 inch) in processing time of PP containing 5×10^{-3} m/100g of (1) tBuNO (2) tBuNO$_2$ (3) TAm (4) TN (5) NDPA and (c) Control - no additive, processed in the closed mixer at 180°C.

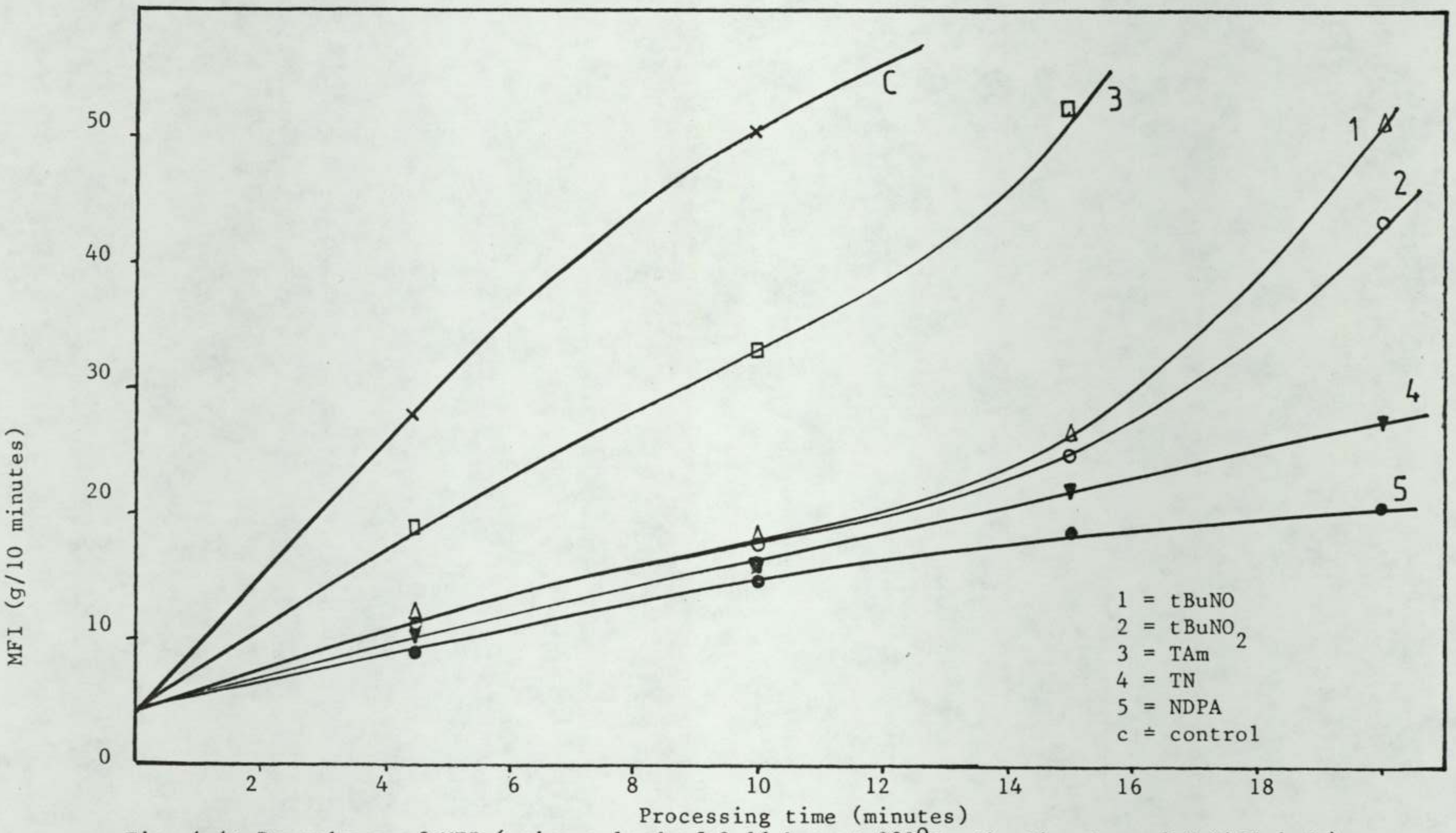


Fig. 4.4: Dependence of MFI (using a load of 2.16 kg; at 230°C, die diameter of 0.0465 inch) on processing time of PP containing 5×10^{-3} m/100g of (1) tBuNO (2) tBuNO$_2$ (3) TAm (4) TN (5) NDPA and (c) control - no additive processed in an open mixer at 180°C.

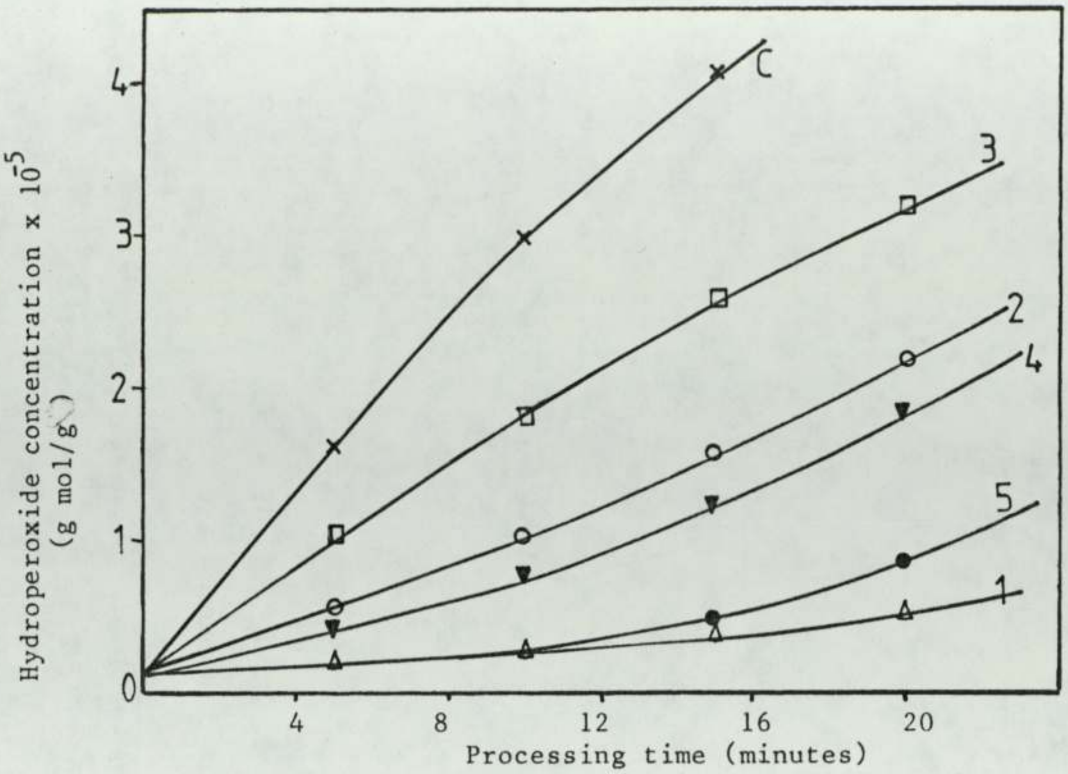


Fig. 4.5: Effect of processing time on the formation of hydroperoxides during processing of PP containing 5x10^{-3} m/100g of (1) tBuNO (2)tBuNO$_2$ (3) TAm (4) TN (5) NDPA, (c) control - no additive, processed in the closed mixer at 180°C.

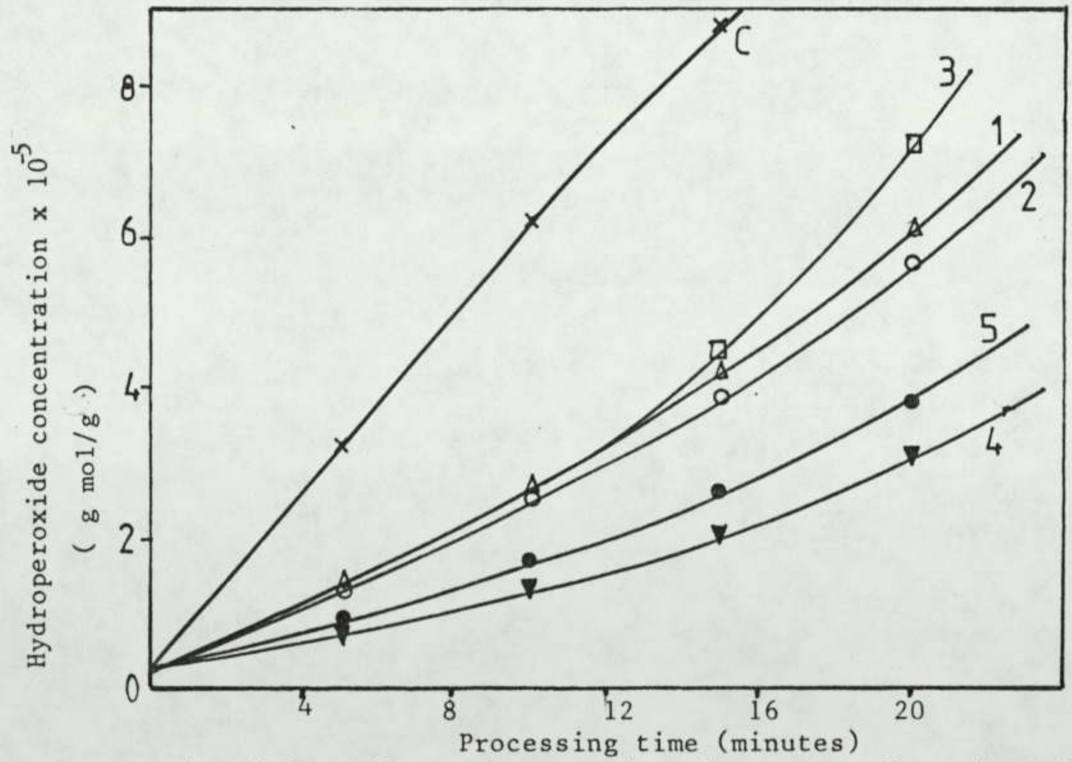


Fig. 4.6: Effect of processing time on the formation of hydroperoxides during processing of PP containing 5x10^{-3} m/100g of (1) tBuNO (2) tBuNO$_2$ (3) TAm (4) TN 9(5) NDPA and (c) control - no additive processed in an open mixer at 180°C.

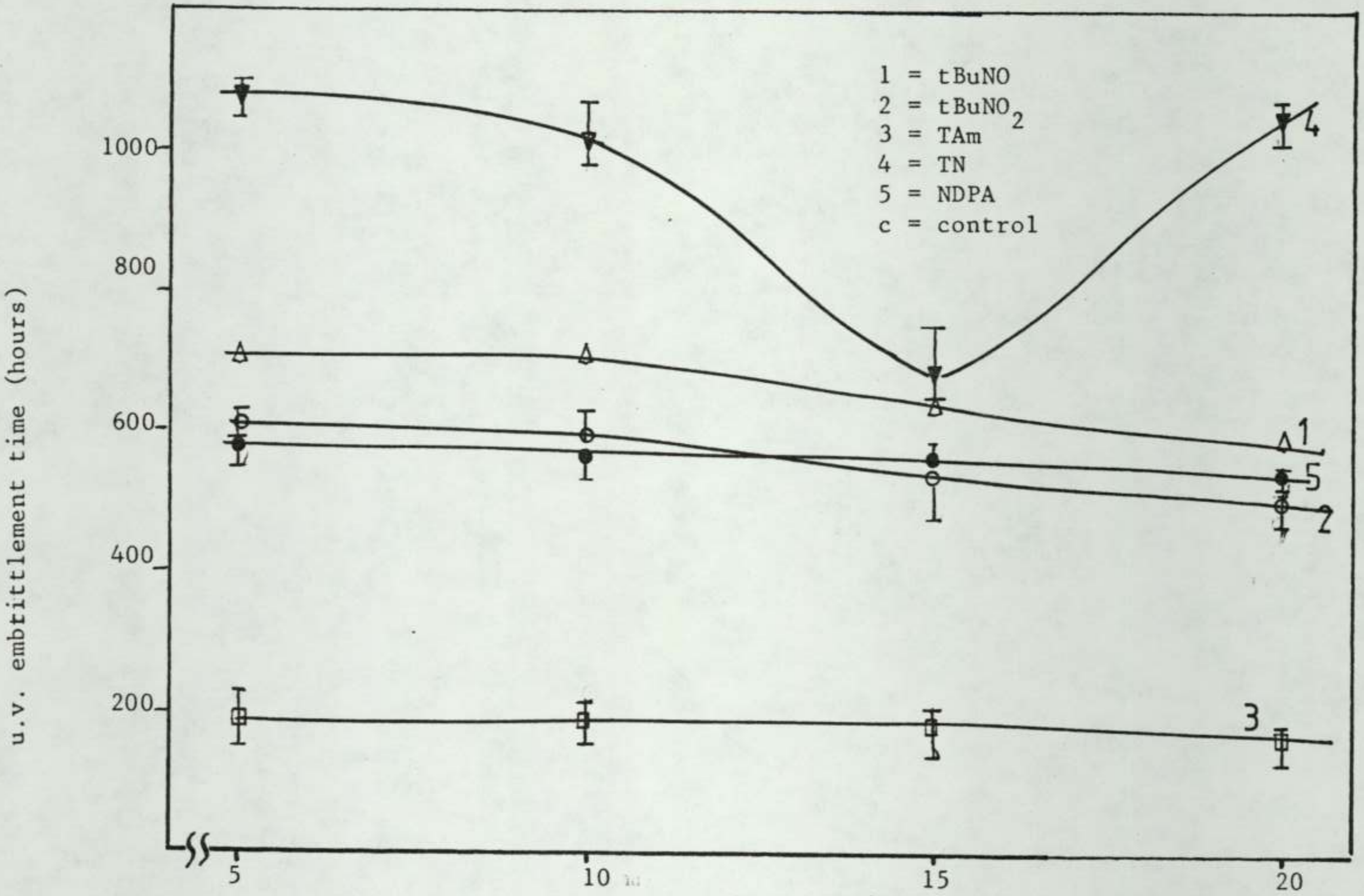


Fig. 4.7: Effect of processing time on u.v. embrittlement time of PP containing $5x10^{-3}$ m/100g of (1) tBuNO (2) tBuNO$_2$ (3) TAm (4) TN (5) NDPA (c) control processed in a closed mixer at 180°C.

Table 4.1 **Dependence of u.v EMT on proc. time in closed mixer**

	u.v. embrittlement times (hours)*				
Proc. Time (minutes)	tBUno	$tBuNO_2$	TAm	TN	NDPA
5	705	610	190	1080	580
10	705	590	190	1020	560
15	635	530	180	680	560
20	585	500	160	1050	540

* concentration = $5x\ 10^{-3}$ mol/100g.

Generally, all additives used (except TN) show little decreases in embrittlement times with processing time (Fig. 4.7). In the case of TN embrittlement time decreases as processing time increases up to 15 minutes, after which an increase in embrittlement was observed at 20 minutes. Fig. 4.8 shows almost the same relationship in irradiation time to a constant level (0.3) of carbonyl growth with processing time, (0.4 in the case of TN to compensate for an initial rapid carbonyl growth, which will be discussed in the next section).

Figures 4.9 - 4.13 show the effect of processing times on carbonyl formation under the effect of u.v. light in PP films containing the additives processed in a closed mixer. Films containing tBuNO and $tBuNO_2$ (Figs. 4.9 and 4.10 respectively) showed some induction period in which there was little or no carbonyl formation (though longer in

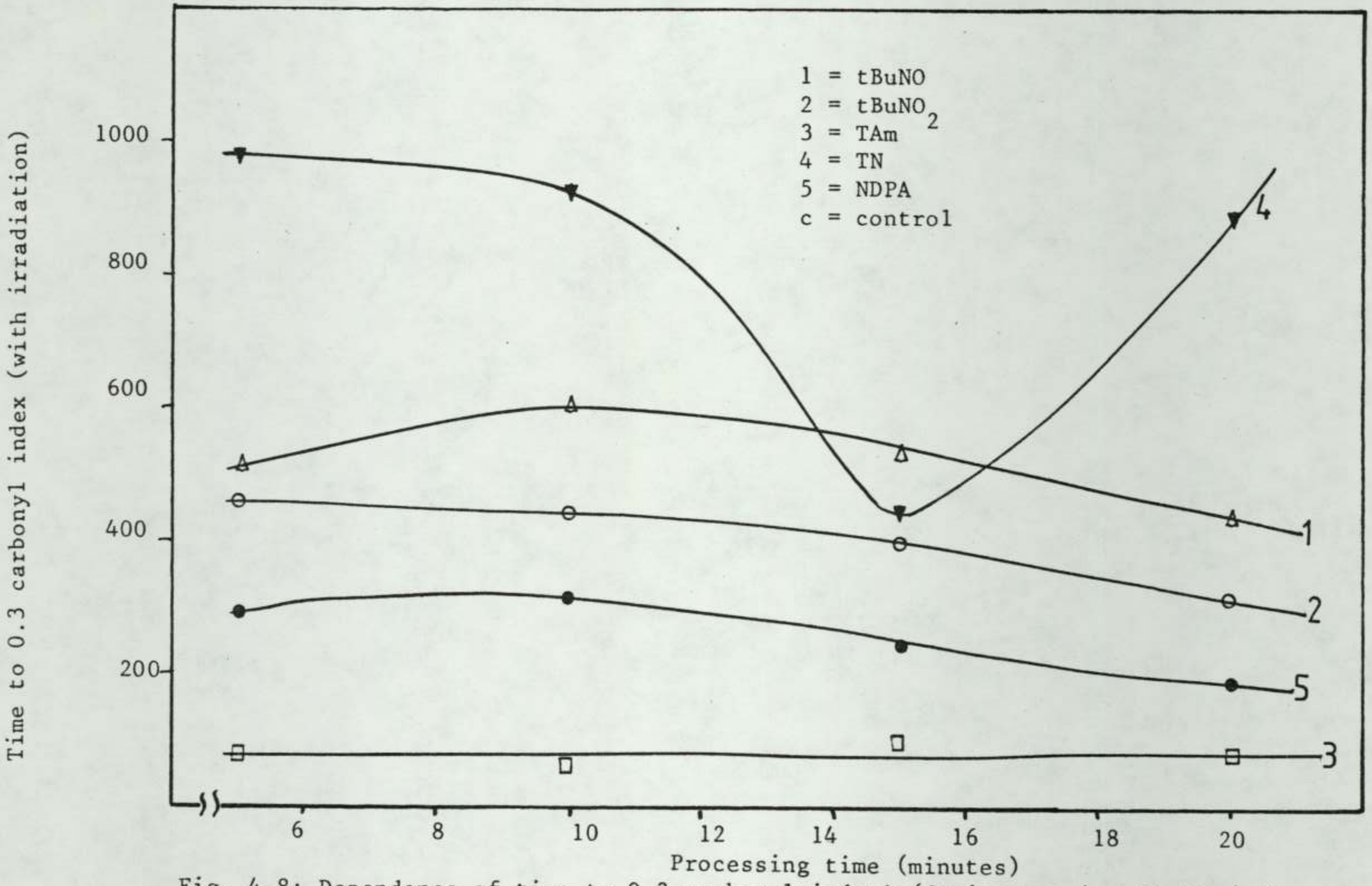


Fig. 4.8: Dependence of time to 0.3 carbonyl index* (during u.v irradiation) in processing time of PP containing 5×10^{-3} mol/100g of (1) tBuNO (2) tBuNO$_2$ (3) TAm (4) TN, (5) NDPA
* 0.4 in the case of TN.

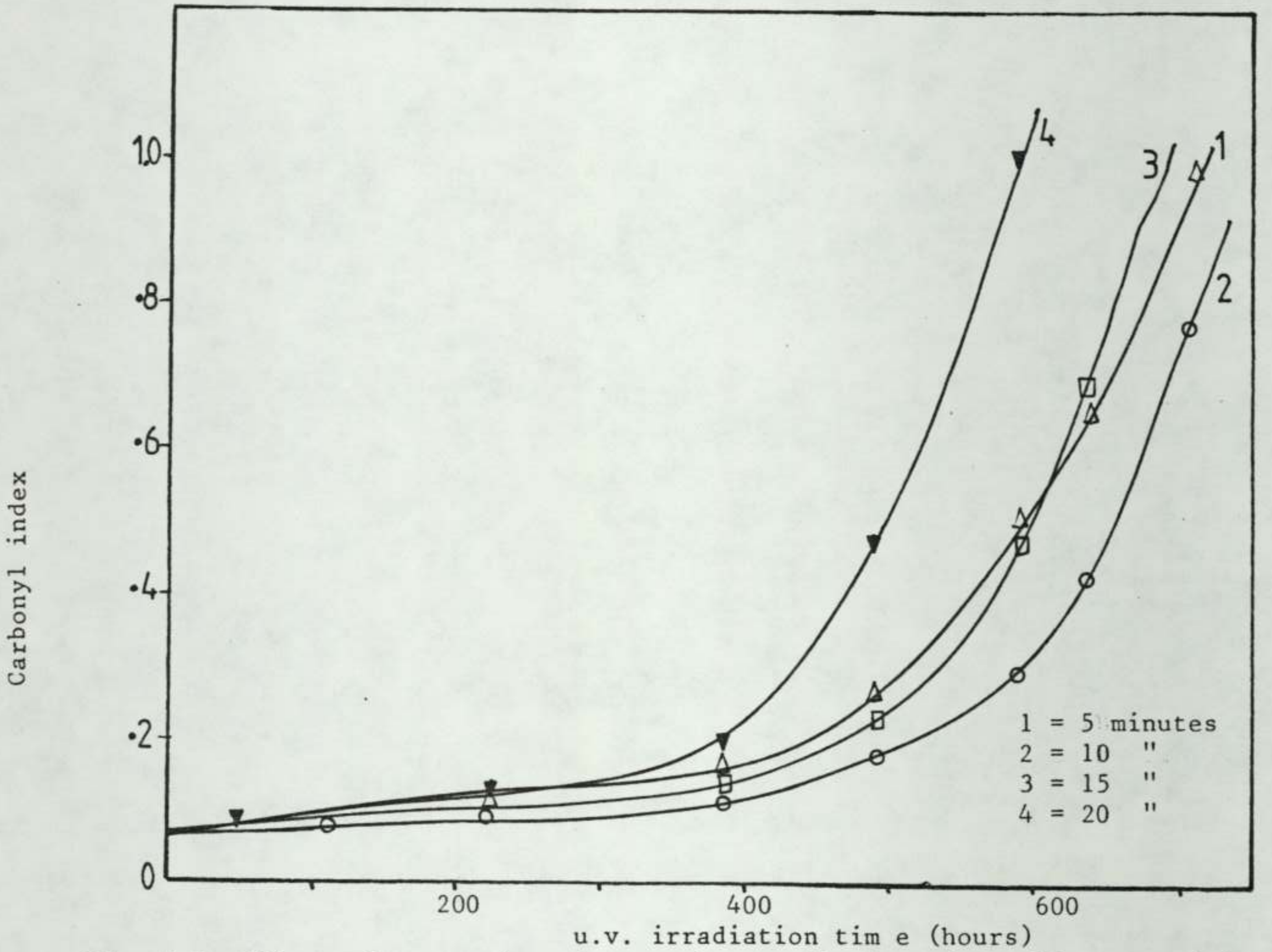


Fig. 4.9: Effect of processing time on photo-oxidation of PP films containing 5×10^{-3}m/100g tBuNO processed in the closed mixer.

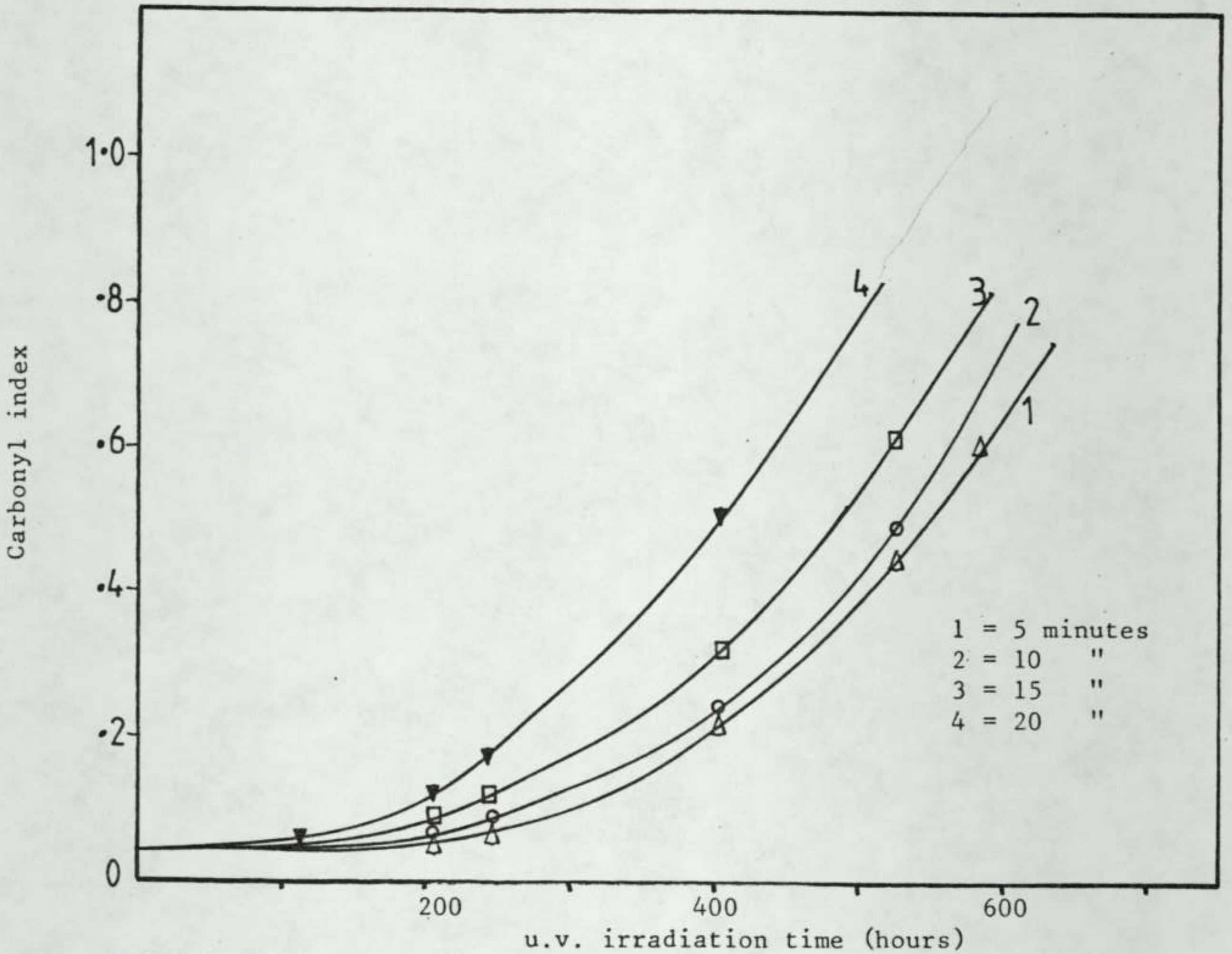


Fig. 4.10: Effect of processing time on photo-oxidation of PP films contianing 5 x 10^{-3} m/100g tBuNO$_2$ processed inthe closed mixer.

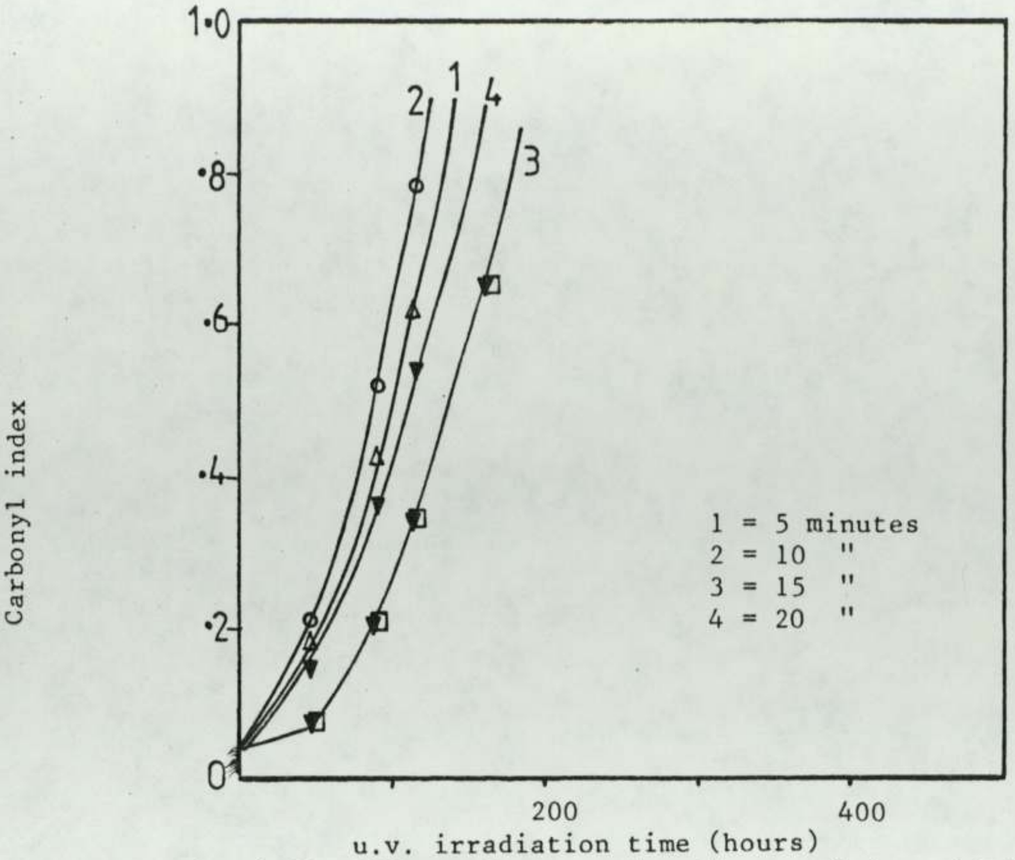


Fig. 4.11: Effect of processing time on photo-oxidation of PP films containing tris amino TAm processed in the closed mixer. (conc. $5x10^{-3}$mol/100g)

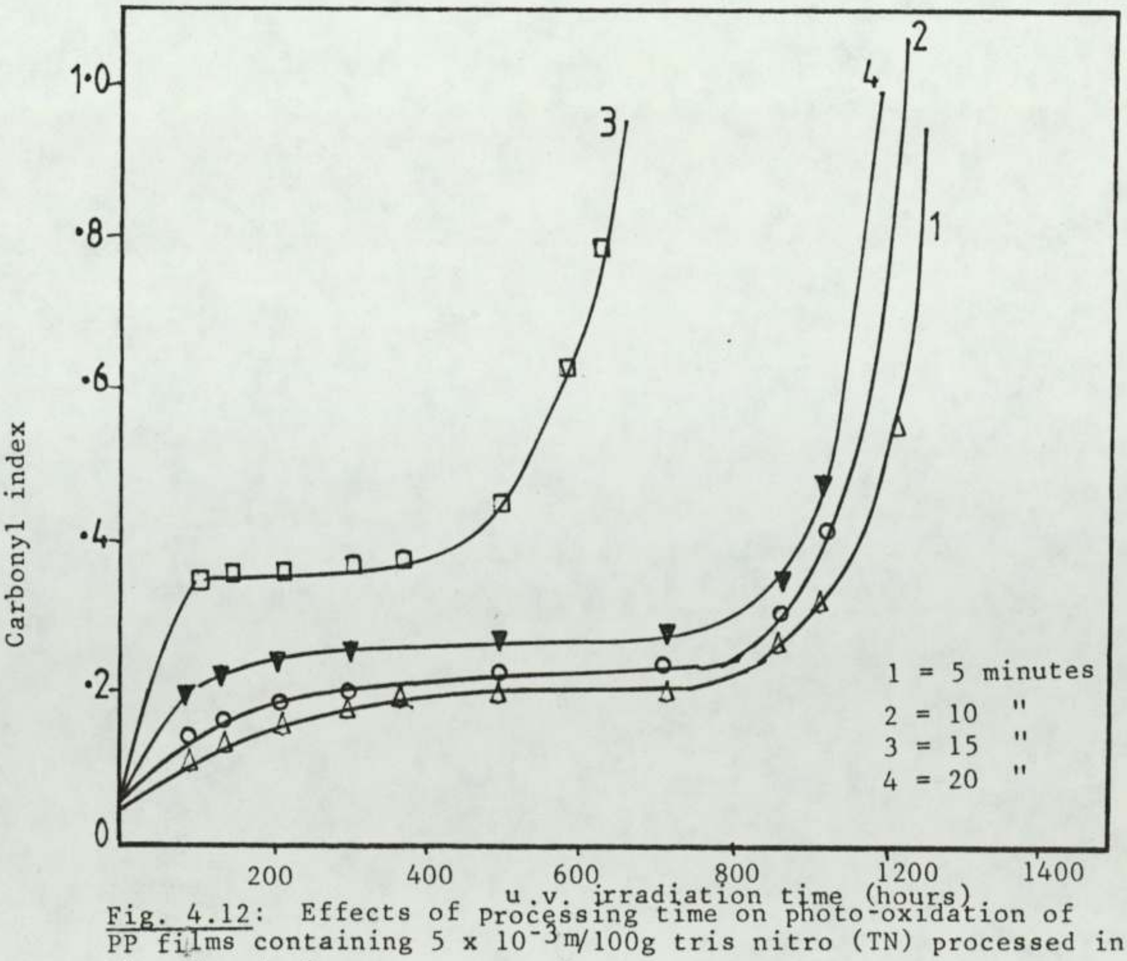


Fig. 4.12: Effects of processing time on photo-oxidation of PP films containing 5 x 10^{-3}m/100g tris nitro (TN) processed in the closed mixer.

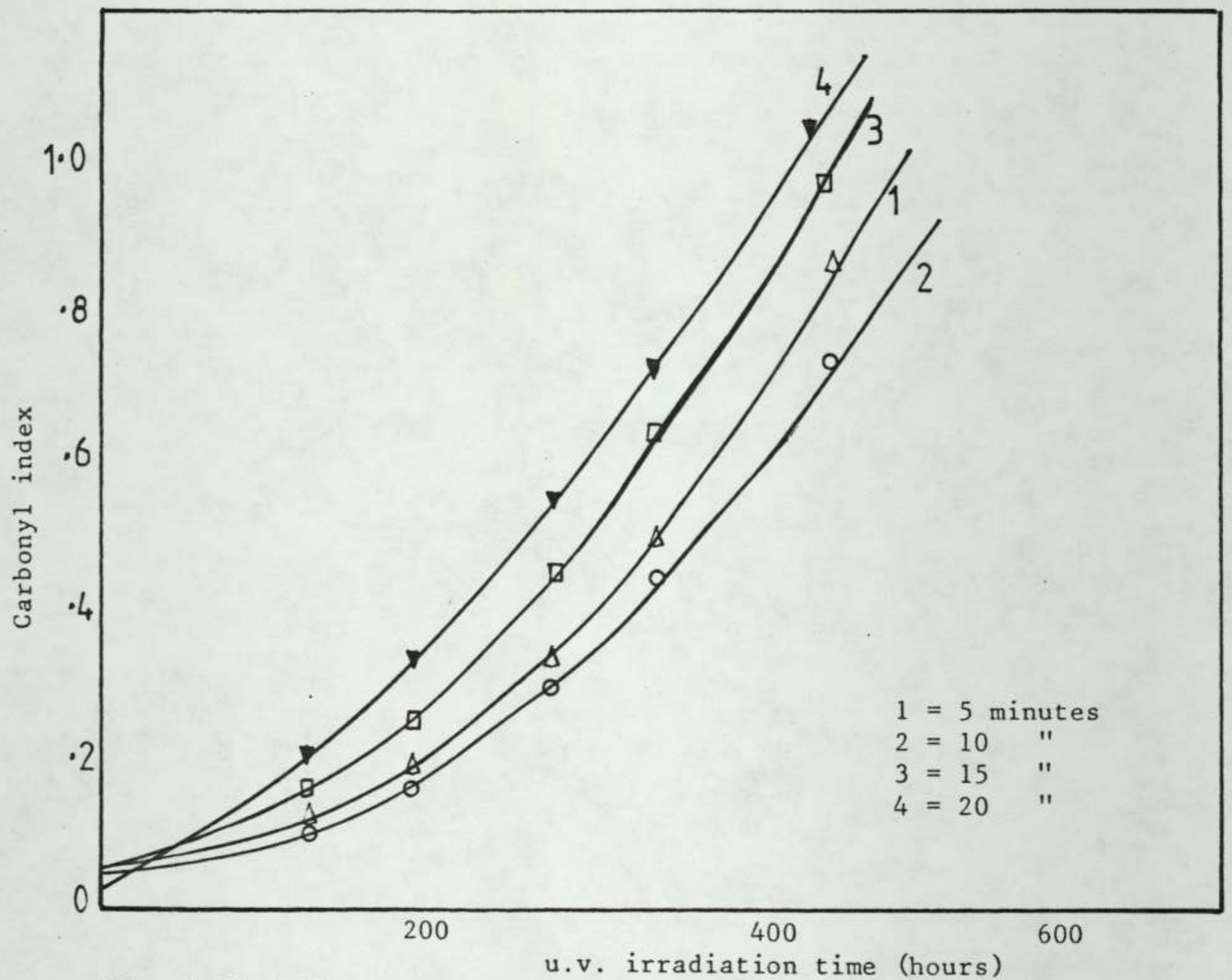


Fig. 4.13: Effect of processing time on photo-oxidation of PP films containing 5 x 10^{-3} m/100g NDPA processed in the closed mixer.

tBuNO than $tBuNO_2$), while films containing TAm and NDPA - (Figs. 4.11 and 4.13) showed no induction periods. Films containing TN (Fig. 4.12) on the other hand showed an initial rapid carbonyl growth followed by a period of gradual growth. (See Fig. 4.49, which shows the spectral changes in PP containing TN under photo irradiation).

The effect of processing time on the u.v. embrittlement time of PP containing 5×10^{-3}mol/100g of the additives processed in an open mixer (excess oxygen) is shown in Table 4.2 and Fig. 4.14.

Table 4.2 **Dependence of u.v. EMT on processing time (in open mixer)**

	u.v. embrittlement times (hours)*				
Proc. Time (minutes)	tBuNO	$tBuNO_2$	TAm	TN	NDPA
5	590	410	145	700	480
10	230	220	140	590	395
15	120	150	120	480	360
20	90	140	109	350	320

* concentration = 5×10^{-3} mol/100g.

A sharper decrease in u.v. embrittlement time with increasing processing time was obtained (compared with those procesed in the closed mixer - Fig. 4.7). An almost similar picture was obtained when irradiation time to a constant level of carbonyl growth (e.g. 03) was measured against processing times (Fig. 4.15).

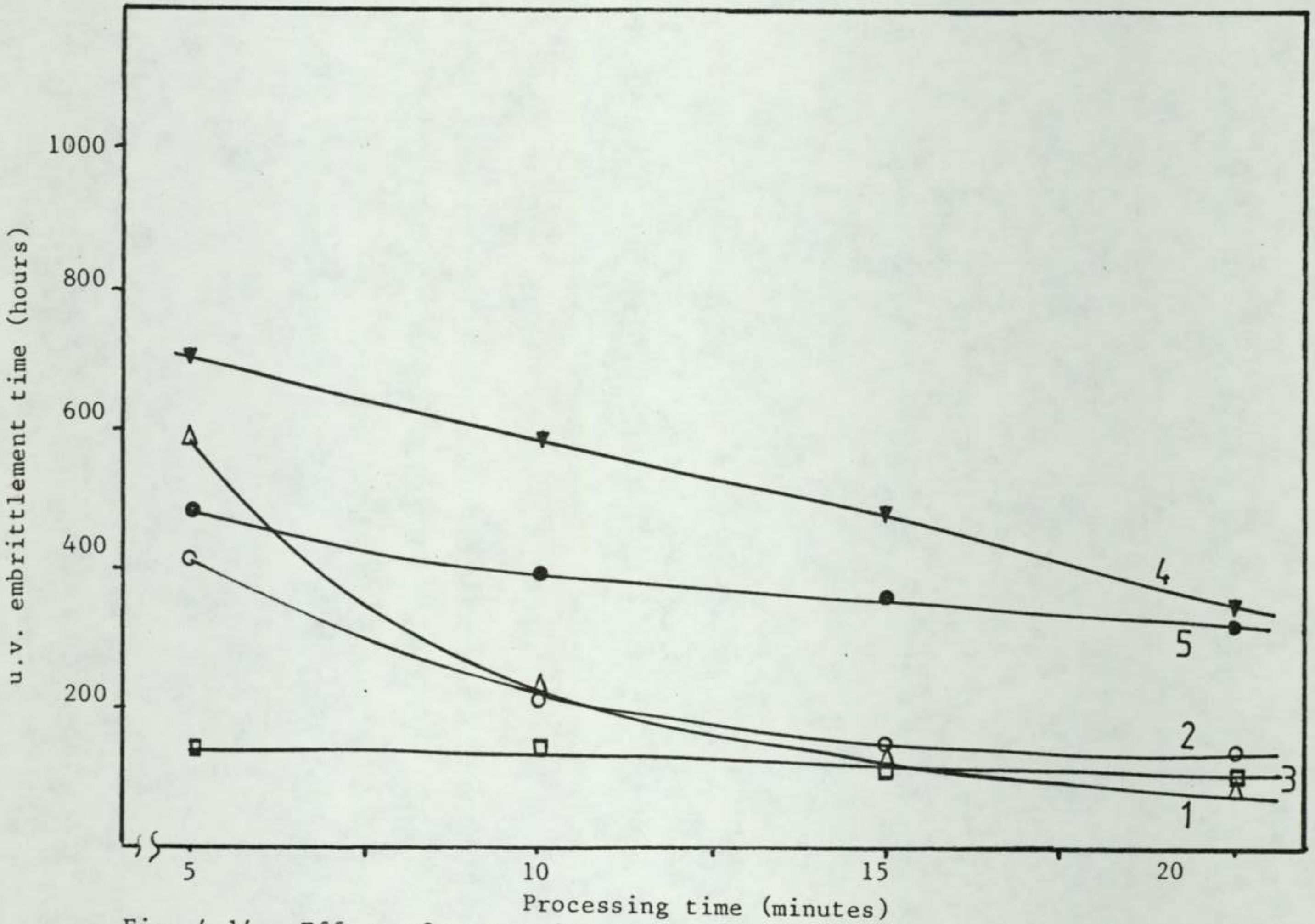


Fig. 4.14: Effect of processing time on u.v. embrittlement time of PP containing 5×10^{-3}mol/100g (1) tBuNo (2) $tBuNO_2$ (3) TAm (4) TN (5) NDPA processed in an open mixer at 180°C.

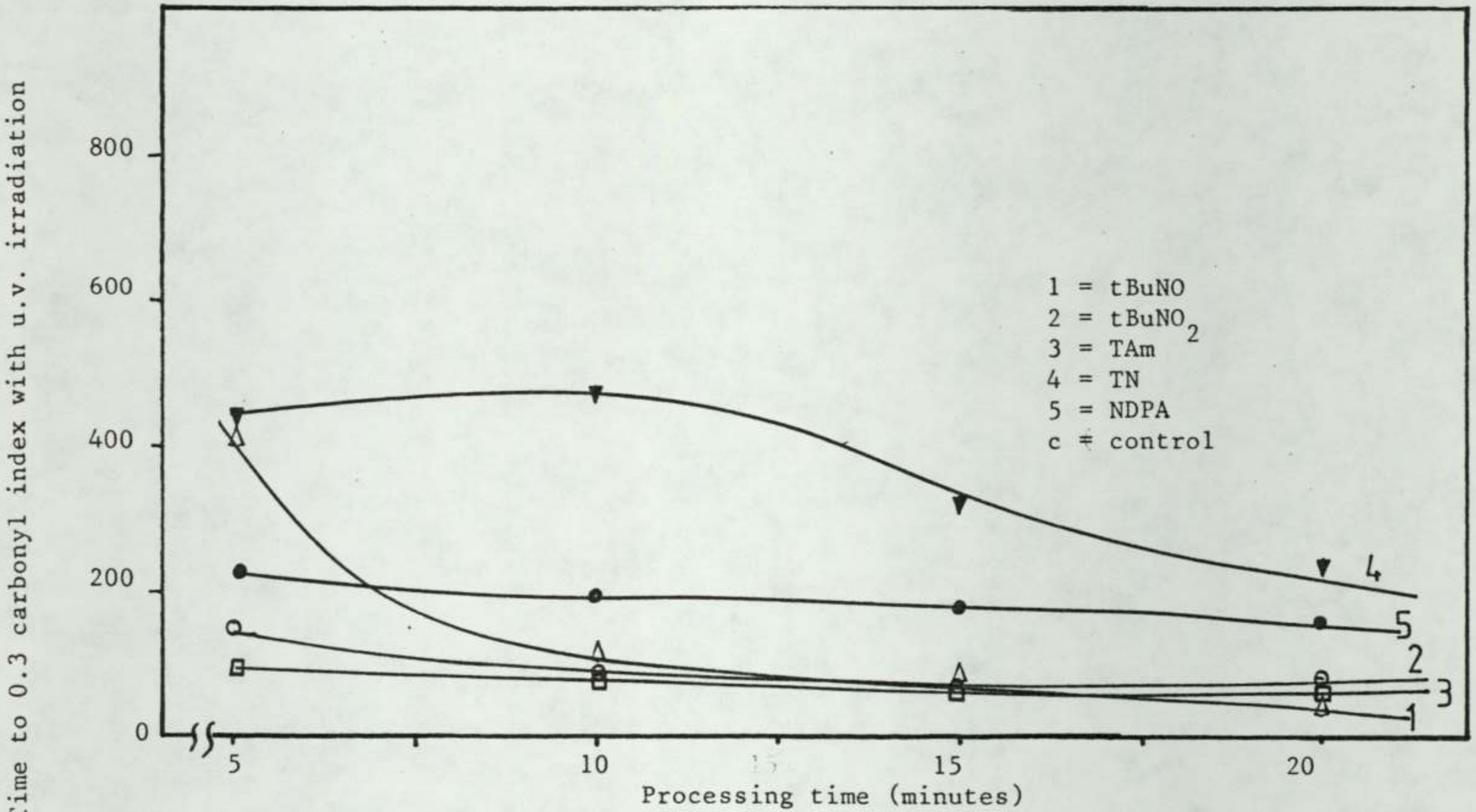


Fig. 4.15: Dependence of time to 0.3 carbonyl index* (during u.v. irradiation) on processing time of PP containing 5×10^{-3} m/100g of (1) tBuNo (2) tBuNO$_2$ (3) TAm (4) TN (5) NDPA processed in an open mixer at 180°C.
* 0.4 in the case of TN.

Figures 4.16 - 4.20 show the effect of processing times on carbonyl formation under the effect of u.v. light in PP films containing the additives (processed in the open mixer). Films containing $tBuNO_2$ and TAm (Fig. 4.17 and 4.18 respectively) showed no induction period. In the case of tBuNO (Fig. 4.16) only the film processed for 5 minutes (curve 1) showed a slow rate of carbonyl formation. In NDPA however (Fig. 4.20) a very short induction period was observed while films containing TN (Fig. 4.19) show an initial rapid carbonyl formation, similar to that observed in closed-mixer-processed films (Fig. 4.12), but on a larger scale than those processed in the closed mixer.

The effect of additive concentration on the photostability of PP processed both in the closed and open mixers is shown in Tables 4.3 - 4.7 for tBuNO, $tbuNo_2$, TAm, TN, and NDPA, respectively. These are summarised in Figures 4.21 (for closed mixer) and 4.22 (for open mixer).

Table 4.3 tBuNO

Concentration* $x10m^{-3}/100g$	u.v. EMT (Hours) CM	OM
1 (0.087)	580	105
1.15 (0.01)	590	115
2.5 (0.22)	630	140
5 (0.44)	705	240
10 (0.87)	910	630

Table 4.4 $tBuNO_2$

Concentration* $x10m^{-3}/100g$	u.v. EMT (Hours) CM	OM
1 (0.1)	570	150
5 (0.5)	590	220
10 (1.0)	640	405
15 (1.5)	700	480
20 (2.0)	890	500

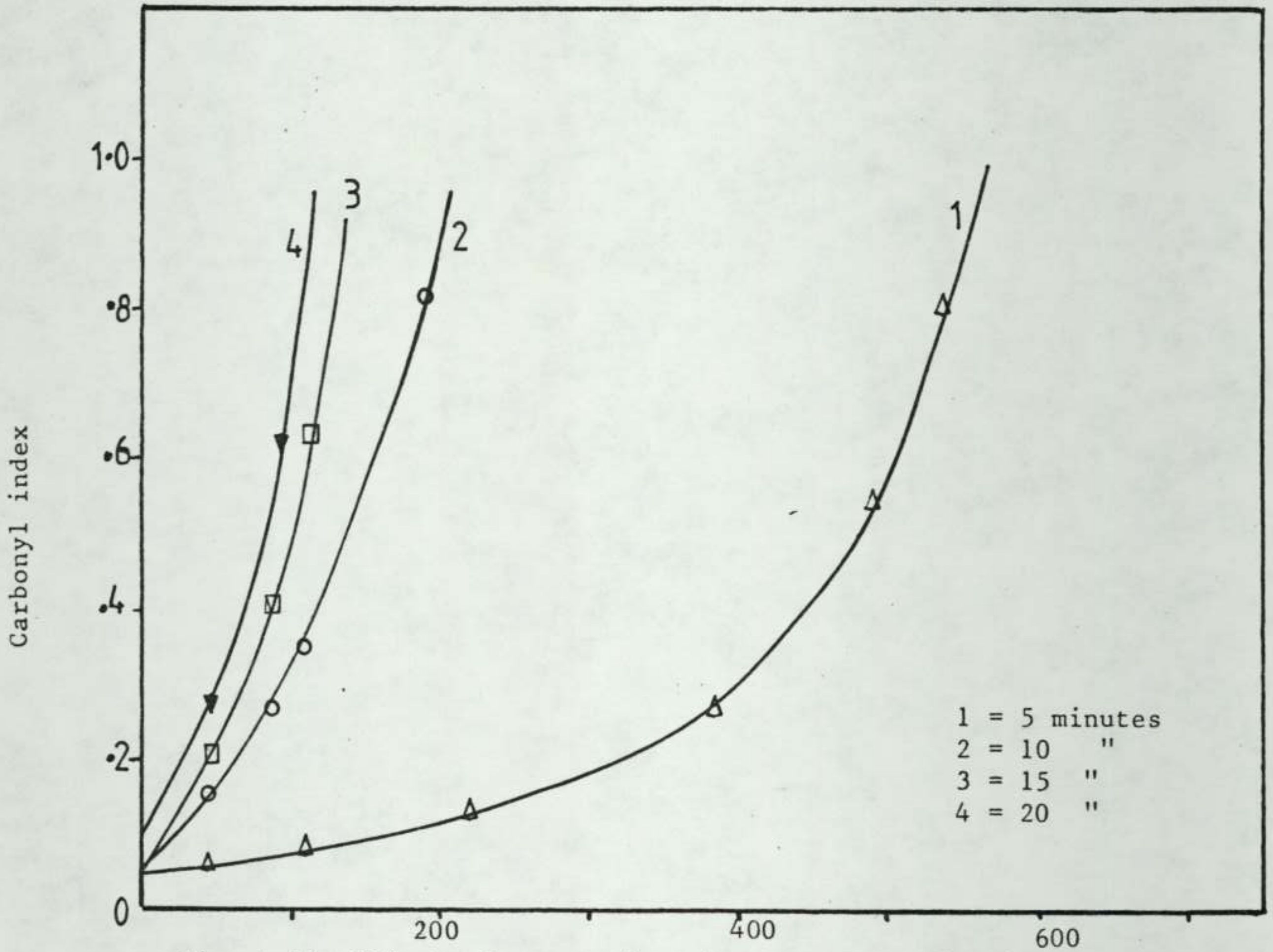


Fig. 4.16: Effect of processing time on photo-oxidation of PP films containing 5 x 10^{-3}m/100g tBuNO processed in the open mixer at 180°C.

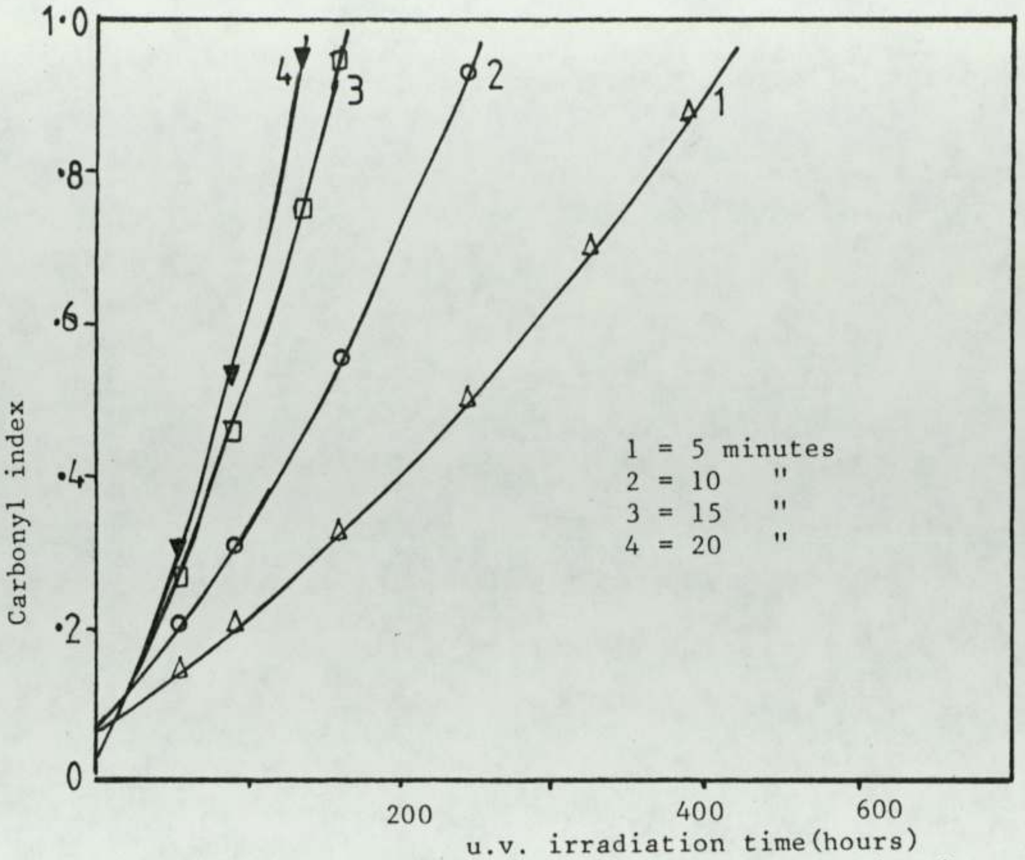


Fig. 4.17 Effect of processing time on photo-oxidation of PP films containing 5x10^{-3} mol/100g tBuNO$_2$ processed in the open mixer.

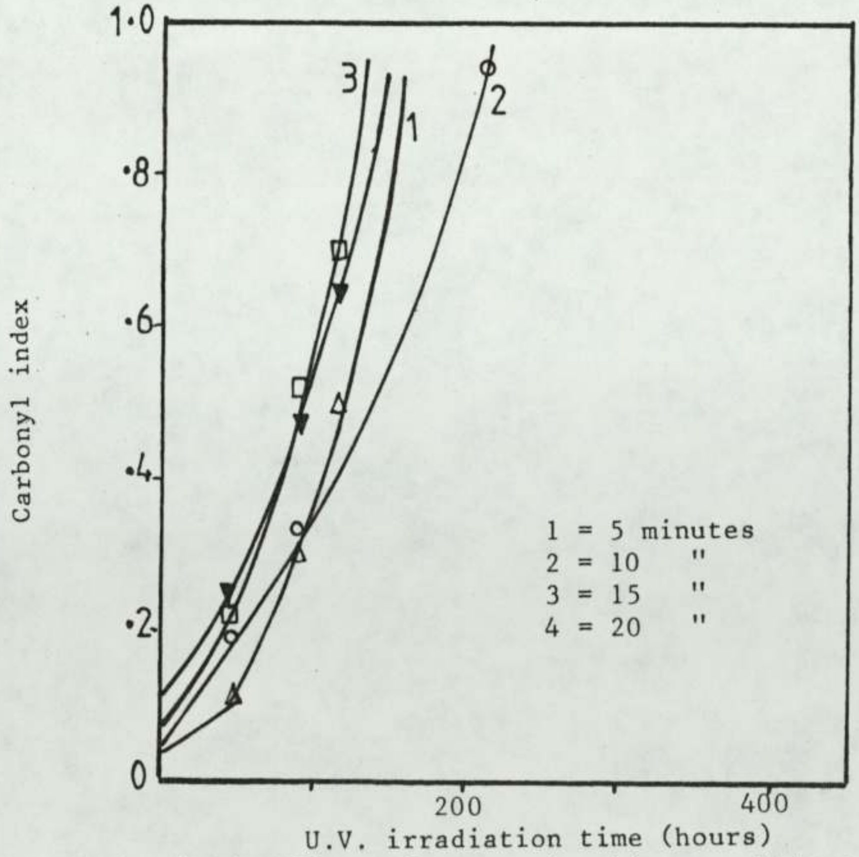


Fig. 4.18: Effect of processing time on photo-oxidation of PP films containing tris-amino (TAM) processed in the open mixer. (conc. 5x10^{-3}mol/100g.)

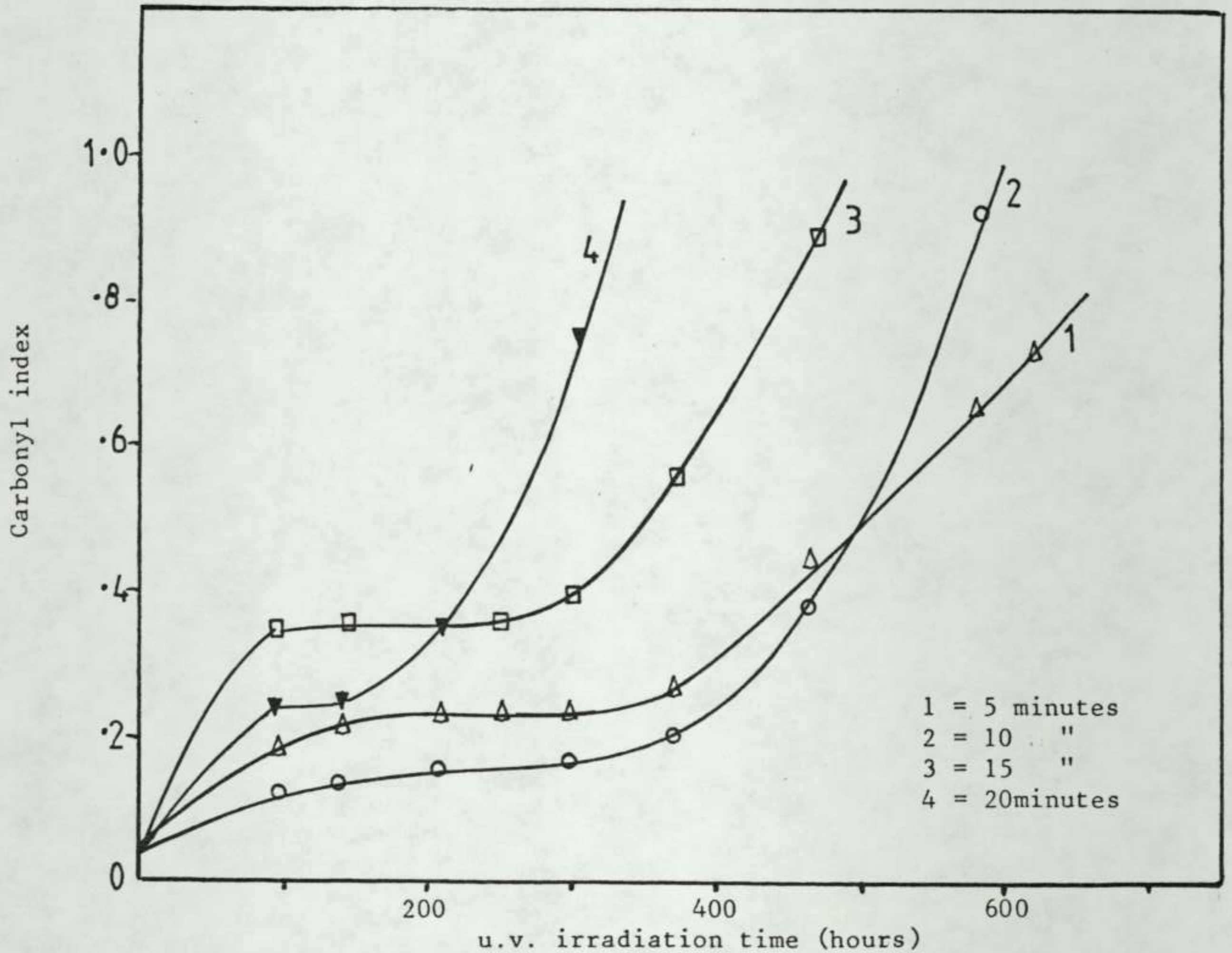


Fig. 4.19: Effect of processing time on photo-oxidation of PP films containing 5×10^{-3}m/100g tris nitro processed in theopen mxer at 180°C.

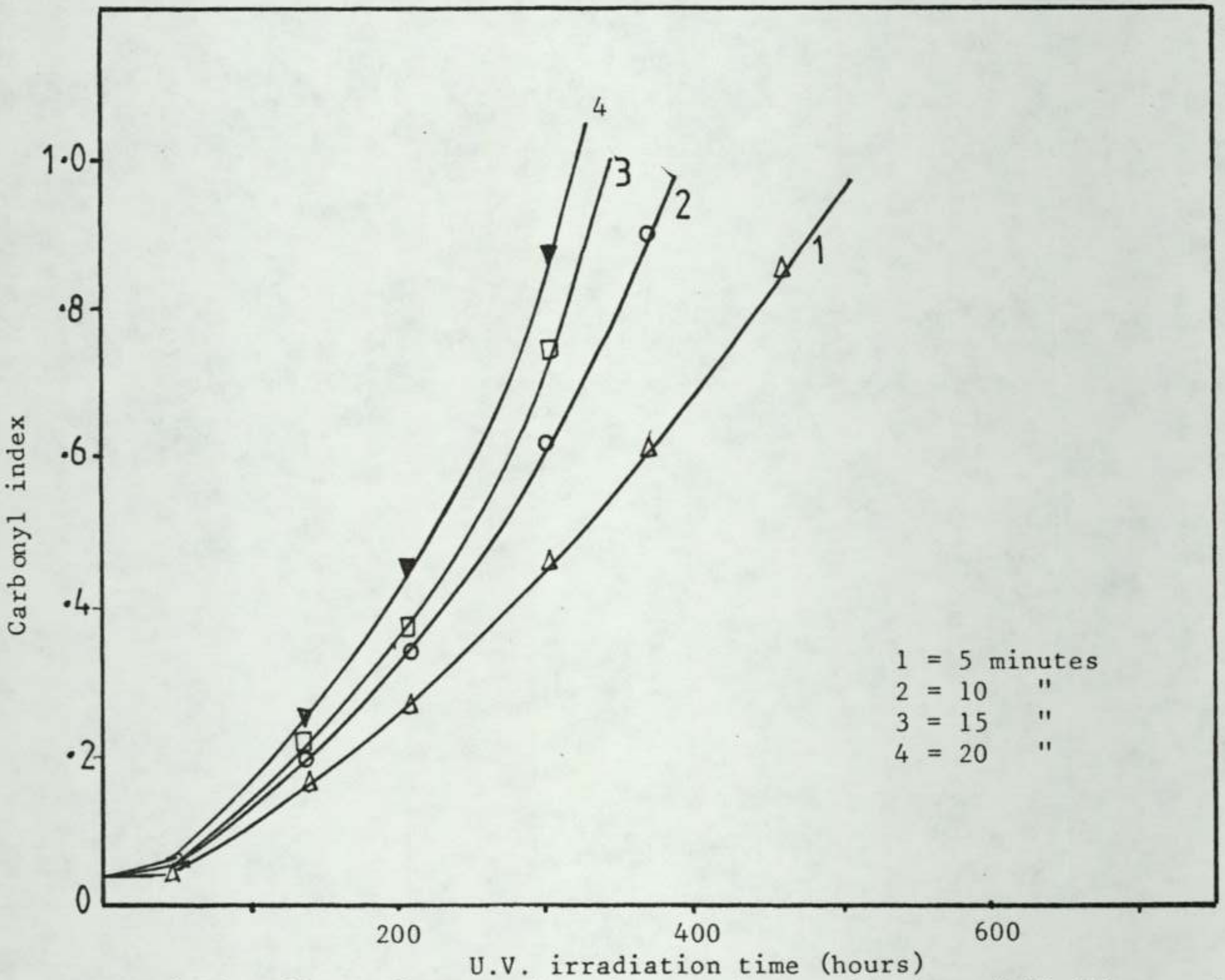


Fig. 4.20: Effect of processing time on photo-oxidation of PP films containing 5×10^{-3}m/100g NDPA processed in the open mixer at 180°C.

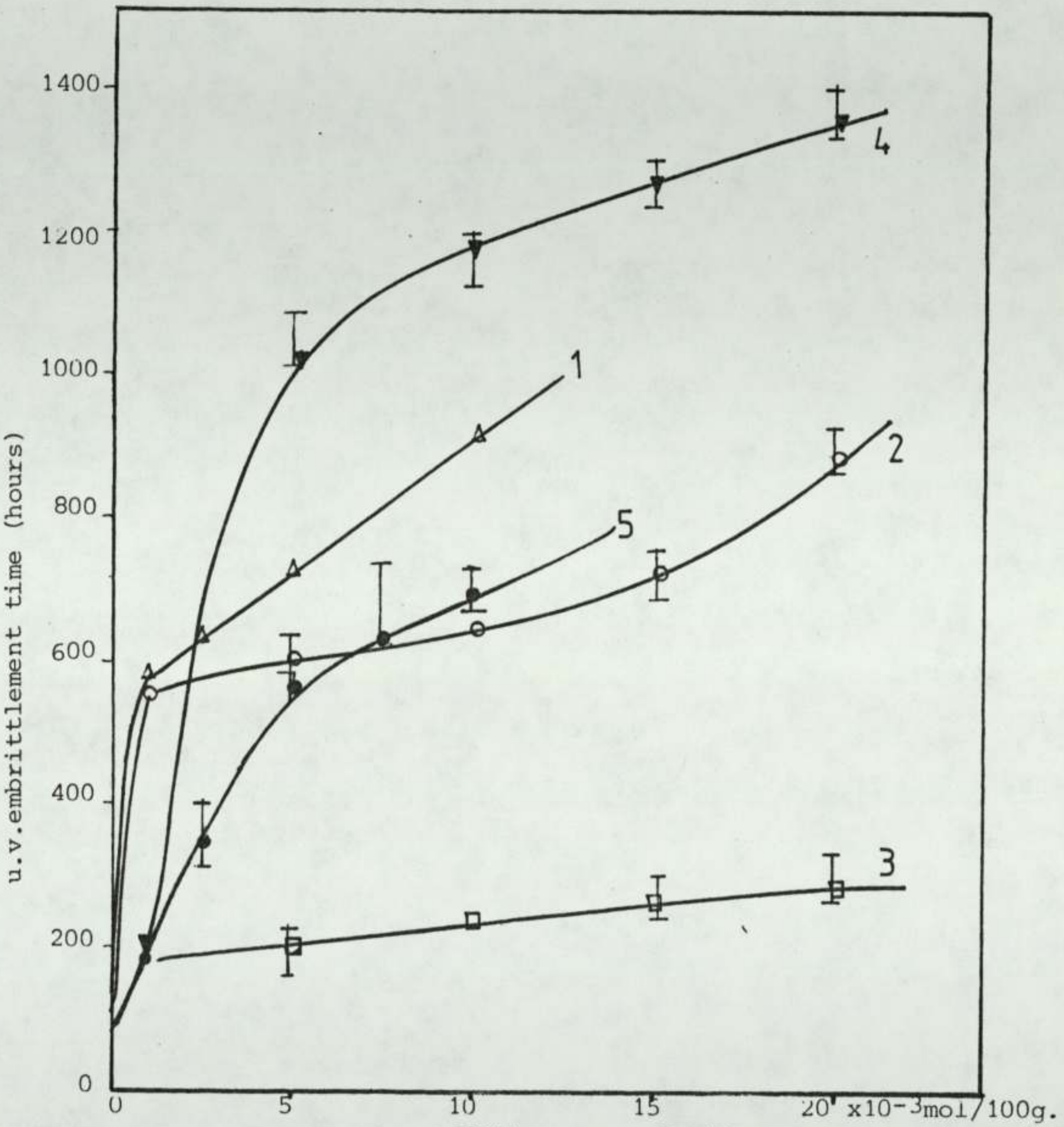


Fig. 4.21 : Effect of additive concentration on u.v.embrittlement time of PP processed with (1)tBuNO (2)$tBuNO_2$ (3)TAm (4)TN (5)NDPA for 10 mins. in a closed mixer at 180oC.

Table 4.5 TAm

Concentration*	u.v. EMT (Hours)	
x10m^{-3}/100g	CM	OM
1 (0.12)	180	115
5 (0.6)	120	140
10 (1.2)	230	165
15 (1.8)	255	180
20 (2.4)	280	210

Table 4.6 TN

Concentration*	u.v. EMT (Hours)	
x10^{-3}mol/100g	CM	OM
1 (0.15)	205	200
5 (0.75)	1020	585
10 (1.5)	1175	680
15 (2.26)	1250	740
20 (3.0)	1350	765

Table 4.7 NDPA

Concentration*	u.v. EMT (Hours)	
x10m^{-3}/100g	CM	OM
1 (0.2)	230	210
2.5 (0.5)	400	270
5 (1.0)	645	520
7.5 (1.5)	730	570
10 (2.0)	790	630

* Figures in brackets are weight percentages in polymer. All samples were processed for 10 minutes at 180°C.

In samples procesed in a closed mixer, all the additives show a positive concentration effect i.e. photostability increased with increasing concentration-sharply at low concentrations, but more gradual at higher concentrations. Similarly in the open mixer (Fig. 4.22) phostability increased with increasing concentration although to a lesser degree than in the closed mixer but gradually; except in the case of tBuNO in which a sharp increase in embrittlement time was observed with increasing concentration. The same relationship was established when the irradiation time to a constant level of carbonyl growth was examined with additive concentrations in films processed in the closed and open mixers (Figs. 4.23 and 4.24 respectively).

Figures 4.25-4.29 show the effect of additive concentration on the carbonyl formation (under u.v. light) in PP containing the additives processed in the closed mixer. Both tBuNO (Fig. 4.25) and $tBuNO_2$ (fig. 4.26) showed induction periods (longer in tBuNO) while both TAm (Fig. 4.27) and NDPA (Fig. 4.29) had no induction periods at all, though the higher the concentration, the slower the rate of carbonyl formation. In the case of TN (Fig. 4.28) an initial rapid carbonyl formation was observed, followed by a period during which the carbonyl growth slowed down. (See Fig. 4.49 for a typical spectral change in PP containing TN). In the open mixer, however, (Figs. 4.30 - 4.34) only PP film containing 10×10^{-3}mol/100g of tBuNO (Fig. 4.30) showed an induction period of any significance, although generally, the higher the concentration, the slower the rate of carbonyl formation.

4.3. DISCUSSION

The relation between torque and the thermal processing time may be dependent on a number of factors such as the physical state of the additive and/or its transformational products, and molecular mass. Liquid additives may have lubricating/plasticising effects. tBuNO for

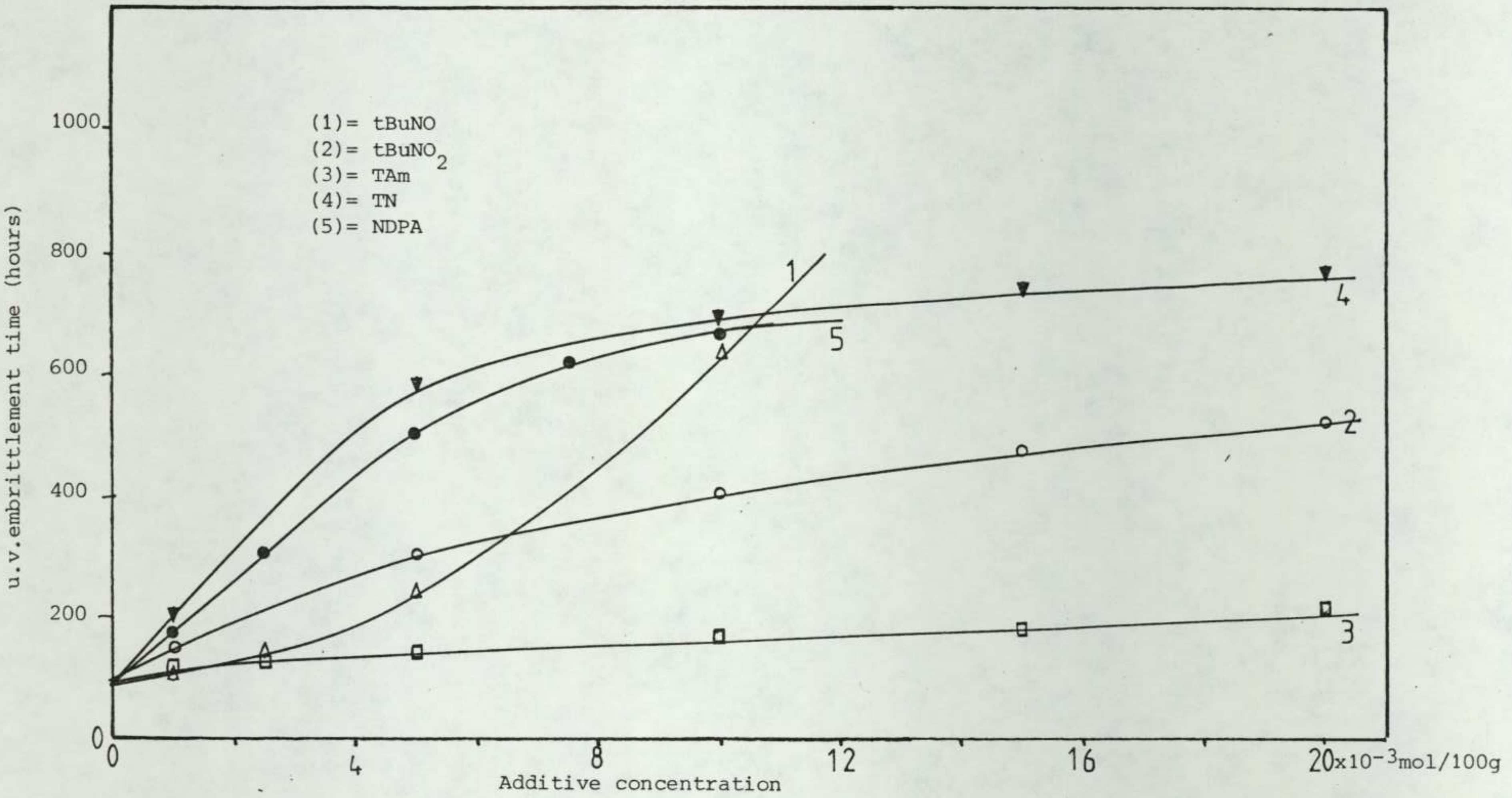


Fig. 4.22 : Effect of additive concentration on u.v.embrittlement time of PP processed with additives for 10 mins. at 180°C in an open mixer.

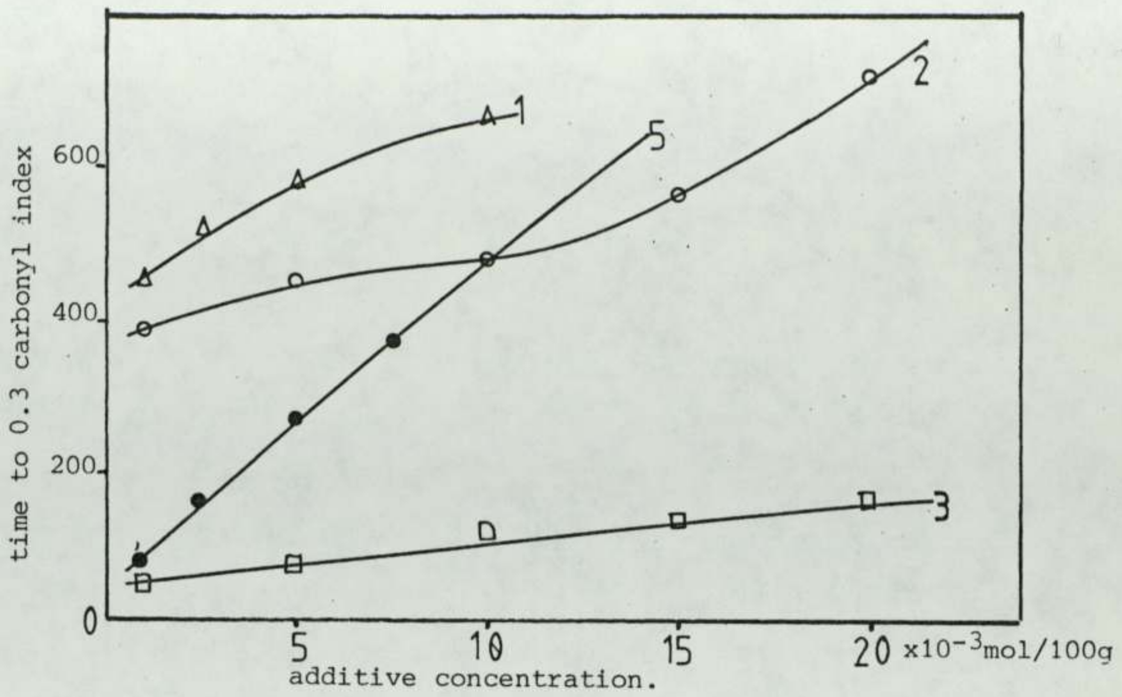


Fig. 4.23: Dependence of time to 0.3 carbonyl index with u.v.irradiation of PP processed with (1)tBuNO (2)tBuNO$_2$ (3)TAm (5)NDPA, in a closed mixer for 10 mins. at 180^{o}C.

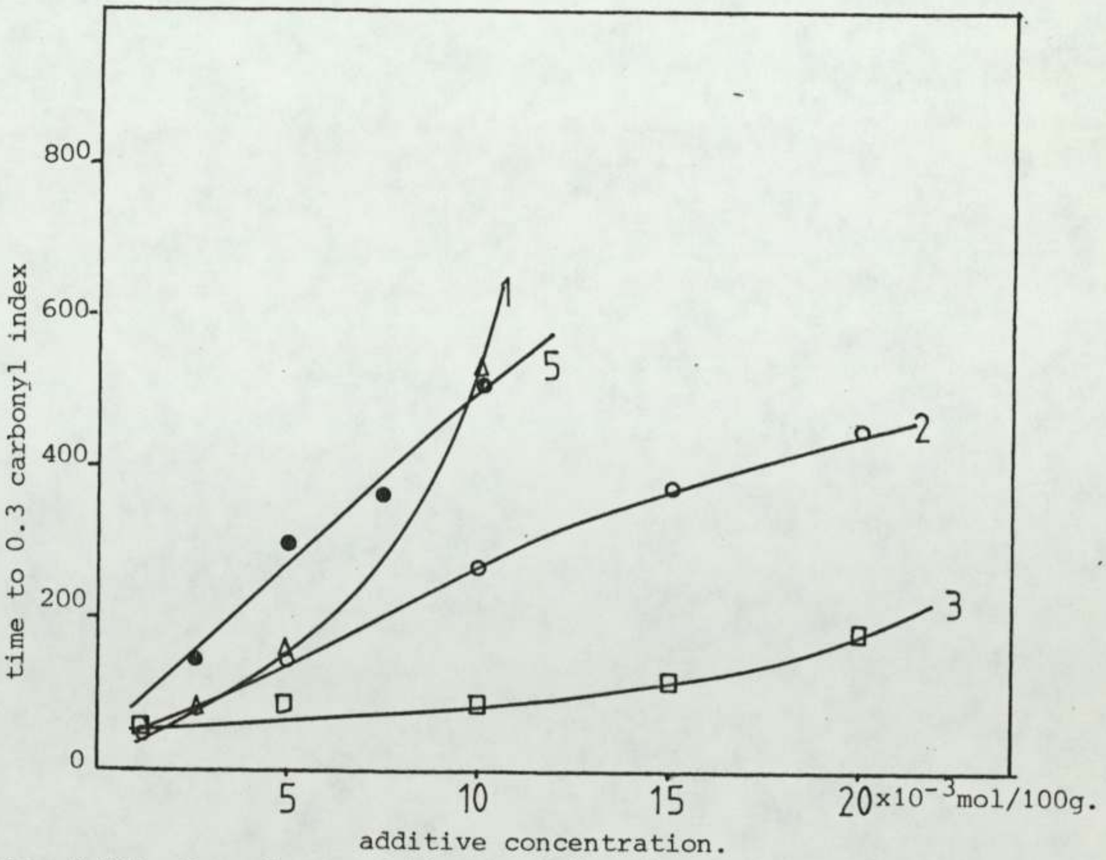


Fig. 4.24: Dependence of time to 0.3 carbonyl index with u.v.irradiation of PP processed with (1)tBuNO (2)tBuNO$_2$ (3)TAm (5) NDPA for 10 mins. in an open mixer at 180^{o}C.

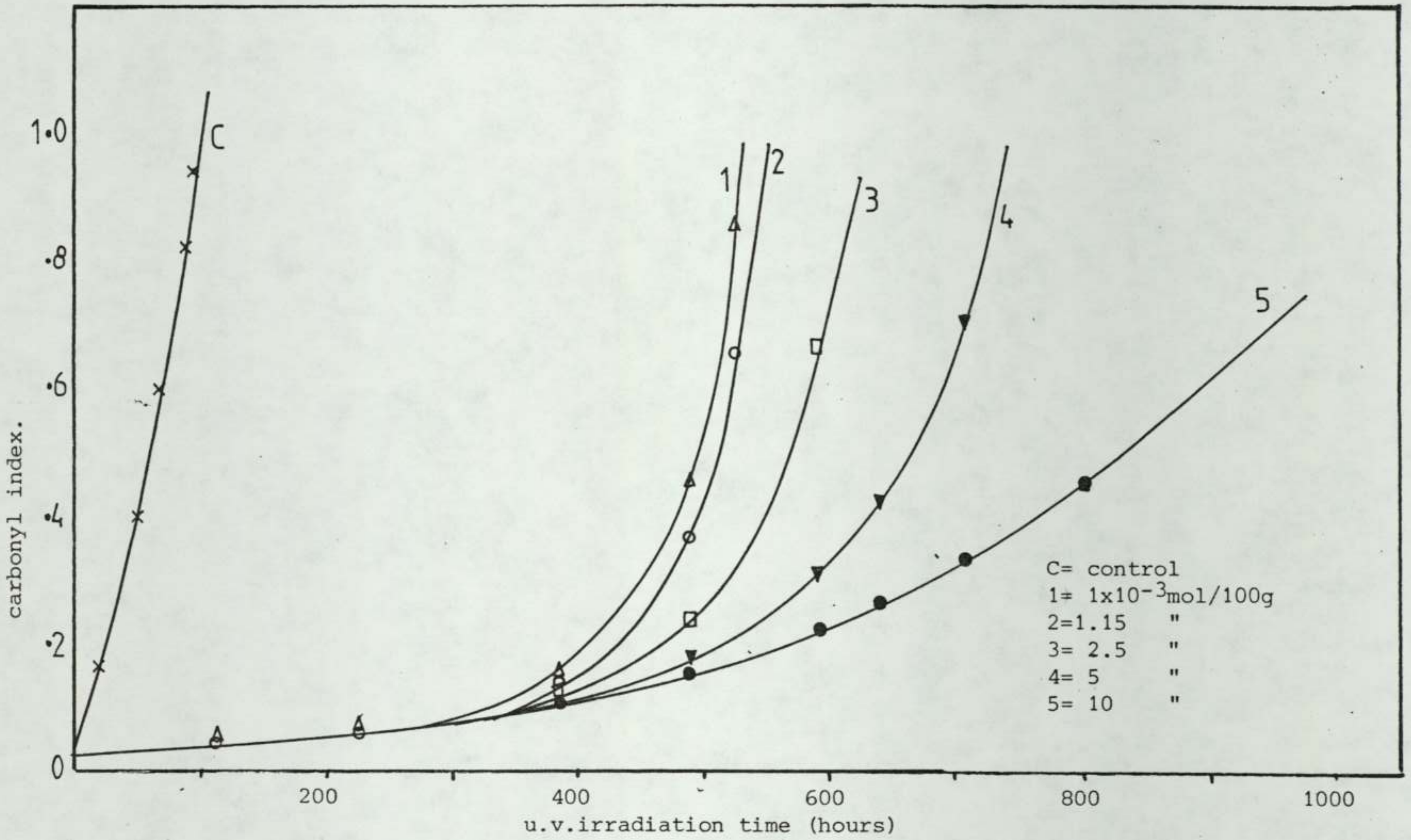


Fig. 5.25 : Effect of additive concentration on photo-oxidation of PP processed with tBuNO in a closed mixer for 10 mins. at 180°C.

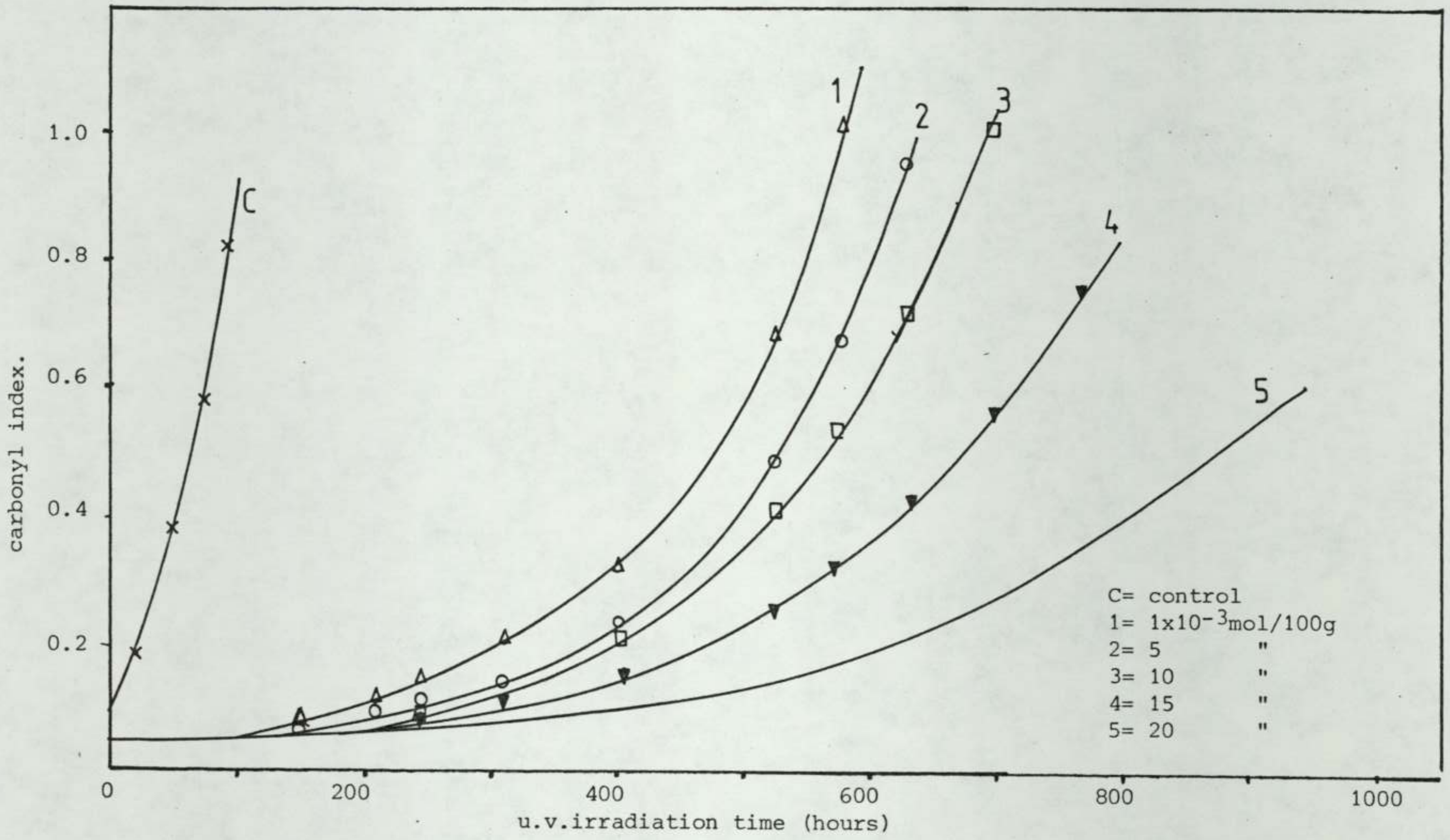


Fig. 4.26 : Effect of additive concentration on photo-oxidation of PP processed with $tBuNO_2$ in a closed mixer for 10 mins. at 180°C.

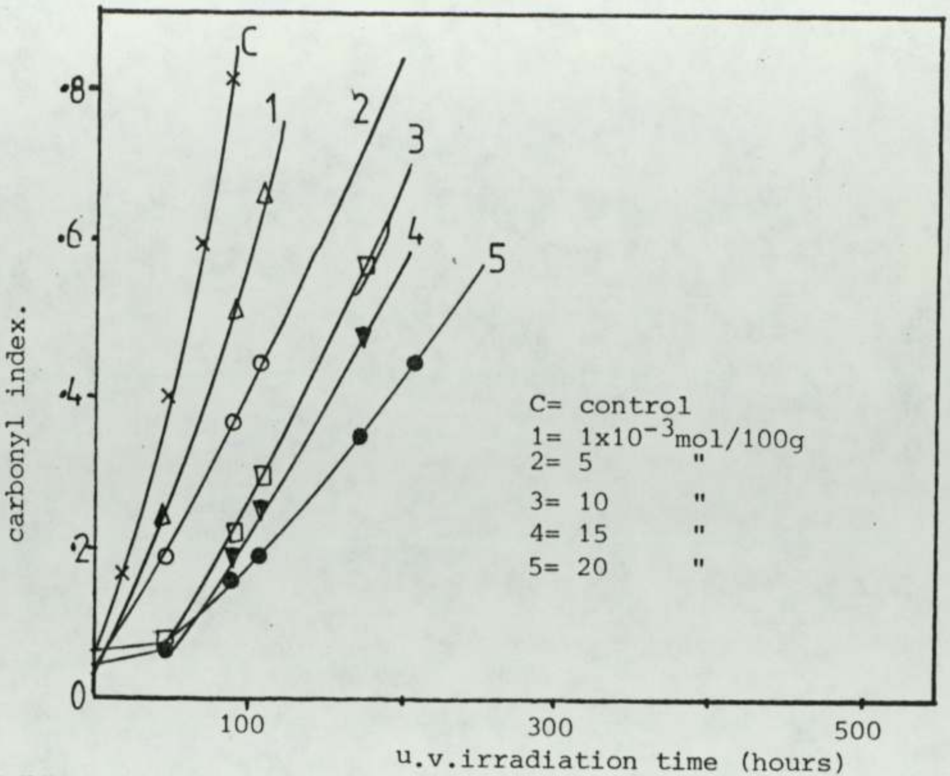


Fig 4.27 : Effect of additive conc. on photo-oxidation of PP processed with TAm in a closed mixer for 10 minsat 180° C.

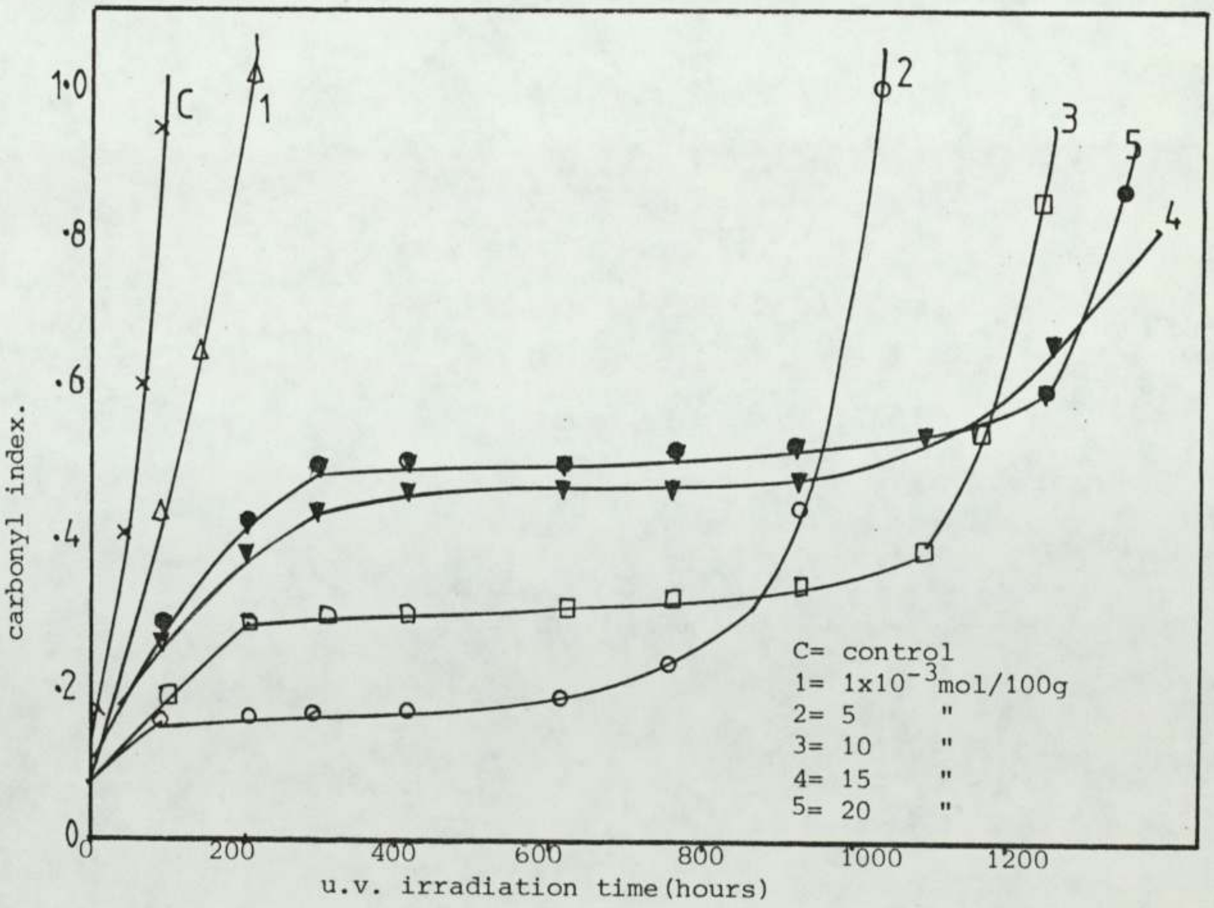


Fig 4.28 : Effect of additive conc. on photo-oxidation of PP processed with TN in a closed mixer for 10 mins. at 180°C.

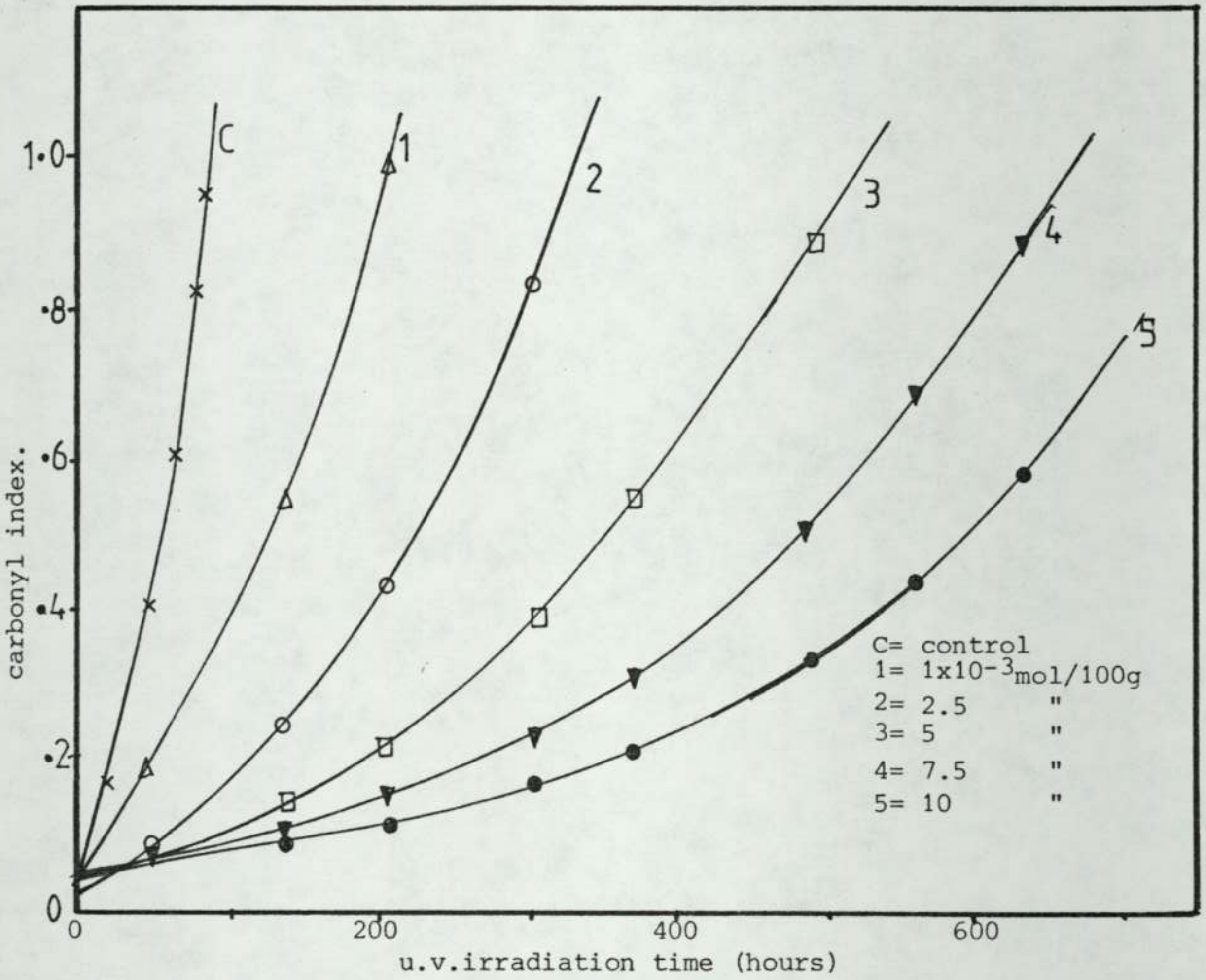


Fig. 4.29 : Effect of additive conc. on photo-oxidation of PP processed with NDPA in a closed mixer for 10 mins. at 180°C.

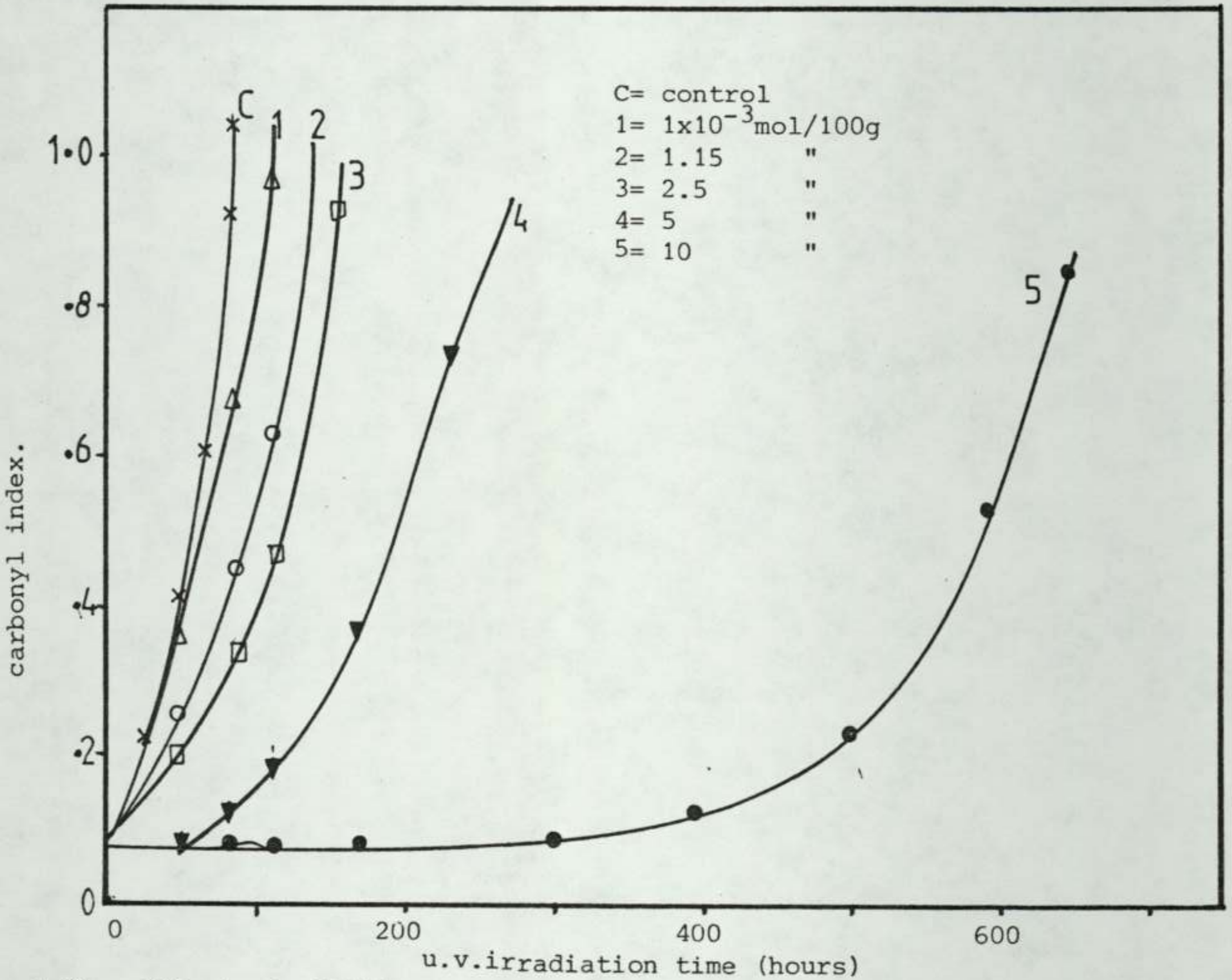


Fig. 4.30 : Effect of additive conc. on photo-oxidation of PP processed with tBuNO in an open mixer for 10 mins. at 180°C.

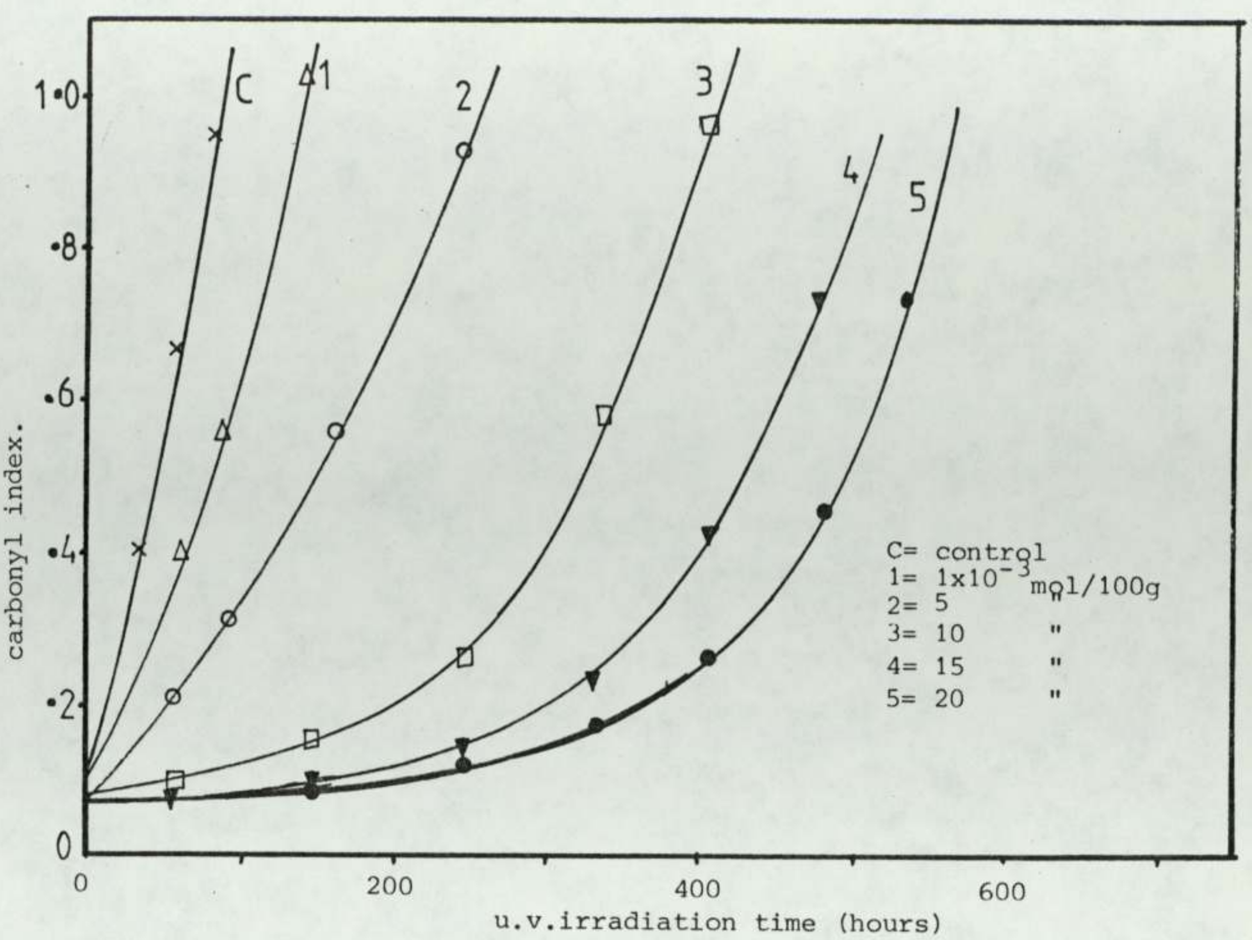


Fig. 4.31 : Effect of additive conc. on photo-oxidation of PP processed with $tBuNO_2$ in an open mixer for 10 mins. at 180°C.

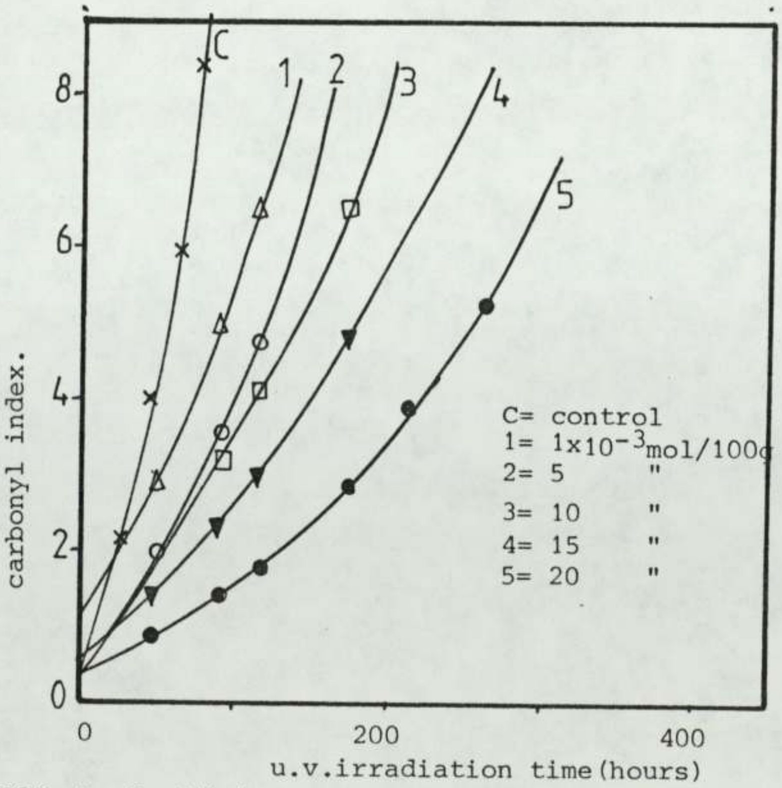


Fig. 4.32: Effect of additive conc. on photo-oxidation of PP processed with TAm in an open mixer for 10 mins. at 180°C.

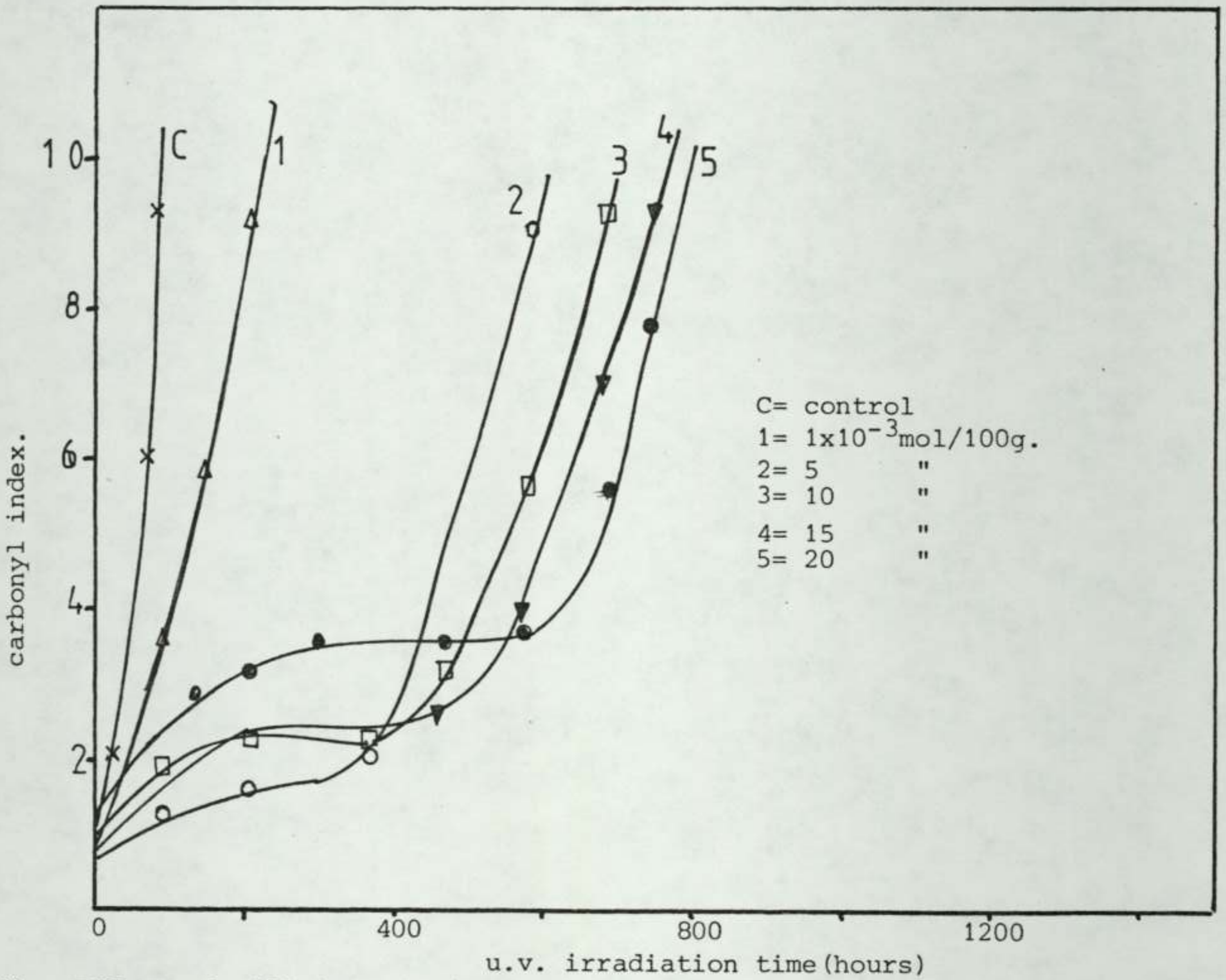


Fig. 4.33 : Effect of additive conc. on photo-oxidation of PP processed with TN in an open mixer for 10 mins. at 180°C.

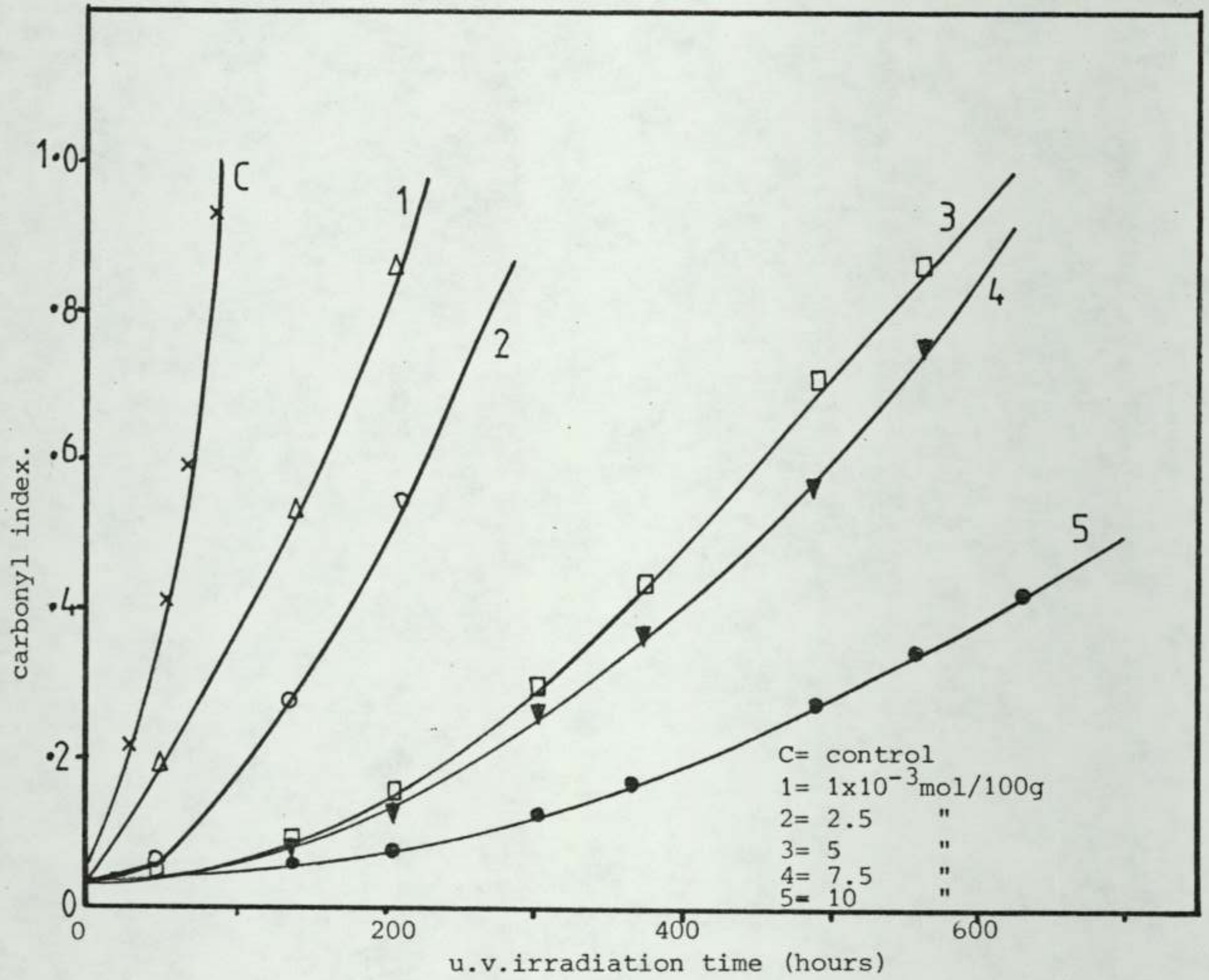


Fig. 4.34 : Effect of additive conc. on photo-oxidation of PP processed with NDPA in an open mixer for 10 mins. at 180°C.

example exists in either the dimer (solid) or monomer (liquid) form. The later predominates at high temperatures(163) (usually so above $80^{o}C$). Thus, the relatively low maximum torque of PP containing tBuNO (Fig. 4.1 - inset) may be due to a plasticising effect or its low molecular mass as the maximum torque was found to increase with increasing molecular mass of additive.

The relatively good melt stabilising activity of both tBuNO and NDPA in PP (processed in a closed mixer- Fig. 4.3) and the subsequent relatively low level of hydroperoxides in the processed samples (Fig. 4.5) suggest that they either interfere with the chain-propagation of PP during processing or that they decompose the formed hydroperoxides. The latter is less likely to be the case as results obtained from model compounds studies clearly demonstrates that even at high reaction ratio (1:1) none of the additives effectively decompose hydroperoxides (Fig. 4.35).

Electron spin resonance (e.s.r.) examinations of PP films containing tBuNO and NDPA showed signals characteristics of nitroxyl radicals as shown in Figs. 4.36 and 4.37 respectively. The signals in each case are triplets with calculated g-valves of 2.005 and 2.0046 for tBuNO and NDPA respectively and a calculated splitting factor (aN) of 16 and 1.51 which are not uncharacteristic of alkyl nitroxyl radicals(65).

The formation of nitroxyl radicals in PP containing tBuNO is almost certainly due to the 'trapping' of macro-alkyl radicals by the nitroso compound(119,152-154)(reaction 1).

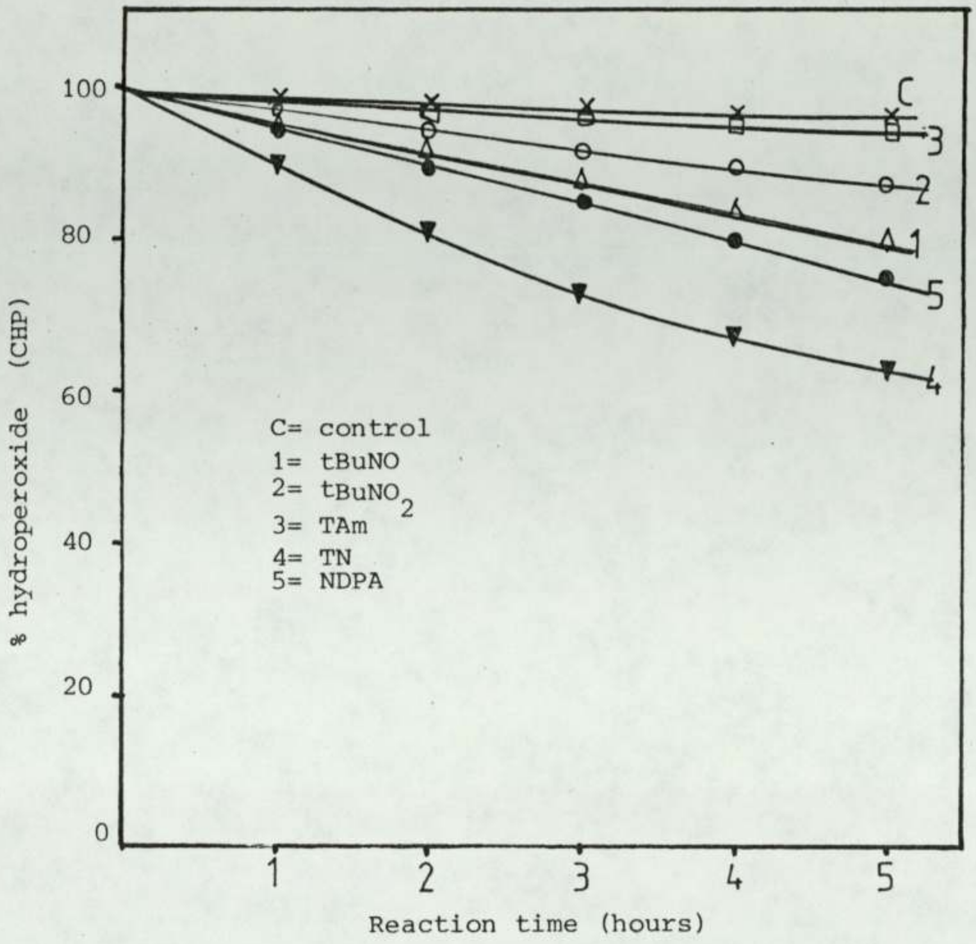


Fig. 4.35: Effect of (1)tBuNO (2)tBuNO$_2$ (3)TAm (4)TN (5) NDPA on thermal decomposition of hydroperoxide (CHP) at 110°C (reaction ratio 1:1) in chlorobenzene

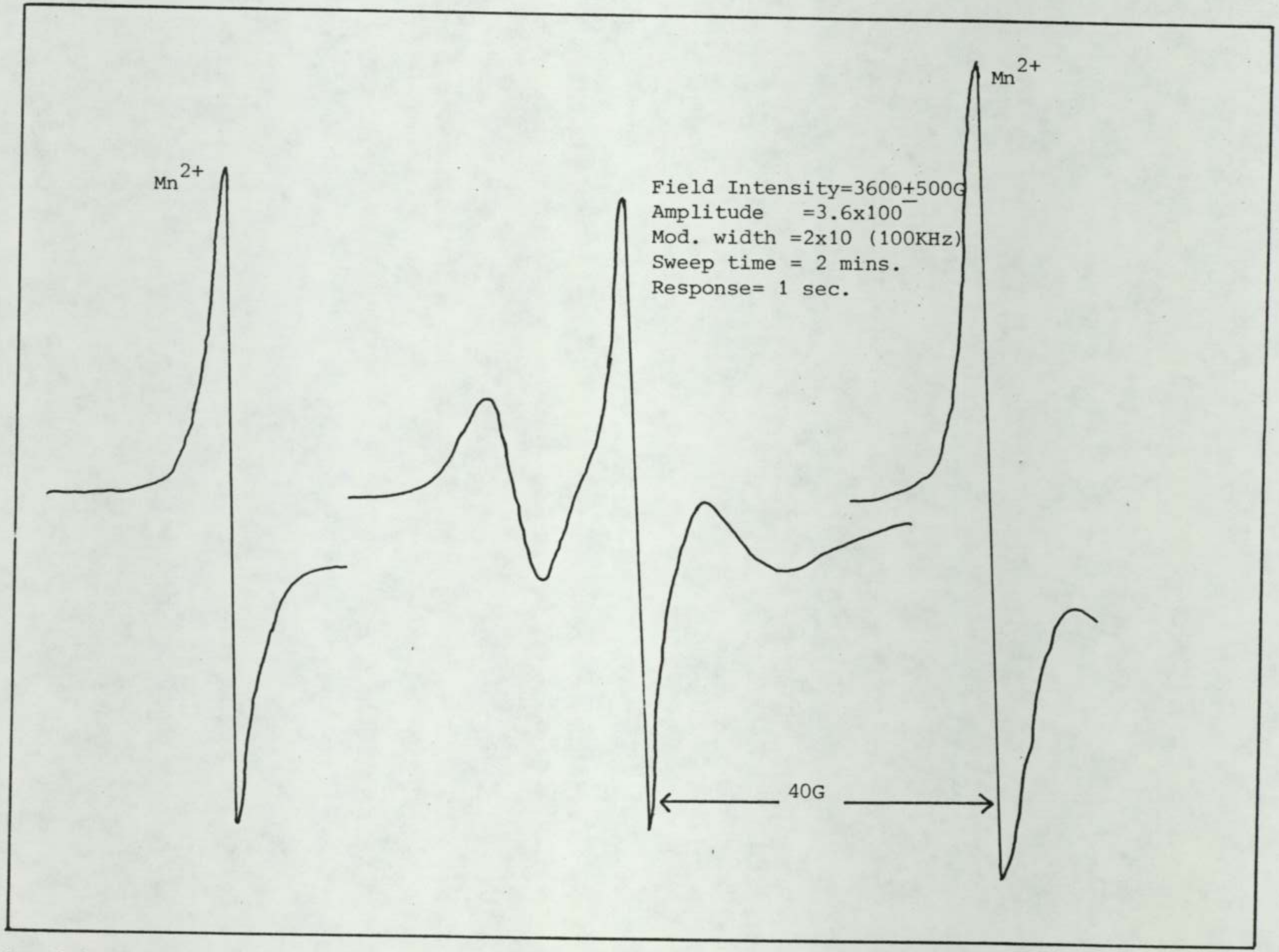
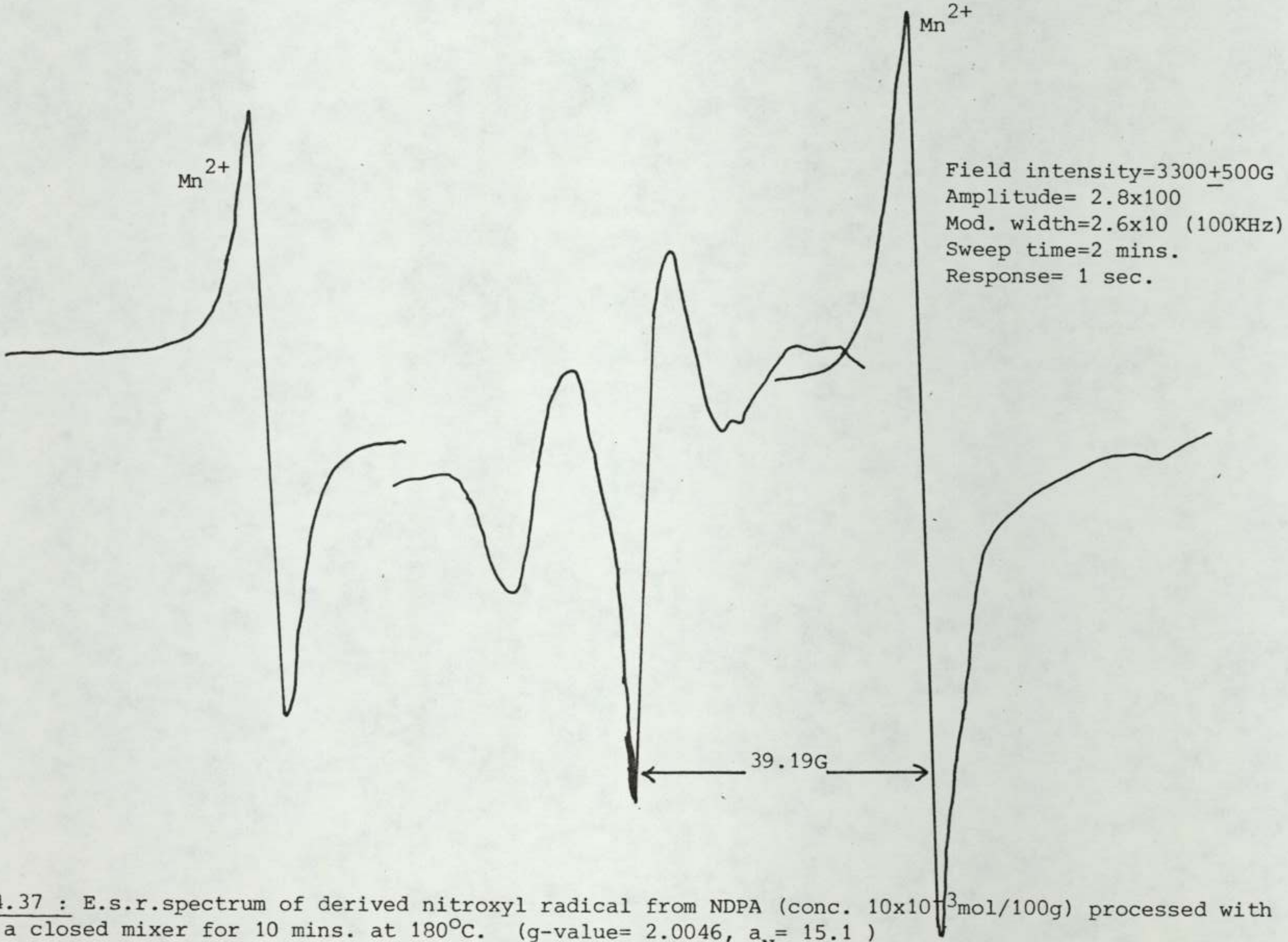
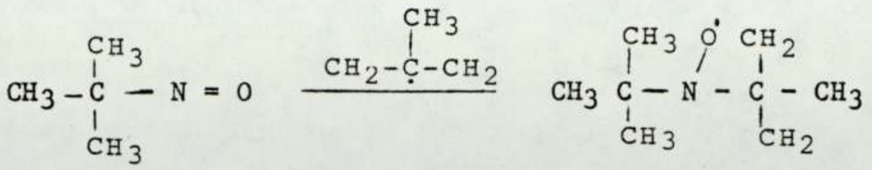


Fig. 3.36 : E.s.r.spectrum of nitroxyl radical derived from tBuNO (conc. 10×10^{-3}mol/100g)processed with PP in a closed mixer for 10 mins. at 180°C. (g-value=2.005, a_N= 16.0)



Field intensity=3300$\pm$500G
Amplitude= 2.8x100
Mod. width=2.6x10 (100KHz)
Sweep time=2 mins.
Response= 1 sec.

Fig. 4.37 : E.s.r.spectrum of derived nitroxyl radical from NDPA (conc. 10x10^{-3}mol/100g) processed with PP in a closed mixer for 10 mins. at 180°C. (g-value= 2.0046, a_N= 15.1)

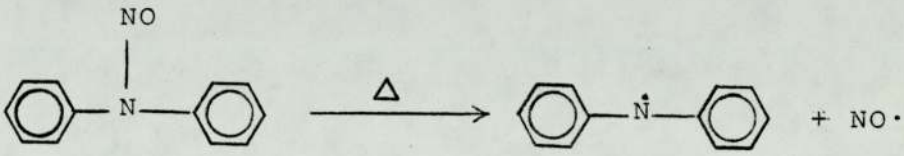


$$CH_3-\underset{CH_3}{\overset{CH_3}{C}}-N=O \xrightarrow{CH_2-\overset{CH_3}{\dot{C}}-CH_2} CH_3\,\underset{CH_3}{\overset{CH_3}{C}}-\overset{\dot{O}}{N}-\underset{CH_2}{\overset{CH_2}{C}}-CH_3$$

-(1)

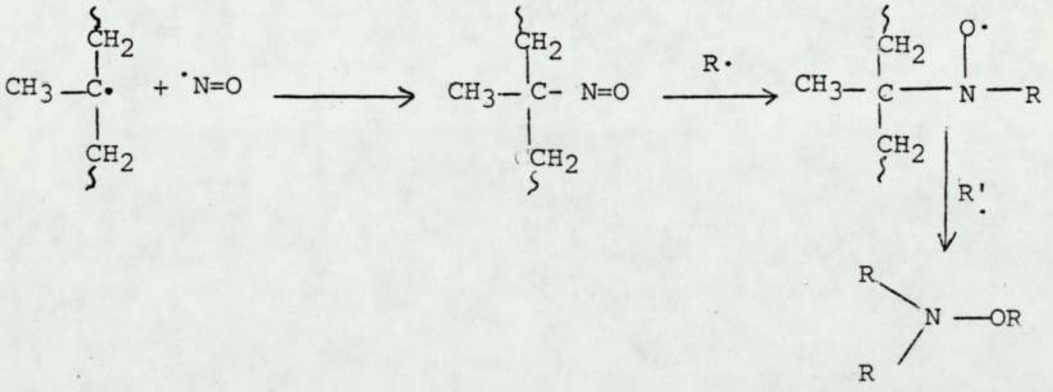
The derived nitroxyl is stable and thus detectable, and can also 'trap' more alkyl radicals to give alkyl hydroxylamines.(121)

In the case of NDPA, literature suggests(125,161,162,164) that the N-NO bond cleaves to give nitric oxide radicals and an imino radical.



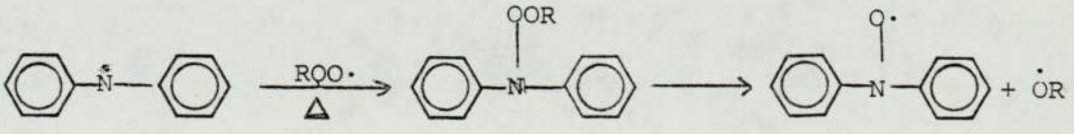
-(2)

The produced nitric oxide radical may react with an alkyl radical to form the nitroso derivative(121) then nitroxyl radical and eventually alkyl hydroxylamine derivative as shown in reaction (3).



- (3)

Although it was thought(165,166) that the imino radical produced in reaction (2) could scavenge alkyl peroxyl radicals (ROO$^\cdot$), thus furnishing nitroxyl and alkoxyl radicals under heat (reaction 4), evidence here does not support this, since the diphenyl nitroxyl radical thereby produced will have a characteristic splitting factor(aN) of 28-29(167).



-(4)

The splitting factor obtained here (15.1) is in agreement with a nitric-oxide- derived radical(168,169) (see reaction 3).

Fig. 4.38 shows the concentration of the derived nitroxyl radical with processing time for PP containing 5 x 10^{-3}mol/100g of tBuNO and of NDPA. The decrease in concentration with increasing processing time may be due to the ability of the initially formed radical to 'trap' alkyl radicals thus reducing the nitroxyl concentration in the system. Additionally, the eventual consumption of the initially added introso compound and produced nitric oxide (in reactions with macro-alkyl radicals) may account for the decrease since new nitroxyls are not being formed.

There is a correlation between the nitroxyl radical concentration and processing time (in a closed mixer - fig. 4.38) and the u.v. embrittlement time with processing (Fig. 4.7) which suggests that the derived nitroxyl radical is responsible for photostabilisation of PP as concentration of nitroxyl radicals decreases with u.v. irradiation time (with increasing carbonyl formation) in both PP films containing tBuNO and NDPA (Fig. 4.39). There is also a correlation between the concentration of the derived nitroxyl radical with additive concentration (Fig. 4.40) and the u.v. embrittlement times with additive concentration (Fig. 4.21).

Although small concentrations of the nitro analogue has been reported(25) in PP processed with tBuNO (upon hot soxhlet extraction after processing) there is no evidence that its contribution to the overall photostability of PP is of any significance. A decrease in nitroxyl radical concentration in PP films containing tBuNO and NDPA after extraction (dichloromethane, 35°C) was observed (Fig. 4.38). This

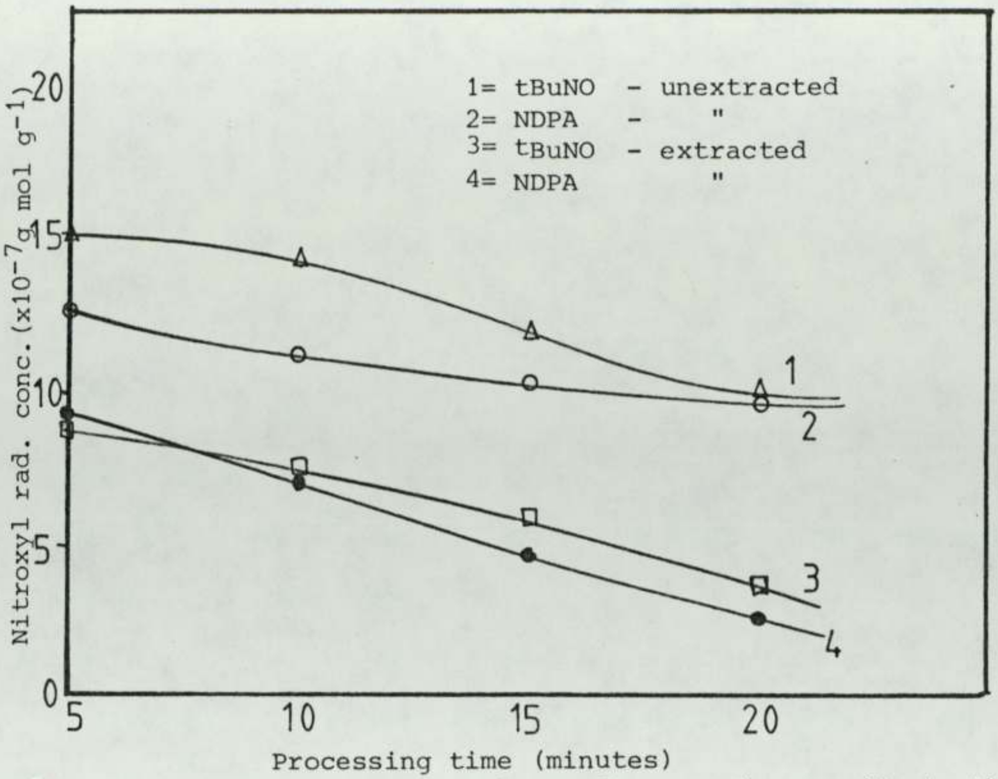


Fig. 4.38 : Effect of processing time and extraction on (derived) nitroxyl conc.in PP processed with 5×10^{-3}mol/100g of tBuNO and NDPA in a closed mixer at 180°C. (extr. in dichloromethane, 35°C)

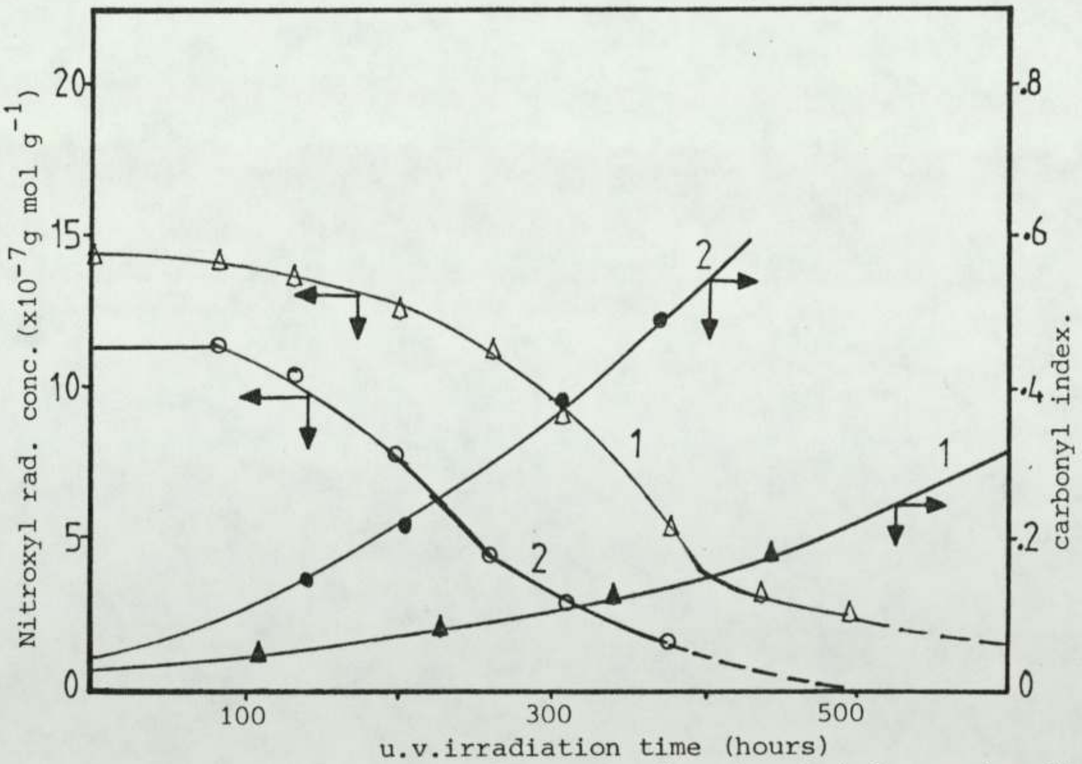


Fig. 4.39: Dependence of nitroxyl conc. and carbonyl index on irradiation time of PP processed with 5×10^{-3}mol/100g of (1) tBuNO (2)NDPA in a closed mixer for 10 mins. at 180°C.

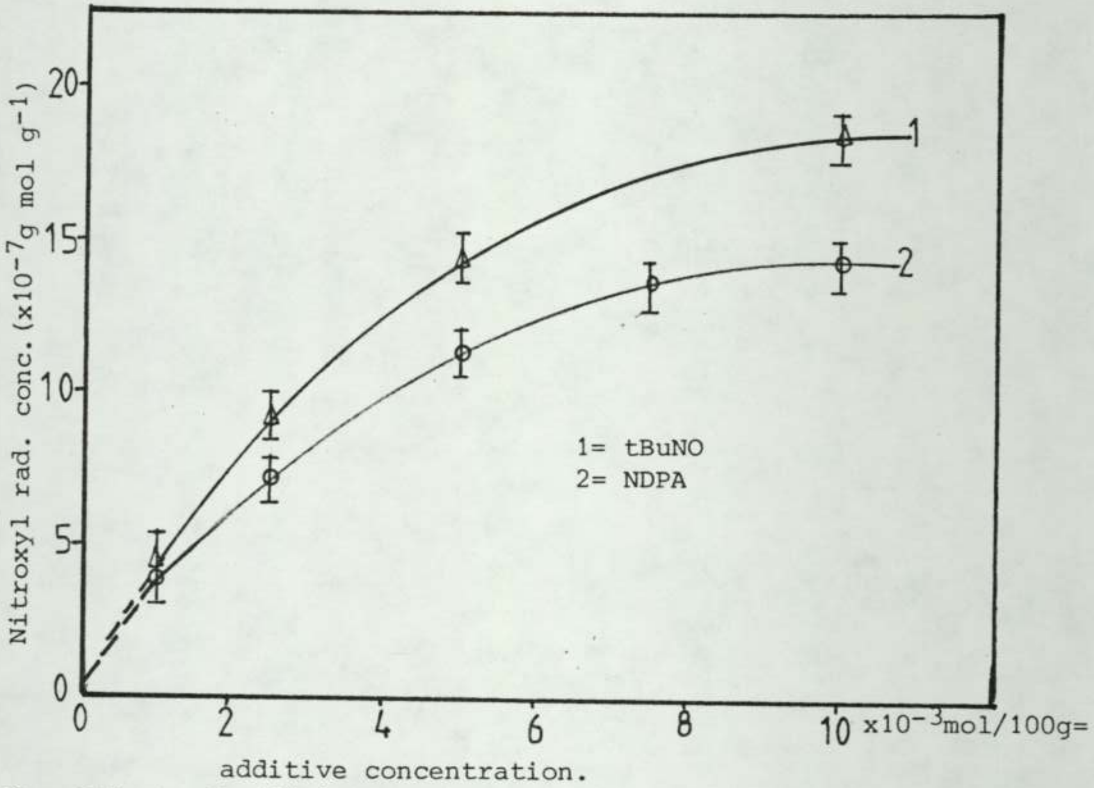


Fig 4.40 : Effect of additive conc. on nitroxyl rad. concentration in PP processed with (1) tBuNO (2) NDPA in a closed mixer for 10 mins. at 180^{o}C.

may be due to the removal of unbound radicals derived from the reaction of the nitroso and nitric oxide radicals with small alkyl radicals.

From reactions 1 and 3, it would be expected tht NDPA would be a better photostabiliser than tBuNO as each molecule of NDPA can scavenge three equivalents of alkyl radicals giving an alkylated hydroxylamine compared to two in tBuNO but results obtained show that tBuNO at the same molar concentration is a better photostabiliser. This is probably due to low stability of the nitric oxide radical or its volatility as it may be given off as brown fumes(160) - (faintly noticeable immediately after processing). The imino radicals on the other hand may dimerise, which may be responsible for the intense colouration observed in PP after processing.

PP containing $tBuNO_2$ did not give any signal in e.s.r. This contradicts some observations(170,171) that nitro compounds react with alkyl radicals through a mechanism of nitroso formation and subsequent formation of nitroxyl radicals. It is probably this non interference with alkyl radicals that accounts for the hydroperoxide formation with increasing processing time (Fig. 4.5). However, nitro compounds are generally thermally stable(173) at temperatures up to 200°C which probably accounts for the observed absorption in infra-red (in PP containing $tBuNO_2$) at 1540 cm^{-1} corresponding to a nitro group absorption (Fig. 4.41) which is concentration dependent and may be responsible for the increased photostabilisation of PP with increasing concentration (Fig. 4.21)

Under photo irradiation, nitro compounds are known to dissociate into free radicals as a primary reaction(27).

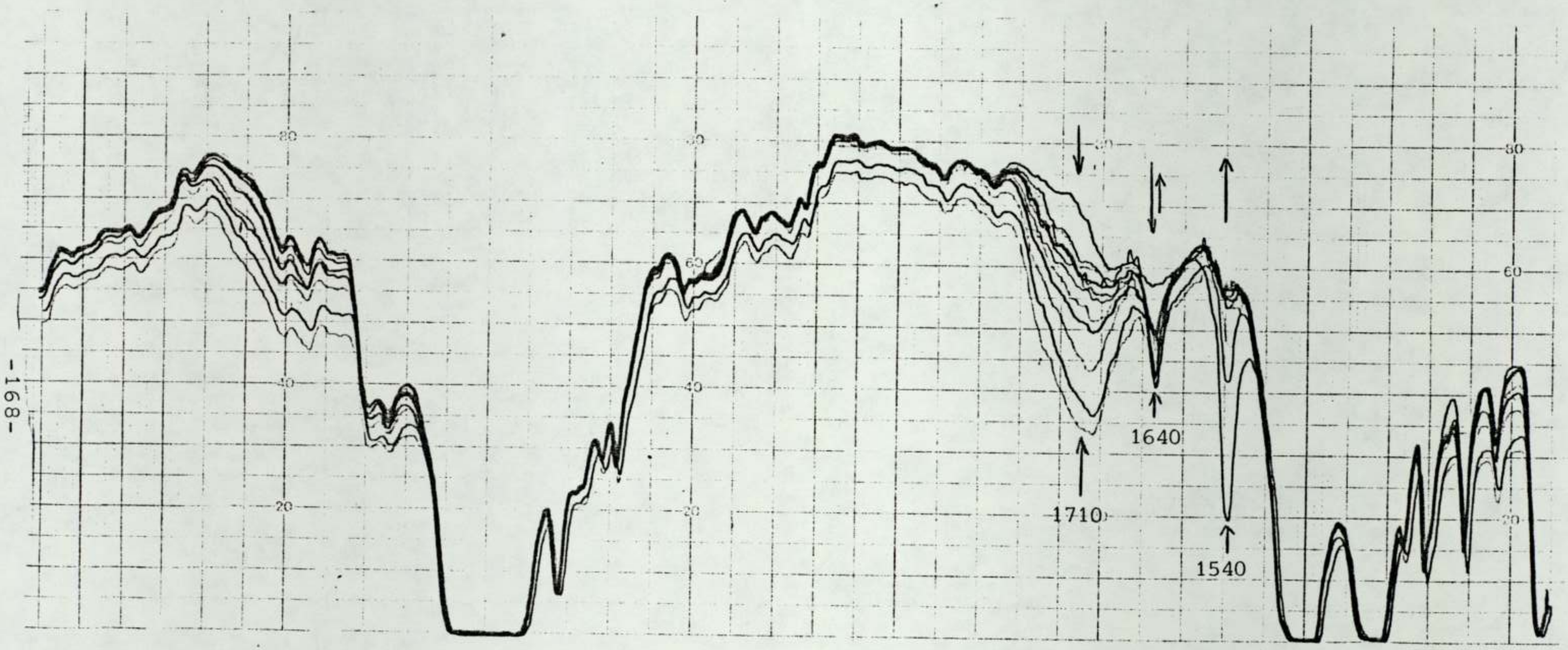


Fig. 4.41 : A typical spectral change (with u.v.irradiation) in PP processed with 15×10^{-3}mol/100g of $tBuNO_2$ in a closed mixer at 180°C for 10 minutes.

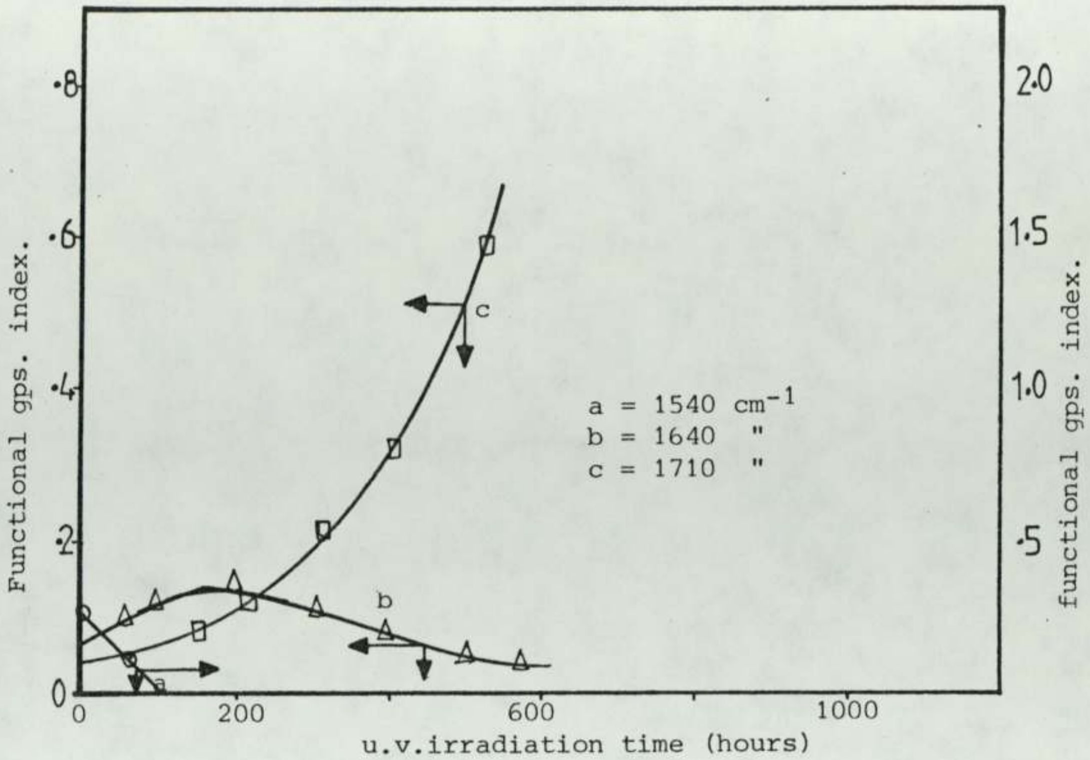


Fig. 4.42. Dependence of functional groups on irradiation time of PP processed with 1x10^{-3}mol/100g of tBuNO$_2$ in a closed mixer for 10 mins. at 180°C.

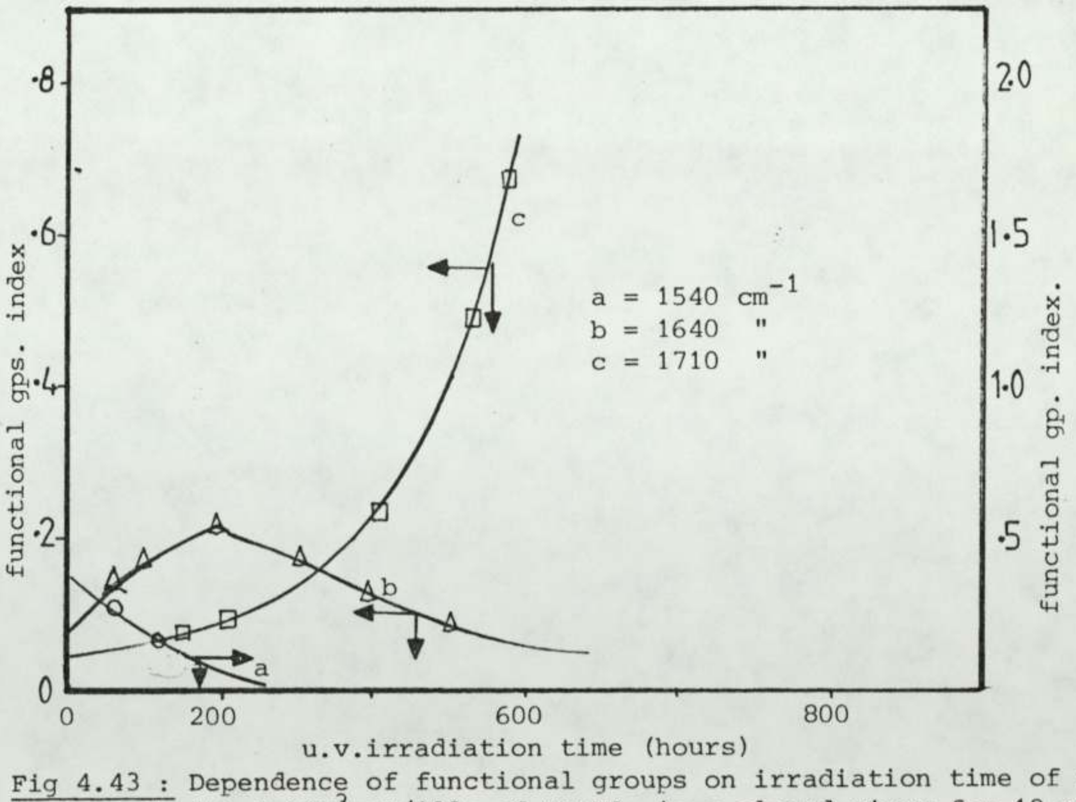


Fig 4.43 : Dependence of functional groups on irradiation time of PP processed with 5x10^{-3}mol/100g of tBuNO$_2$ in a closed mixer for 10 mins. at 180°C.

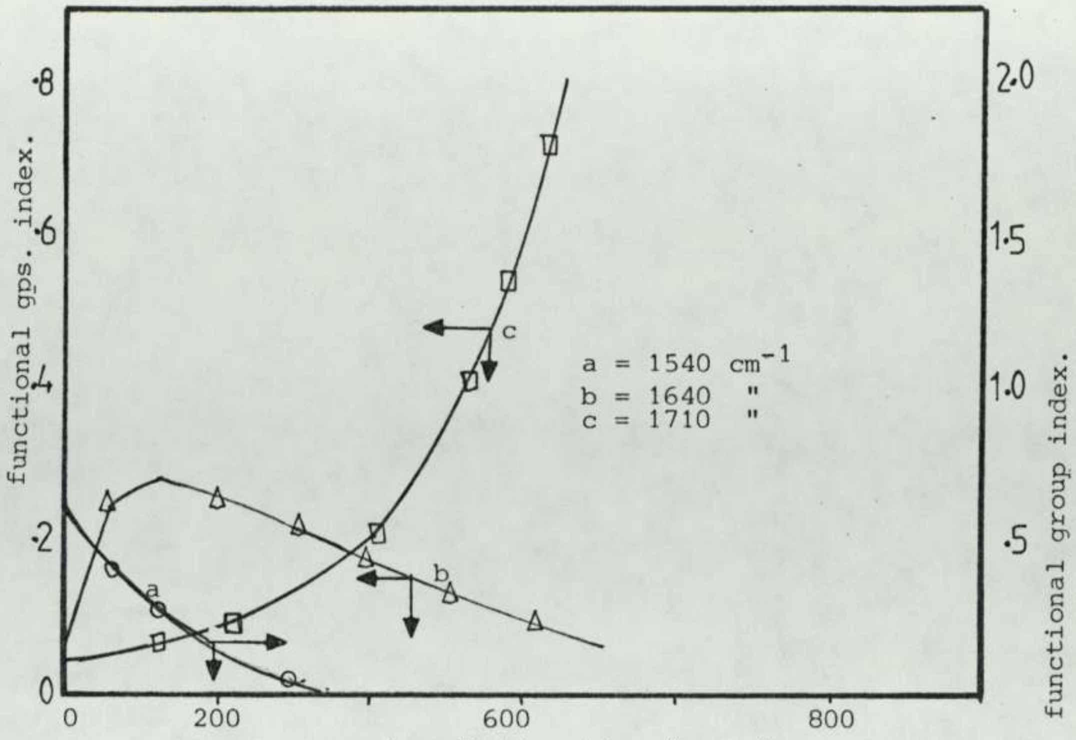


Fig. 4.44 : Dependence of functional groups on irradiation time of PP processed with 10x10^{-3}mol/100g of tBuNO$_2$ in a closed mixer for 10 mins. at 180°C.

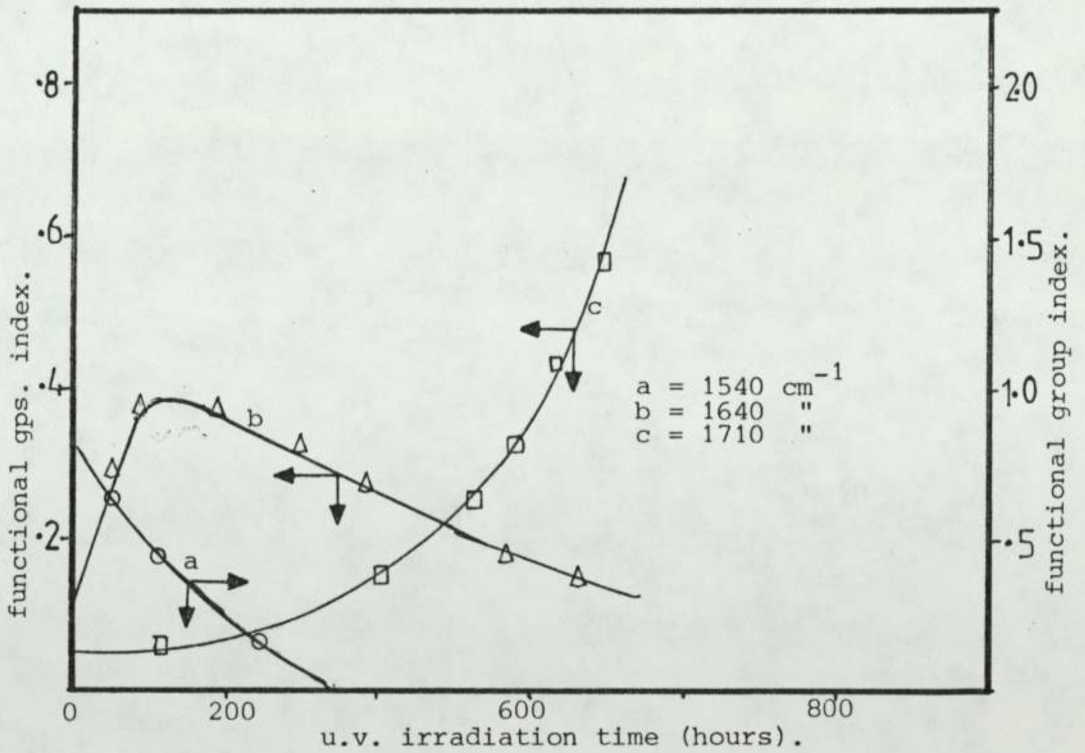


Fig 4.45 : Dependence of functional groups on irradiation time of PP processed with 15x10^{-3}mol/100g of tBuNO$_2$ in a closed mixer for 10 mins. at 180°C.

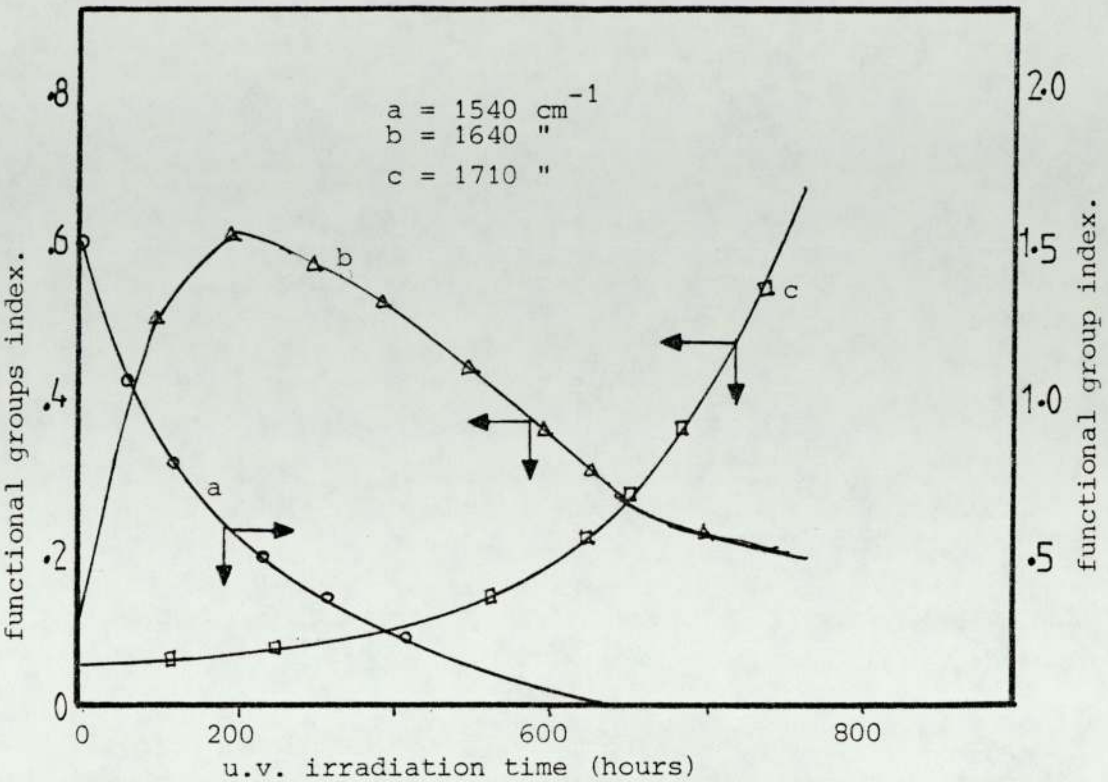


Fig. 4.46 : Dependence of functional groups on irradiation time of PP processed with 20x10^{-3}mol/100g of tBuNO$_2$ in a closed mixer for 10 mins at 180°C.

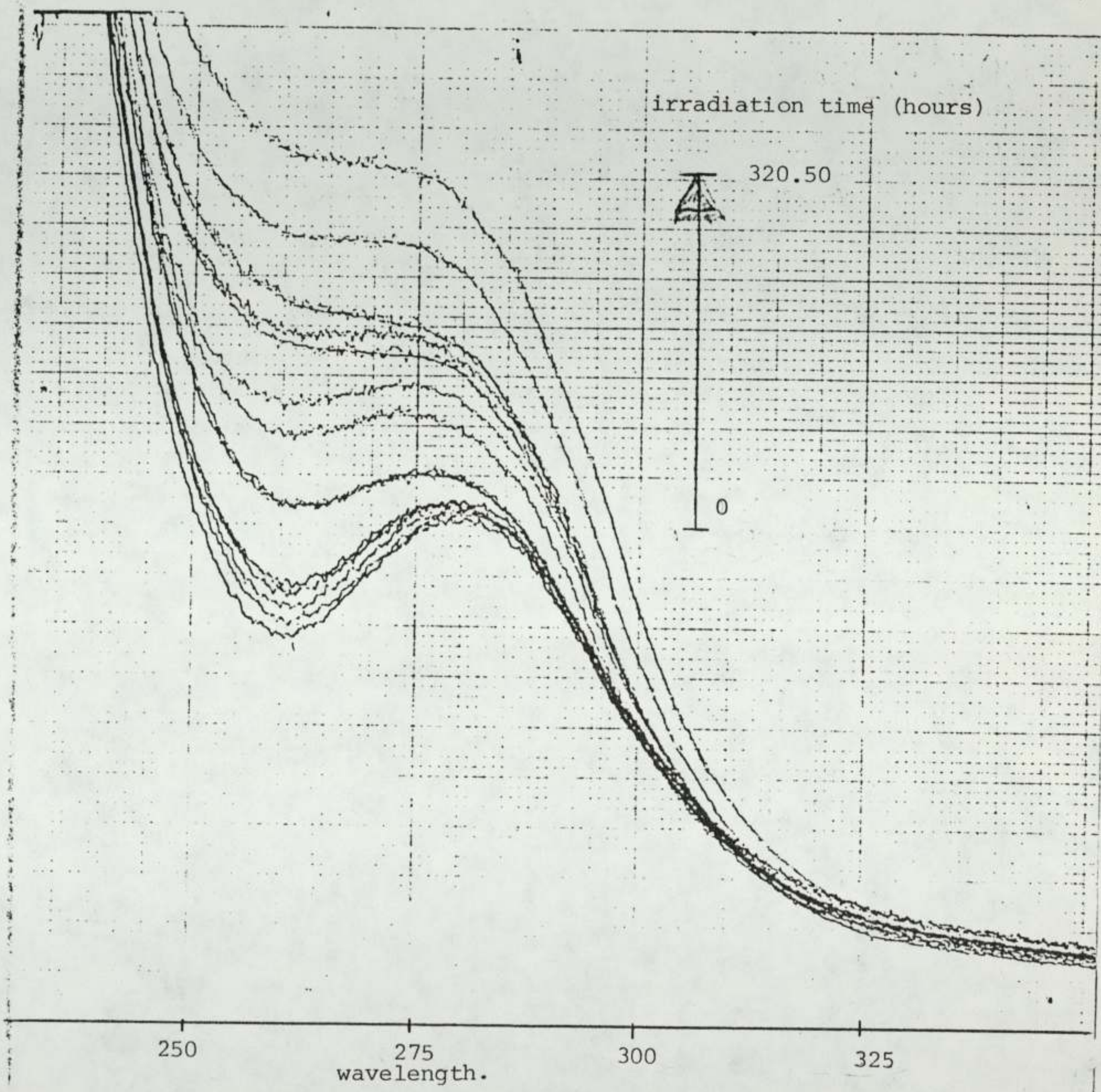


Fig. 4.47 : U.V. absorbance of tBuNO$_2$ (4x10^{-2}M) in hexane with u.v. irradiation time.

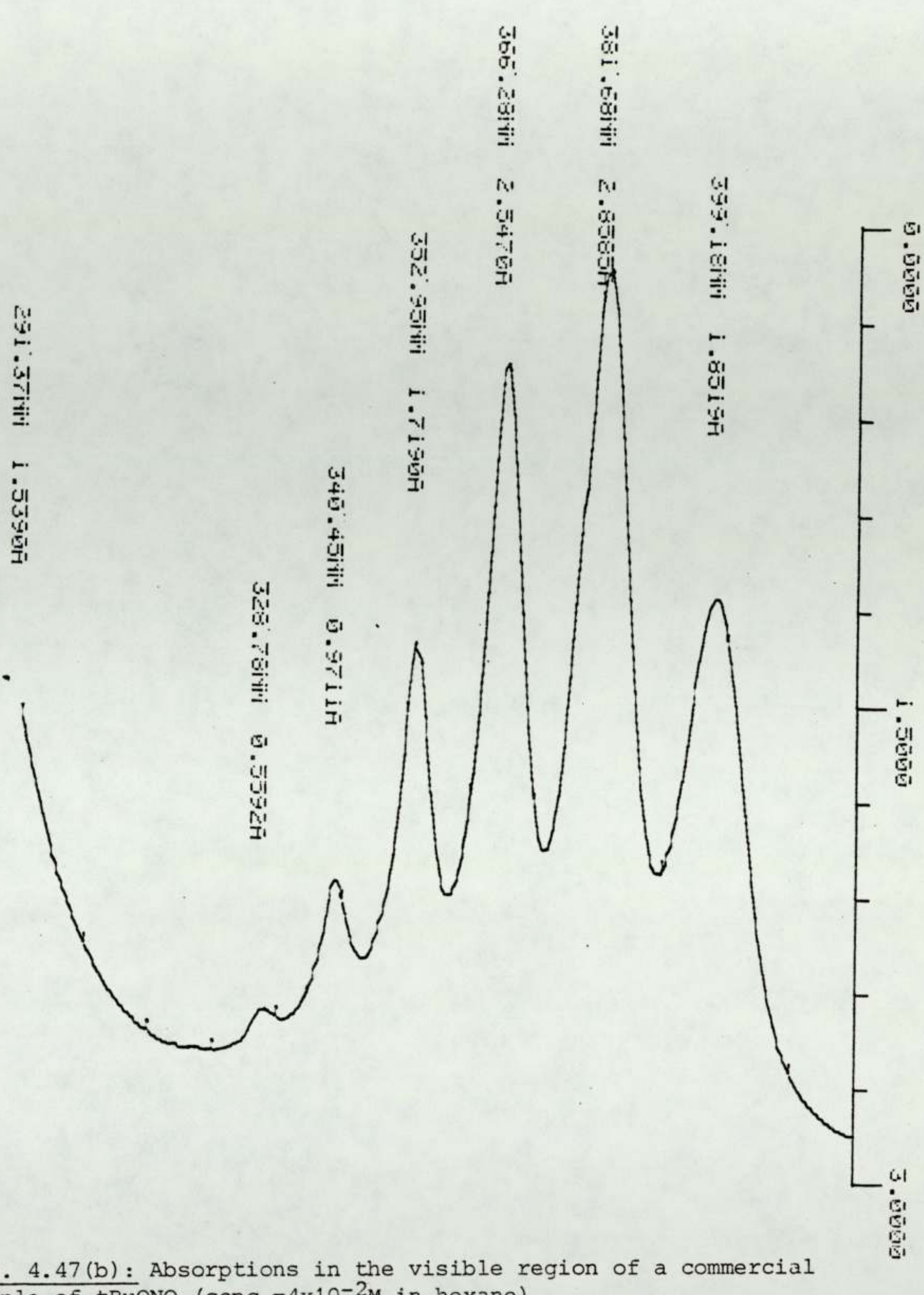


Fig. 4.47(b): Absorptions in the visible region of a commercial sample of tBuONO (conc.=4×10^{-2}M in hexane)

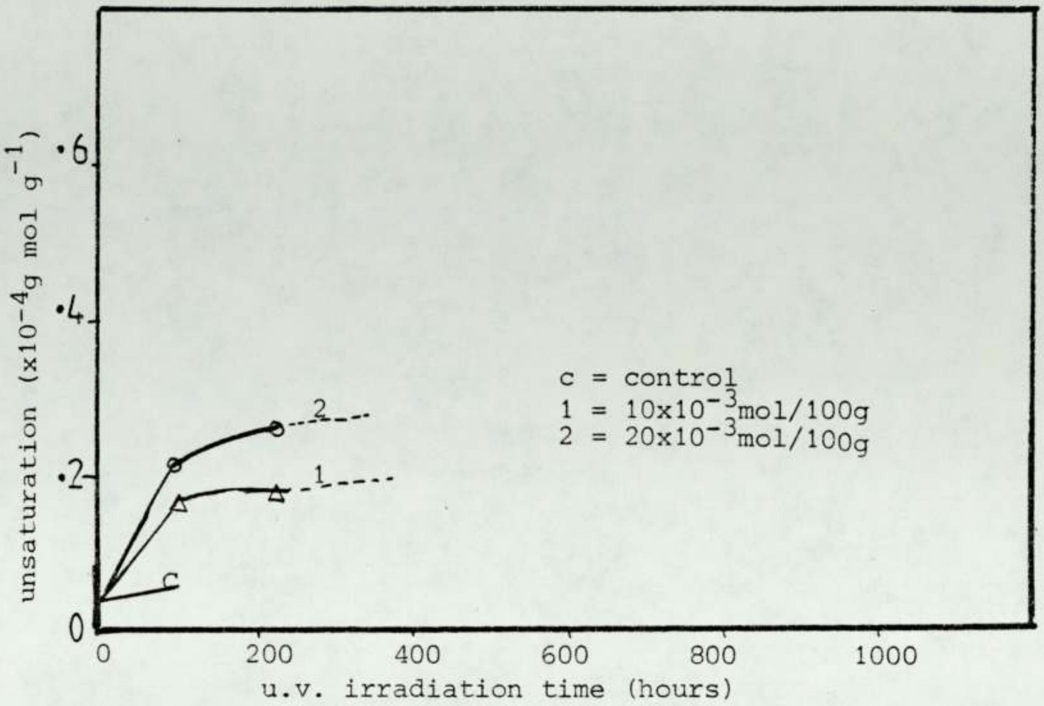


Fig. 4.48 : Dependence of unsaturation (chemical determination) on irradiation time of PP processed with (1) $10x10^{-3}$mol/100g (2) $20x10^{-3}$mol /100g of $tBuNO_2$ in a closed mixer for 10 mins. at 180°C.

$$RNO_2 \xrightarrow{hv} R^{\cdot} + NO_2 \qquad -(5)$$

$$\text{e.g. } (CH_3)_3\ CNO_2 \xrightarrow{hv} (CH_3)_3\ C^{\cdot} + NO_2 \qquad -(6)$$

Recombination of the free radicals may then follow to give the corresponding nitrites(174) which under photo-oxidative conditions give the corresponding nitrates(175).

$$R. + NO_2 \xrightarrow{hv} RONO \xrightarrow[O_2]{hv} RONO_2 \qquad -(7)$$

$$\text{e.g.} (CH_3)_3\ C.+NO_2 \xrightarrow{hv} (CH_3)_3\ CONO \xrightarrow[O_2]{hv} (CH_3)_3\ CONO_2 \qquad -(8)$$

In all samples containing $tBuNO_2$ (e.g. Fig. 4.41) the formation of a new functional group which absorbs in infra-red at 1640 cm^{-1} under photo-irradiation suggested that nitrite/nitrate formation may have occured in the polymer as nitrates absorbs in infra-red in this region(177). Thus, as shown in Figures 4.42 - 4.46 as the nitro index ($1540cm^{-1}$) decreases, the new functional group ($1640cm^{-1}$) increases until a maximum is reached and then followed by a decrease while the carbonyl index increases. But although $tBuNO_2$ absorbs u.v. light (in solution) in the region 270-280 nm (Fig. 4.47) due to its n → n* transition(176), the corresponding nitrite was found to absorb in the visible region (Fig. 4.47b) and the nitrate is not known to absorb above 310 nm(175). Hence the small shift in the u.v. absorbance of $tBuNO_2$ in solution (Fig. 4.47) towards shorter wavelength (under u.v. irradiation) accompanying an increased absorption may be due to possible nitrate formation; and the subsequent reduction in the i.r. absorption at 1640 cm^{-1} (Fig. 4.41) may be due to the volatilisation or decomposition of the nitrate.

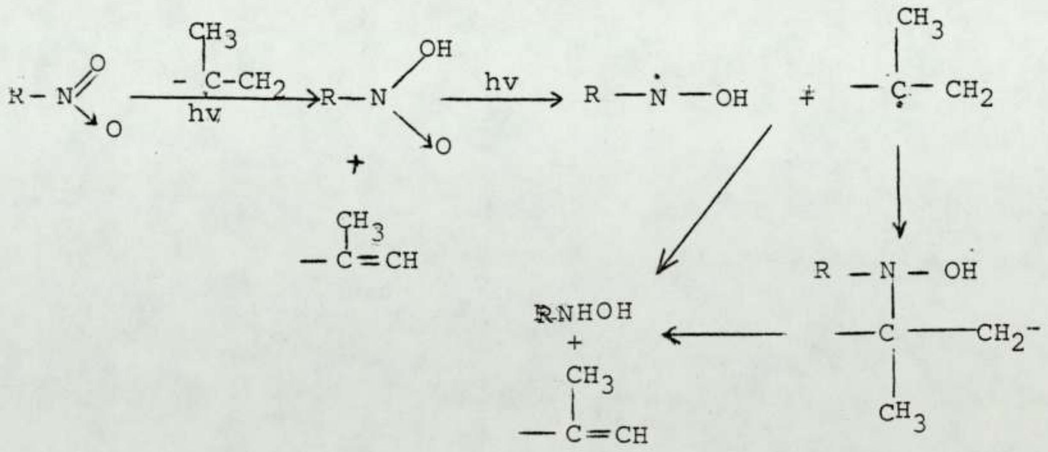
However, the absorbance at $1640\mathrm{cm}^{-1}$ must be partly due to olefinic unsaturation (which may also absorb in this region(177)) as it was found that in PP film containing 10×10^{-3}mol/100g of $\mathrm{tBuNO_2}$ for example, when irradiated in u.v. light (about 100 hours) unsaturation determined by chemical method (See Chapter 2) was found to increase from 0.04 to 0.07×10^{-4}g mol g^{-1}. (Fig. 4.48) hence photostabilisation is almost certainly by a mechanism involving unsaturation formation.

Under photo-irradiation, nitro compounds may undergo N-O bond cleavage as well as hydrogen abstraction(174) as in reactions 9 and 10.

$$\mathrm{RNO_2} \xrightarrow{h\nu} \mathrm{RNO} + \mathrm{O}^{\bullet} \qquad -(9)$$

$$\mathrm{RNO_2} + \mathrm{R'H} \xrightarrow{h\nu} \mathrm{RNO_2H} + \mathrm{R'}. \qquad -(10)$$

These could not be photo-stabilising reactions in themselves as alkyl radicals and elemental oxygen are formed, but a combination of both reactions in the polymer may be responsible for photostabilisation as in the following scheme.



The probable evidence for this mechanism ultimately lies in the unsaturation formation during photo irradiation.

TN has a little effect on melt stabilisation (FIg. 4.3) and hydroperoxide formation in PP (Fig. 4.5) during processing but does not effectively decompose hydroperoxide thermally (Fig. 4.35). The decrease in embrittlement time with processing time (up to 15 minutes) in PP continuing TN (Fig. 4.7) processed in the closed mixer may indicate chain scission with processing followed by cross linking at 20 minutes. TN is known(159,172) to decompose under heat usually giving formaldehyde and nitroparaffin.

$$(HOCH_2)_3CNO_2 \xrightarrow{\Delta} 3HCHO + CH_3NO_2 \qquad -(11)$$

The extent to which this decomposition occurs, and the concentration of the products relative to that of TN is not clear. (Formaldehyde was given off during processing - recognised by smell). These decomposition products may be responsible for the increased photostability of PP (probably due to cross linking) at later stages of processing (e.g. 20 minutes Fig. 4.7). Indeed, TN is known to enhance cross linking in polymer systems(157).

As in the case in $tBuNO_2$, an infra-red absorption at 1540 cm^{-1} in PP containing TN (Fig. 4.49) indicate the presence of a nitro group (either due to TN or a derived product) in the polymer matrix. As shown in Fig. 4.50, TN and a possible decomposition product (nitro-methane) both absorb in u.v. in the same region 275nm (in solution) but the TN absorbance is more intense than that of nitromethane at the same molar concentration.

TN may gradually furnish formaldehyde (even at room temperature, hence its use as embalming fluid)(172), thus the initial rapid carbonyl

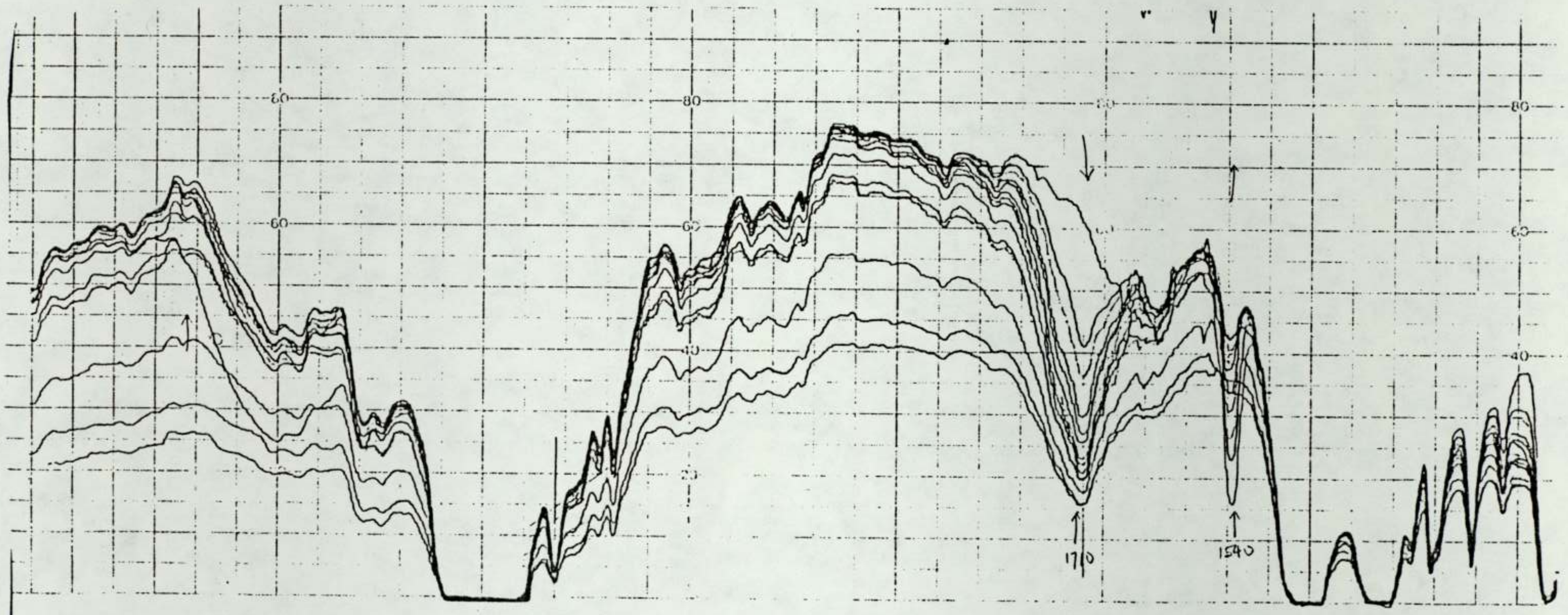
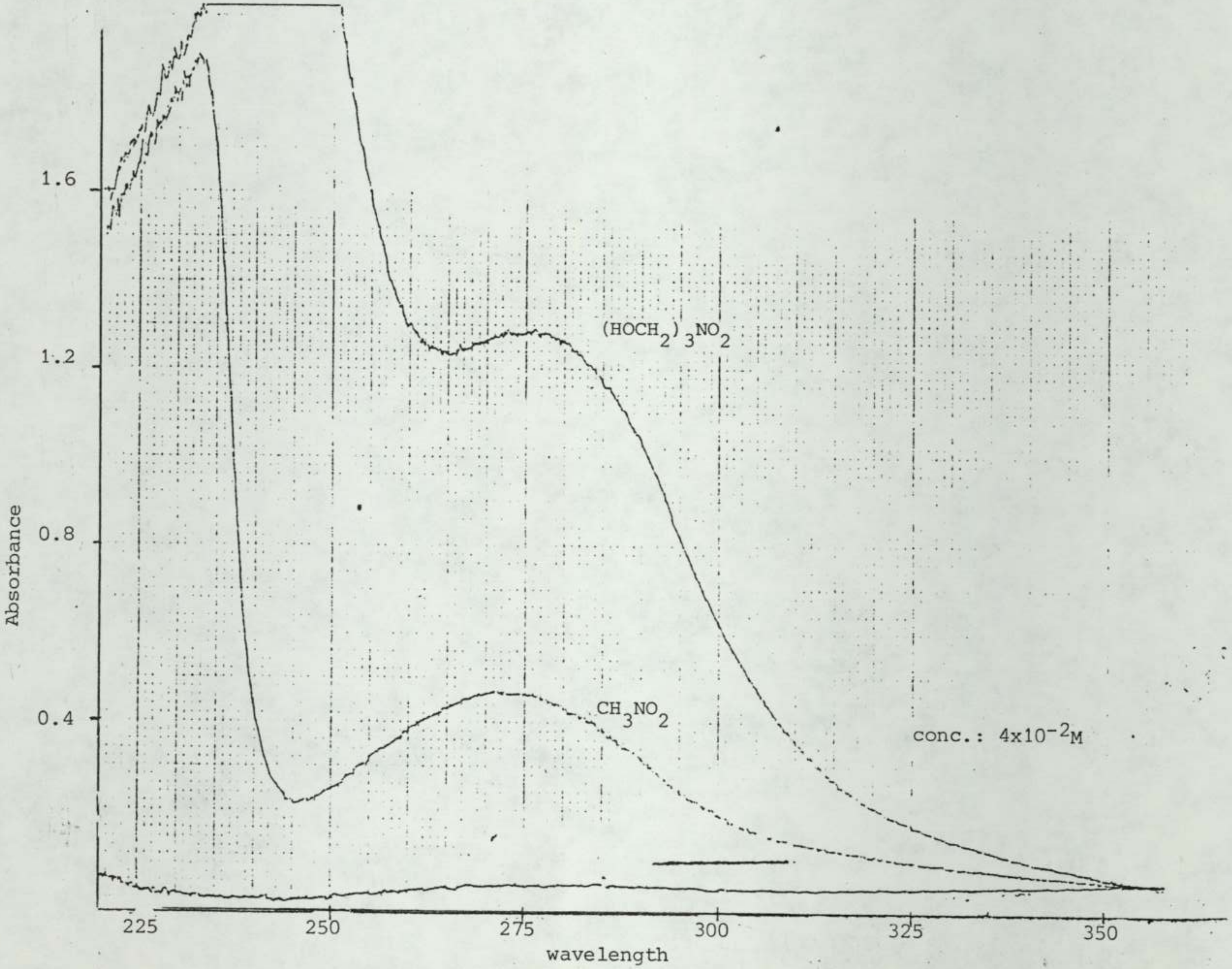


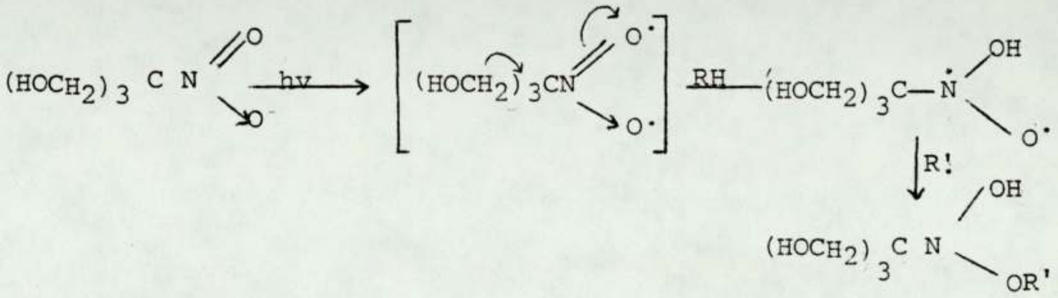
Fig. 4.49 : A typical spectral change (with u.v irradiation in PP processed with 15×10^{-3} mol/100g of TN in a closed mixer at 180°C for 10 minutes.



<u>Fig. 4.50 :</u> u.v. absorbances of TN and Nitromethane in hexane at room temperature.

growth in PP containing TN (e.g. Fig. 4.28) with photo-irradiation (which is concentration dependent) may actually be due to the released formaldehyde and not within the polymer matrix as this initial carbonyl growth does not seem to affect the overall photostability of PP containing TN.

During photo-irradiation, there was no observed formation of any new functional group; and it did not give any signal in e.s.r. Photostabilisation may be through the excitation of TN to its triplet state as shown in the reaction scheme below.



U.v. absorption/screening by TN may also contribute, though marginally to PP photostability as the photostability of unstabilised PP was found to increase from an embrittlement time of 90 hours to about 160 hours (Fig. 4.51) when screened with PP film containing 20×10^{-3} mol/100g of TN.

Like in $tBuNO_2$ and TN, PP films containing TAm gave no signals in e.s.r, thus no nitroxyl radical was produced unlike in the case of secondary amines. TAm is thermally stable(156) up to temperatures of about 200°C. There is no evidence however that it interferes in the radical-chain propagation of PP during thermal processing as indicated by the high concentration of hydroperoxide build-up with processing time (Fig. 4.5) and neither is there evidence that it decomposes

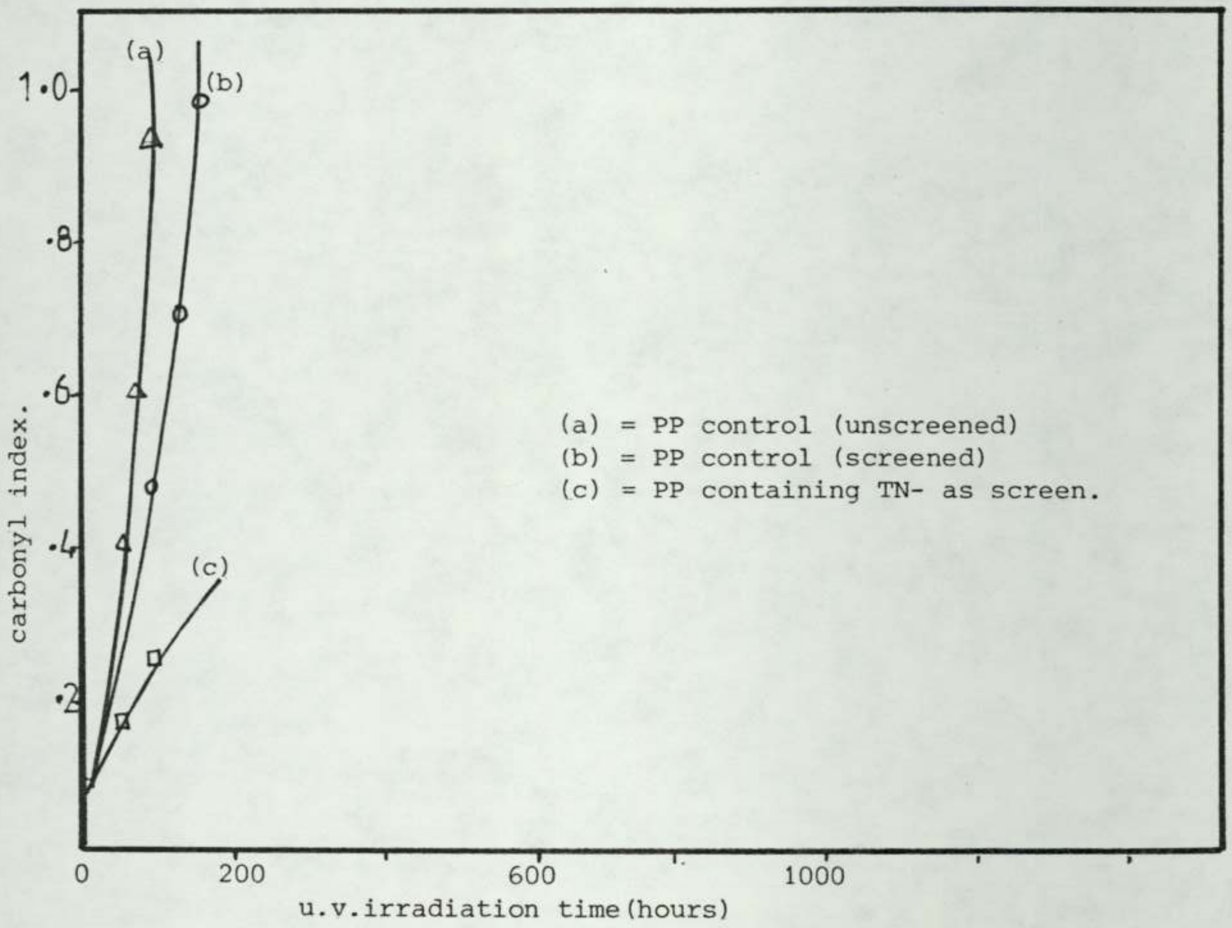


Fig. 4.51 : Effect of u.v.screening on unstabilised PP by stabilised PP containing 20×10^{-3}mol/100g of TN, processed in a closed mixer for 10 mins. at 180°C.

hydroperoxides under heat, even at high reaction ratio (Fig. 4.35), U.v. spectroscopy showed that solutions of TAm either in water or methanol do not absorb u.v. light either in the u.v. or visible regions.

The absence of an induction period in all PP films containing TAm suggests that the high hydroperoxide concentration in the films was immediately photo-cleaved in a process that initiates photodegradation, hence the generally low photostability of PP by TAm.

4.4 Photostabilisation of PP from 4% masterbatches of tBuNO and $tBuNO_2$.

The desirability of stabilisation from master-batches, due to ease of handling and economic advantage cannot be over-emphasised. Master batches of PP containing 4% tBuNO and $tBuNO_2$ were processed in the closed mixer, and diluted with virgin PP to the same concentration range as those in which the additives were added directly. Photostability of the diluted master batches were evaluated and compared with the normal samples (with directly added additives).

Table 4.8 and Fig. 4.52 show the photostability of diluted master batches (DMB) from tBuNO compared to those in which the additive was added directly.

Photostability in the DMB samples was greatly reduced, rather than showing any advantage. This suggest that, contrary to expectation, there is no binding between PP macroradicals and tBuNO or that the reaction involves small alkyl radicals, even at a concentration as high as 4%. It has been shown earlier that nitroxyl generation during processing of PP

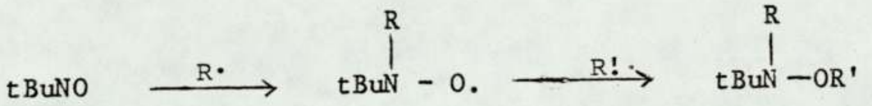
Table 4.8

Concentration* $x10m^{-3}/100g$	u.v. EMT (Hours)	
	N S	DMB
1 (0.087)	580	150
1.15 (0.1)	590	150
2.5 (0.22)	630	150
5 (0.44)	705	150
10 (0.87)	910	520

*figures in brackets are weight percentages

NS - normal samples DMB - diluted master-batch.

with tBuNO accounts for the subsequent photostabilisation. It is therefore possible that during dilution, alkyl radicals produced, rapidly consumed the nitroxyl radicals that might initially have been formed, yielding the substituted (alkyl) hydroxylamine.



$$tBuNO \xrightarrow{R\cdot} tBu\overset{\overset{R}{|}}{N}-O\cdot \xrightarrow{R'\cdot} tBu\overset{\overset{R}{|}}{N}-OR'$$

-(11)

However, alkyl hydroxylamines are known(112) to be thermally unstable and there is no evidence that they can withstand the double thermal processing operations (no e.r.s. signal of nitroxyl radical were obtained in the dilute MB). Additionally, during dilution, some tBuNO may be oxidised to $tBuNO_2$ hence reducing the alkyl-radical-scavenging ability of tBuNO; and being a low molecular weight compound with a low melting point, tBuNO loss due to volatility cannot be ruled out.

Table 4.9 and Fig. 4.53 show the photostability of diluted master batches from $tBuNO_2$ compared to normally processed samples. At low concentrations, the normally processed samples showed slightly better

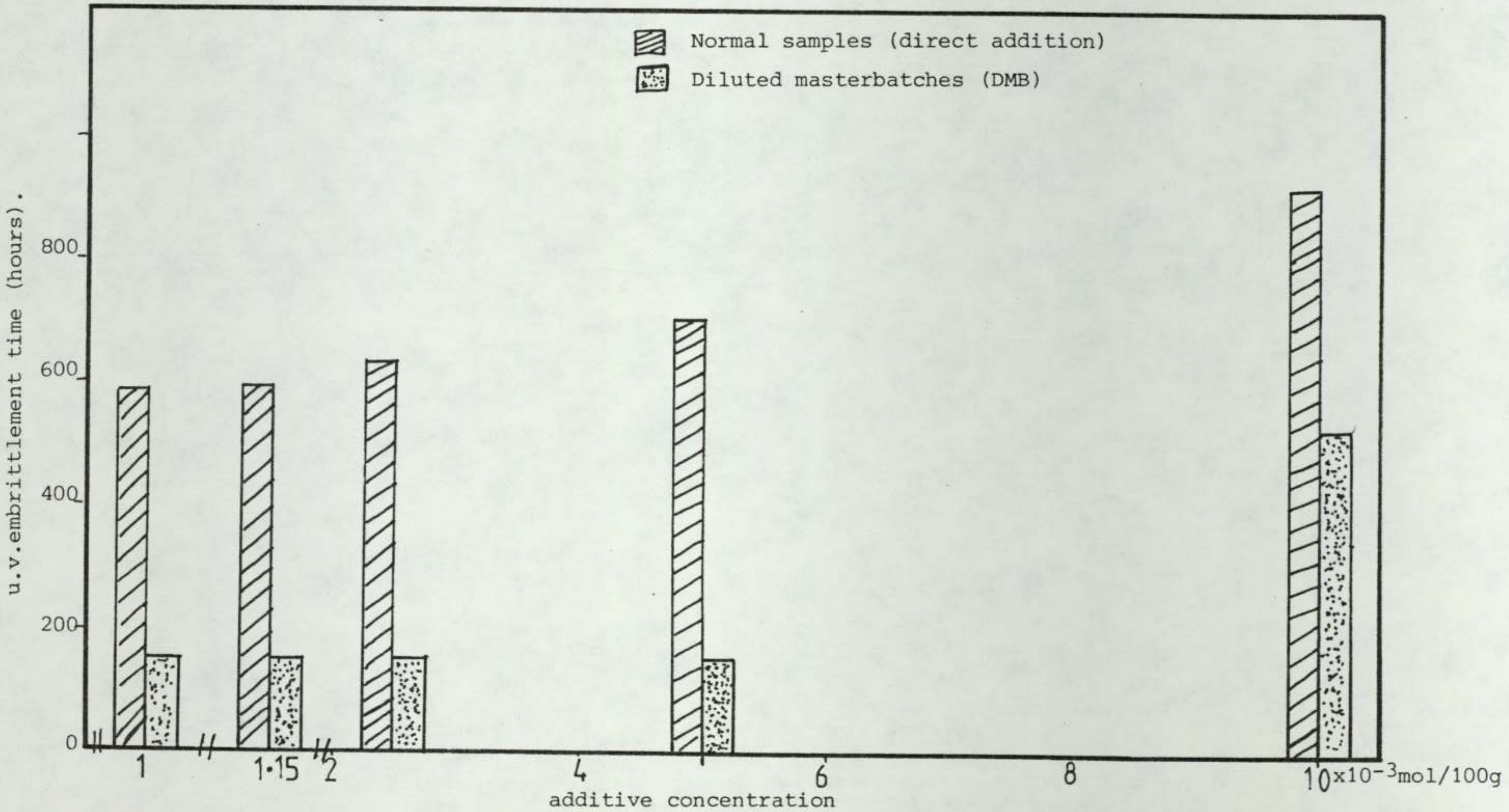


Fig. 4.52 : Comparison between normally processed samples (Direct additive addition) and DMB's (from 4%-masteratch) All processings and dilution for 10 mins. in a closed mixer at 180°C.

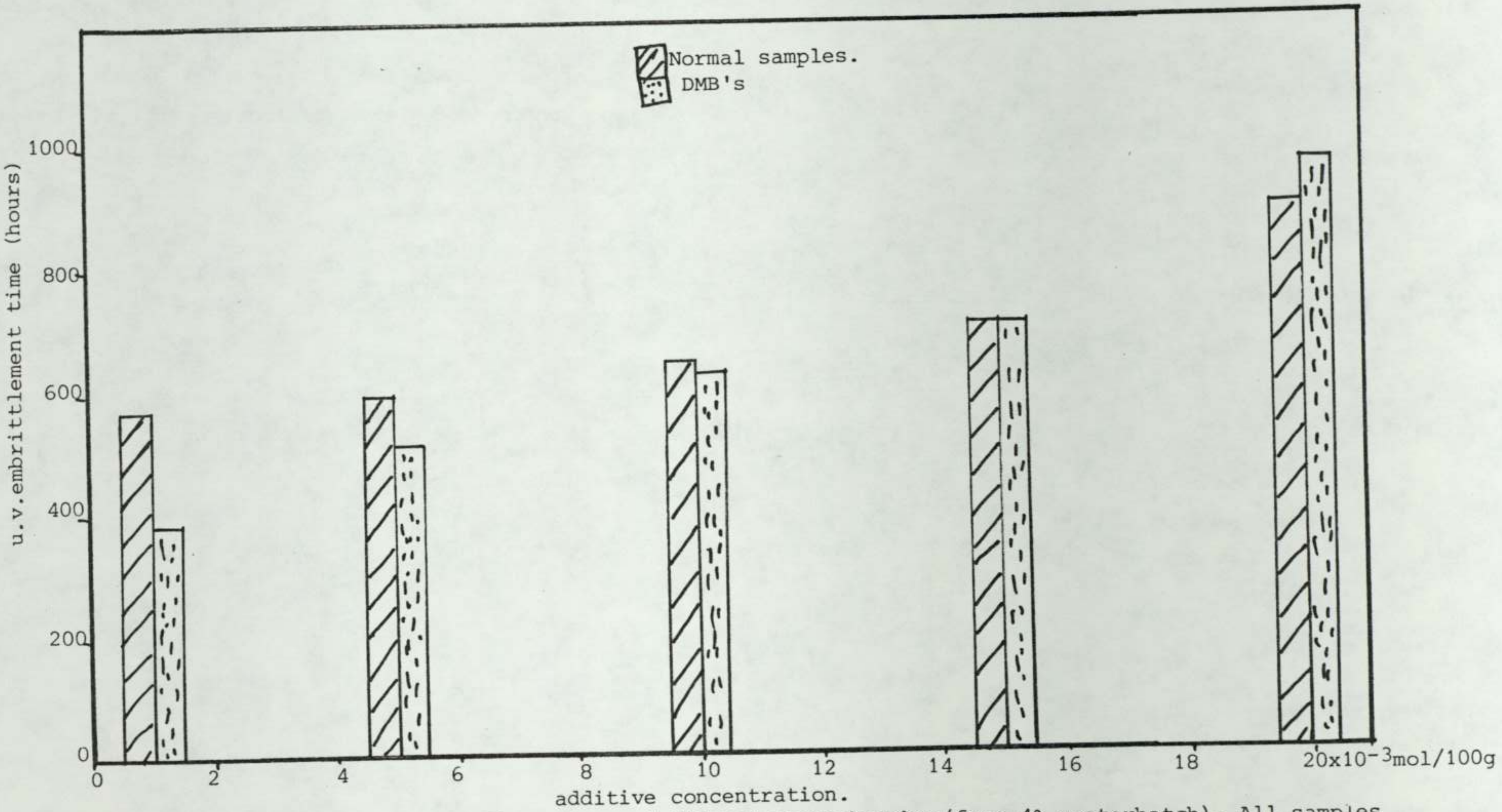


Fig 4.53 : Comparison between normal samples and diluted masterbatches(from 4% masterbatch). All samples processed/diluted in a closed mixer at 180°C for 10 mins.

photostability than the diluted master batches, but as concentration increases, the diluted master batches compares favourably with them.

Table 4.9

Concentration $x100^{-3}$ mol/100g	u.v. EMT (Hours)	
	NS	DMB
1 (0.103)	560	380
5 (0.5)	590	510
10 (1.0)	640	620
15 (1.5)	700	702
20 (2.0)	890	960

* Figures in brackets are weight percentages.

After processing in both normally processed samples and dilute masterbatches, an asborption (in infra-red) was observed at 1530 cm^{-1} corresponding to the nitro function (as in Fig. 4.41). This is in agreement with the earlier assertion that nitro compounds are fairly thermally stable. The nitro absorption were measured as indices and are shown in Fig. 4.54; the trend of the absorptions is fairly correlated to the trend in photostability. Photostabilisation mechanism is thought to be the same for both NS and DMB as previously suggested.

In both tBuNO and $tBuNO_2$ DMB from 4% masterbatches processed in the open mixer gave very little or no improvement compared to unstabilised PP and thus, are of no practical value.

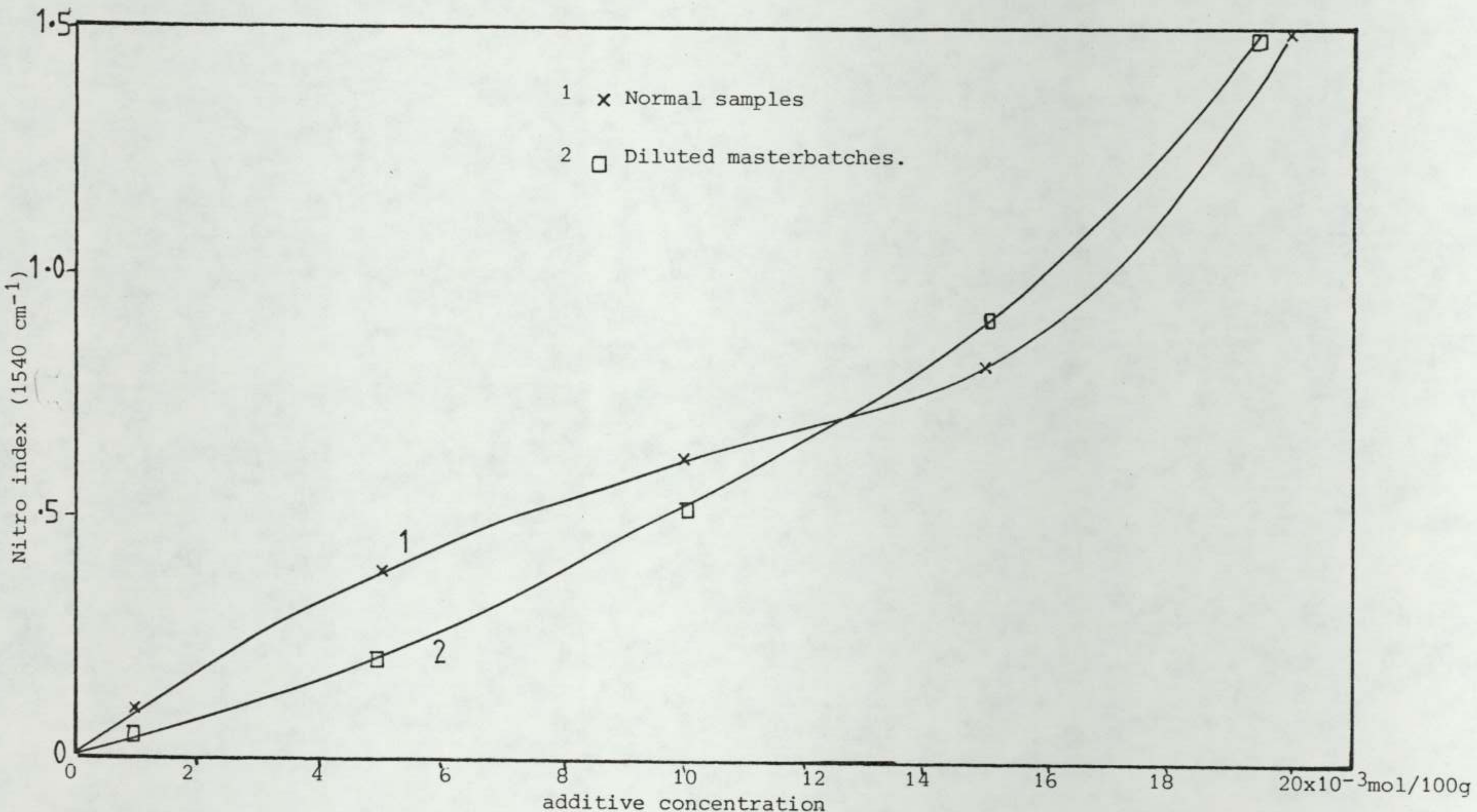


Fig. 4.54 : Dependence of nitro index (1540 cm^{-1}) on additive concentration of PP containing $tBuNO_2$ from diluted masterbatches and normally stabilised samples.

4.5 Synergism with commercial stabilisers and antioxidants

The behaviour of tBuNO, $tBuNO_2$, TN and DHPIN* in the presence of other commercial u.v. stabilisers and antioxidants were evaluated in PP in the same performance tests. Two component synergistic combinations of the additives with HOBP and Tinuvin 770 were examined.

Table 4.10

Concentration $x10^{-4}$ mol/100g	Tinuvin 770	HOBP	tBuNO	TN	$tBuNO_2$	DHPIN
2		260	280	120	205	100
4		510	370	130	380	120
5	2000	590	420	155	420	120
6		685	460	155	450	120
8		740	520	180	540	130
10	3500	800	560	210	570	150

The u.v. embrittlement times of individual compounds at different concentrations are shown in Table 4.10 while those of different synergistic combinations with calculated synergism (%) are shown in Tables 4.11 to 4.18 and summarised in Figs. 4.55 and 4.56. In Fig.4.55 it is shown that tBuNO, $tBuNO_2$ and TN give good synergistic effects with HOBP under u.v. light. The optimum combinations were also found to be close to 1:1 molar ratio in all cases. DHPIN is an effective melt and

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* Structure and code names on pages 36 and 37.

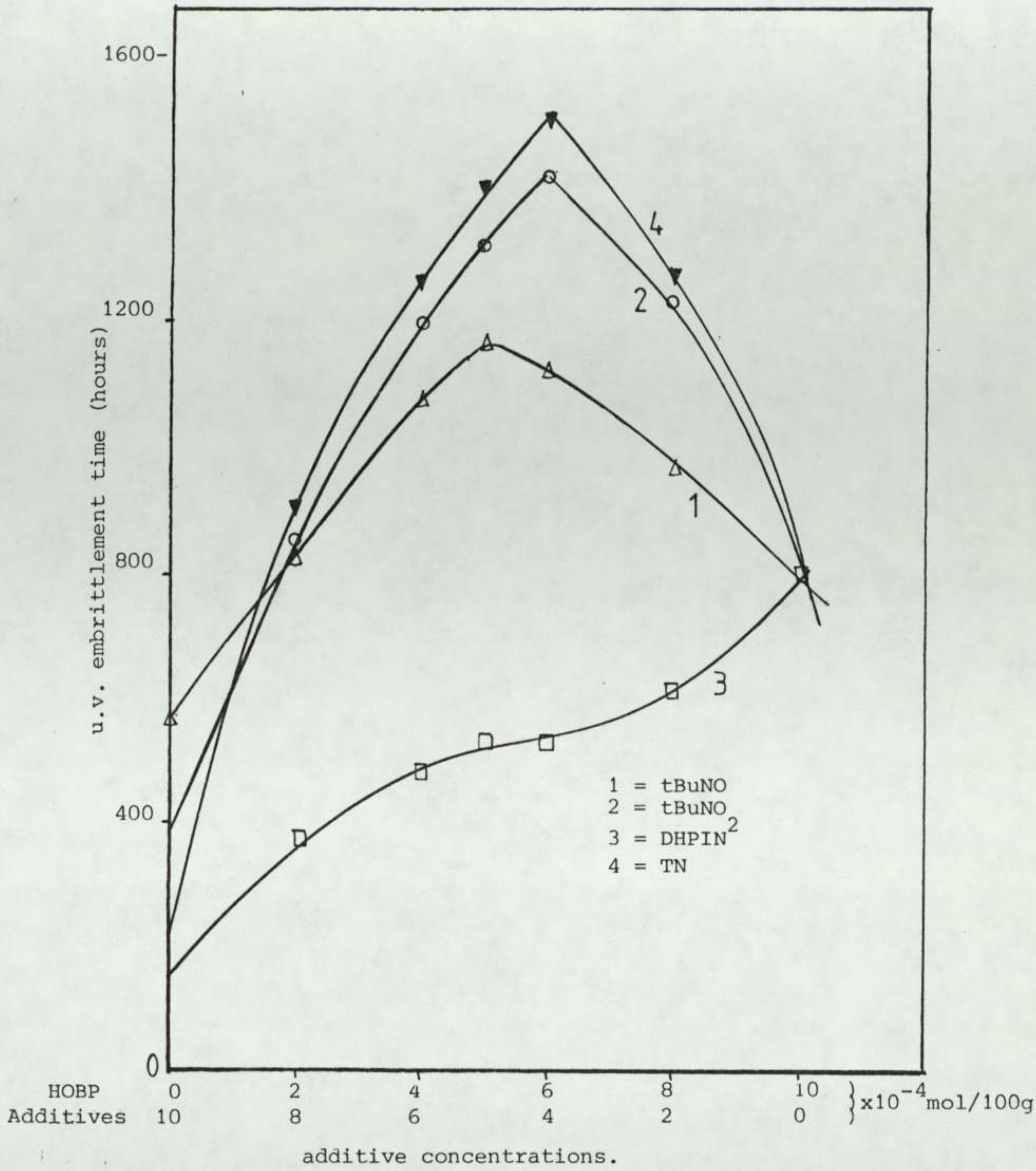


Fig. 4.55 : Additive synergism with HOBP processed in a closed mixer for 10 minutes at 180°C

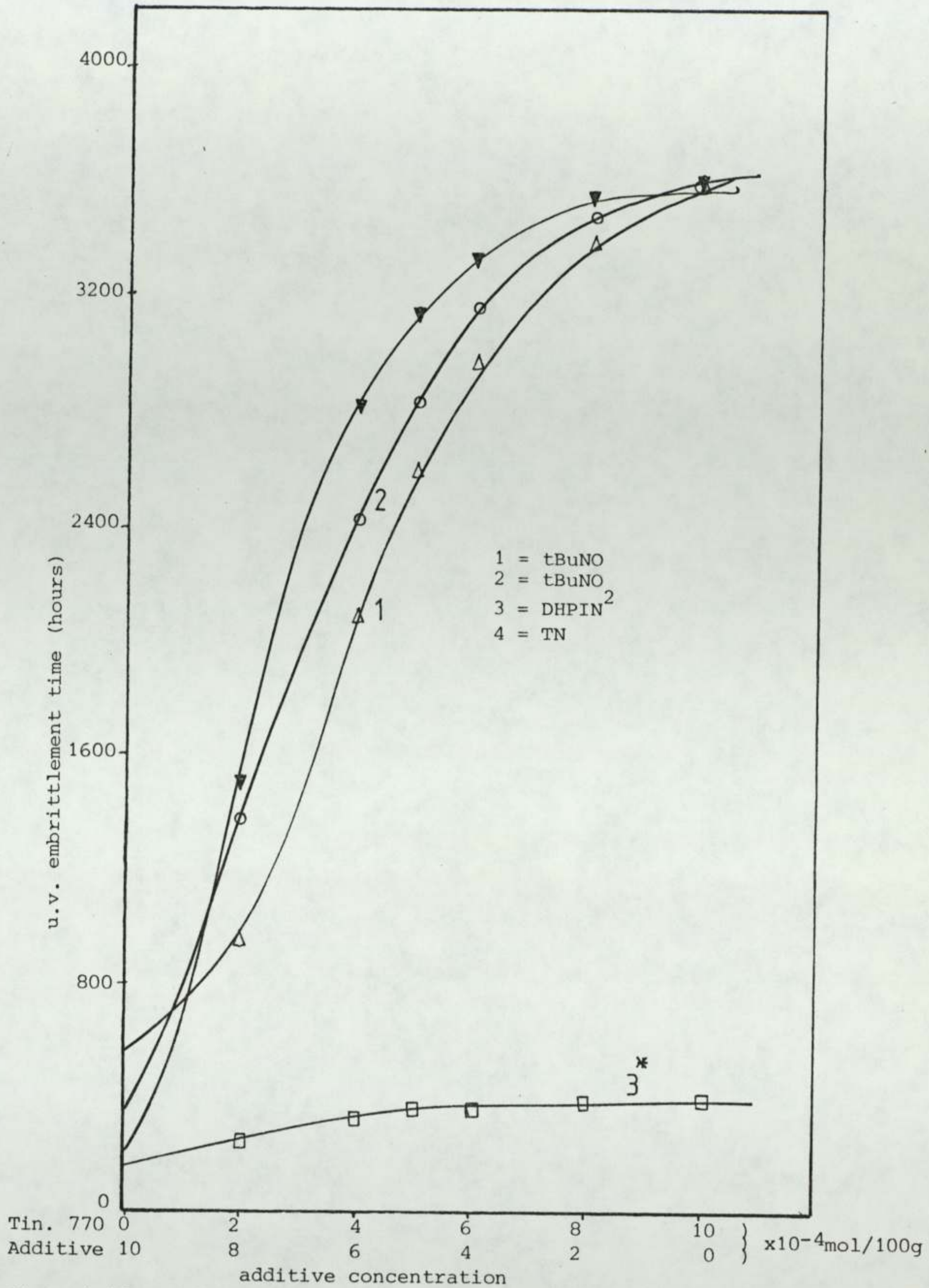


Fig. 4.56 : Additive synergism with Tinuvin 770 (* Tinuvin 327) processed in a closed mixer at 180^{o}C for 10 mins.

thermal stabiliser(126) but lack in u.v. activity compared to tBuNO and $tBuNO_2$, thus its synergism with HOBP was also evaluated. Results show that there's no advantage whatever, over HOBP alone as shown in Fig. 4.55.

HOBP is a known u.v. absorber but in the presence of peroxides, its activity is reduced due to its decomposition by peroxides(150) thus its effectiveness with tBuNO may be due to the known alkyl-radical 'scavenging' by tBuNO, thereby hindering hydroperoxides formation both during processing and photo irradiation; hence synergism may be due to mutual activities of alkyl - radical scavenging (by tBuNO) and u.v. absorbing/screening mechanism (by HOBP). Synergism between other additives and PP may also be due to complimentary mutual activity by both components present in the system. Additionally, the presence of the additives may increase solubility of the synergists in the PP matrix thus increasing their effectiveness, while in the case of DHPIN, the antagonistic effect observed (Table 4.17) may be due to either of the components deactivating the other, or that both compounds form complexes that are ineffective in photostabilisation of PP.

Fig. 4.56 shows that as the concentration of Tinuvin 770 increases, photostability increases; although no combination shows better photostability than Tinuvin 770 alone. As with HOBP (Fog. 4.55) there is no significant advantage of synergism between DHPIN and Tinuvin 327.

Although Tinuvin 770 itself has a pro-oxidant effect to some extent during processing and at initial stages of photo irradiation(150) it is a well known light stabiliser for polyolefins. Thus the synergism of Tinuvin 770 with tBuNO (at equal molar ratio - see Table 4.12) may be due to the enhanced mechanism of radical scavenging.

Table 4.11

tBuNO x10^{-4}mol /100g	HOBP x10^{-4}mol /100g	U.V. EMT Hours	% * synergism
10(0.087)	0 -	560	-
8 (0.07)	2 (0.965)	820	21.67
6 (0.05)	4 (0.13)	1070	24.05
5 (0.04)	5 (0.16)	1170	30.12
4 (0.034)	6 (0.2)	1130	18.85
2 (0.017)	8 (0.26)	950	2.38
0 -	0 (0.38)	800	-

Table 4.12

tBuNO x10^{-4} mol/100g	Tin.770 x10^{-4}mol/ 100g	u.v. EMT Hrs.	% * synergism.
10 (0.087)	0 -	560	
8 (0.07)	2 (0.1)	930	
6 (0.05)	4 (0.19)	2080	
5 (0.04)	5 (0.24)	2590	11.61
4 (0.034)	6 (0.29)	2970	
2 (0.017)	8 (0.38)	3390	
0 -	10 (0.48)	3600	

Table 4.13

$tBuNO_2$ x10^{-4}mol/ 100g	HOBP x10^{-4}mol/ 100g	u.v. EMT Hours.	% * synergism.
10 (0.1)	0 -	570	-
8 (0.08)	2 (0.065)	850	37.09
6 (0.06)	4 (0.13)	1200	42.31
5 (0.05)	5 (0.16)	1320	48.12
4 (0.04)	6 (0.2)	1430	51.41
2 (0.02)	8 (0.26)	1240	50.33
0 -	10 (0.33)	800	-

Table 4.14

$tBuNO_2$ x10^{-4}mol/ 100g	Tin 770 x10^{-4}mol/ 100g	u.v. EMT Hours	% * synergism.
10 (0.1)	0 -	570	
8 (0.08)	2 (0.1)	1360	
6 (0.06)	4 (0.19)	2400	
5 (0.05)	5 (0.24)	2810	21.43
4 (0.04)	6 (0.29)	3130	
2 (0.02)	8 (0.38)	3480	
0 -	10 (0.48)	3600	

Figures in brackets are weight percentages

$$\text{Synergism } \% = \frac{(Es - Ec) - [(E1 - Ec) + (E_2 - E_c)}{(E_1 - Ec) + (E_2 - Ec)} \times 100$$

Es = embrittlement time of synergist

Ec = embrittlement time of control

E_1= embrittlement time of component 1

E_2= embrittlement time of component 2

Table 4.15

TN $x10^{-4}$mol/ 100g	HOBP $x10^{-4}$mol/ 100g	u.v. EMT Hours	% * synergism.
10 (0.151)	0 -	210	-
8 (0.12)	2 (0.065)	900	21.15
6 (0.09)	4 (0.013)	1260	141.2
5 (0.08)	5 (0.16)	1410	133.63
4 (0.06)	6 (0.2)	1525	125.98
2 (0.03)	8 (0.26)	1275	74.26
0 -	10 (0.33)	800	-

Table 4.16

TN $x10^{-4}$mol/ 100g	Tin 770 $x10^{-4}$mol/ 100g.	u.v. EMT Hours.	% * synergism.
10 (0.15)	0 -	210	
8 (0.12)	2 (0.1)	1490	
6 (0.09)	4 (0.19)	2820	
5 (0.08)	5 (0.24)	3140	54.43
4 (0.06)	6 (0.29)	3310	
2 (0.03)	8 (0.38)	3540	
0 -	10 (0.48)	3600	

Figures in brackets are weight percentages

$$\text{Synergism } \% = \frac{(Es - Ec) - [(E1-Ec) + (E_2 - E_C)}{(E_1 - Ec) + E_2 - Ec} \times 100$$

Es = embrittlement time of synergist

Ec = embrittlement time of control

E_1= embrittlement time of component 1

E_2= embrittlement time of component 2

Table 4.17

DHPIN x10^{-4}mol/ 100g	HOBP x10^{-4}mol/ 100g	u.v EMT Hours	% syner- gism.
10 (0.21)	0 -	150	-
8 (0.17)	2 (0.065)	375	35.71
6 (0.12)	4 (0.13)	470	-15.56
5 (0.10)	5 (0.16)	530	-16.98
4 (0.08)	6 (0.2)	530	-29.6
2 (0.04)	8 (0.26)	610	-21.21
0 -	10 (0.33)	800	-

Table 4.18

DHPIN x10^{-4}mol/ 100g	Tin 327 x10^{-4}mol/ 100g	u.v. EMT Hours.
10 (0.21)	0 -	150
8 (0.17)	2 (0.065)	230
6 (0.12)	4 (0.13)	320
5 (0.10)	5 (0.16)	350
4 (0.08)	6 (0.19)	350
2 (0.04)	8 (0.26)	280
0 -	10 (0.32)	390

Table 4.19

Irg.1076 x10^{-4}mol/ 100g	tBuNO$_2$ x10^{-3} mol/ 100g	u.v. EMT (Hrs)
10 (0.53)	0 -	360
8 (0.42)	2 (0.2)	645
6 (0.32)	4 (0.4)	840
5 (0.27	5 (0.5)	920
4 (0.21)	6 (0.6)	895
2 (0.11)	8 (0.8)	795
0 -	10 (1.0)	640

Table 4.20

Irg. 1010 x10^{-4}mol/ 100g	tBuNO$_2$ x10^{-3} mol/ 100g	u.v. EMT (hrs)
5 (0.59)	0 -	205
4 (0.47)	2 (0.2)	630
3 (0.35)	4 (0.4)	880
2.5 (0.29)	5 (0.5)	970
2 (0.24)	6 (0.6)	950
1 (0.12)	8 (0.8)	840
0 -	10 (1.0)	640

Figures in brackets are weight percentage

Table 4.21

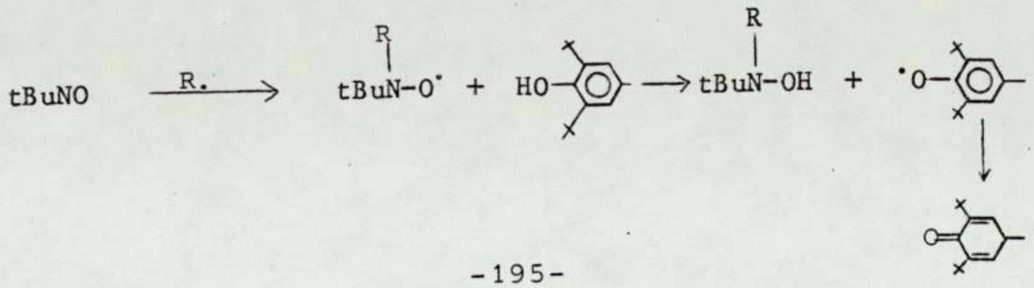
Irganox 1076 x10^{-4}mol/ 100g	tBuNO x10^{-3} mol/ 100g	u.v. EMT Hours
10 (0.53)	0 -	360
8 (0.42)	2 (0.17)	510
6 (0.32)	4 (0.35)	620
5 (0.27	5 (0.4)	660
4 (0.21)	6 (0.5)	660
2 (0.11)	8 (0.7)	800
0 -	10 (0.87)	900

Table 4.22

Irg. 1010 x10^{-3}mol/ 100g	tBuNO x10^{-3}mol/ 100g	UV EMT% (hrs)
5 (0.59)	0 -	205
4 (0.47)	2 (0.17)	415
3 (0.35)	4 (0.35)	560
2.5 (0.29)	5 (0.4)	620
2 (0.24)	6 (0.5)	640
1 (0.12)	8 (0.7)	670
0 -	10 (0.87)	900

Figures in brackets are weight percentages

From Tables 4.11- 4.14 and Figs. 4.55 and 4.56, it can be seen that HOBP and Tinuvin 770 synergised with both tBuNO and tBuNO$_2$, but both systems lack in thermal antioxidant activity. Thus, synergism between tBuNO, tBuNO$_2$ and thermal antioxidant (Irganox 1076 and Irganox 1010) was evaluated. The results are shown in Tables 4.19- 4.22 and demonstrated in Figures 4.57 and 4.58. The effectiveness of tBuNO is reduced in the presence of both Irganox 1076 and 1010 and that as thermal antioxidant concentration increases, photostability decreased markedly. This may be due to the fact that nitroxyl radicals produced from tBuNO during processing and photo irradiation may abstract hydrogen from the phenols thus producing phenoxyl radicals and possibly quinones (which are known to sensitize photo-oxidative degradation of PP$^{(178)}$ under u.v. irradiation.



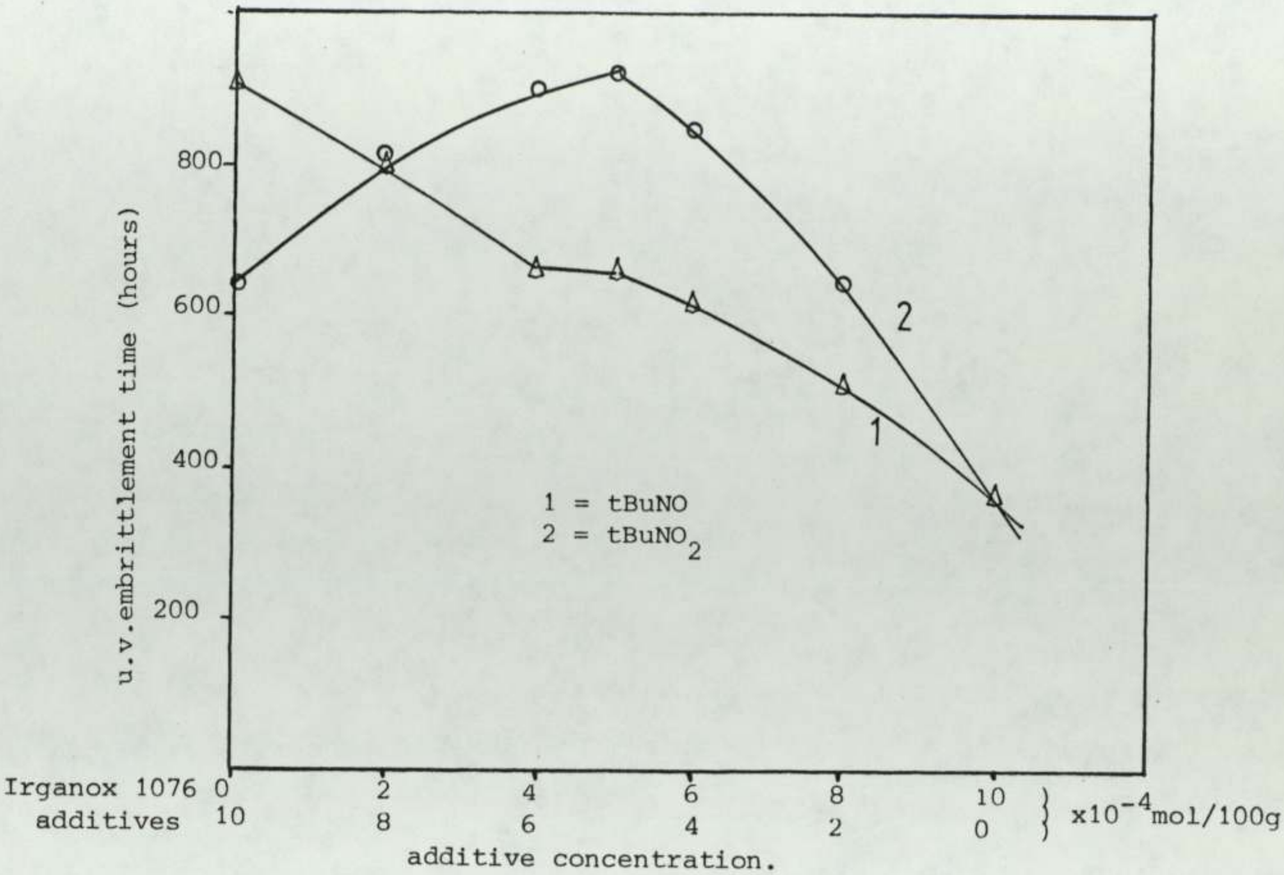


Fig 4.57: Synergism of tBuNO and $tBuNO_2$ with Irganox 1076 processed in a closed mixer at 180°C for 10 minutes.

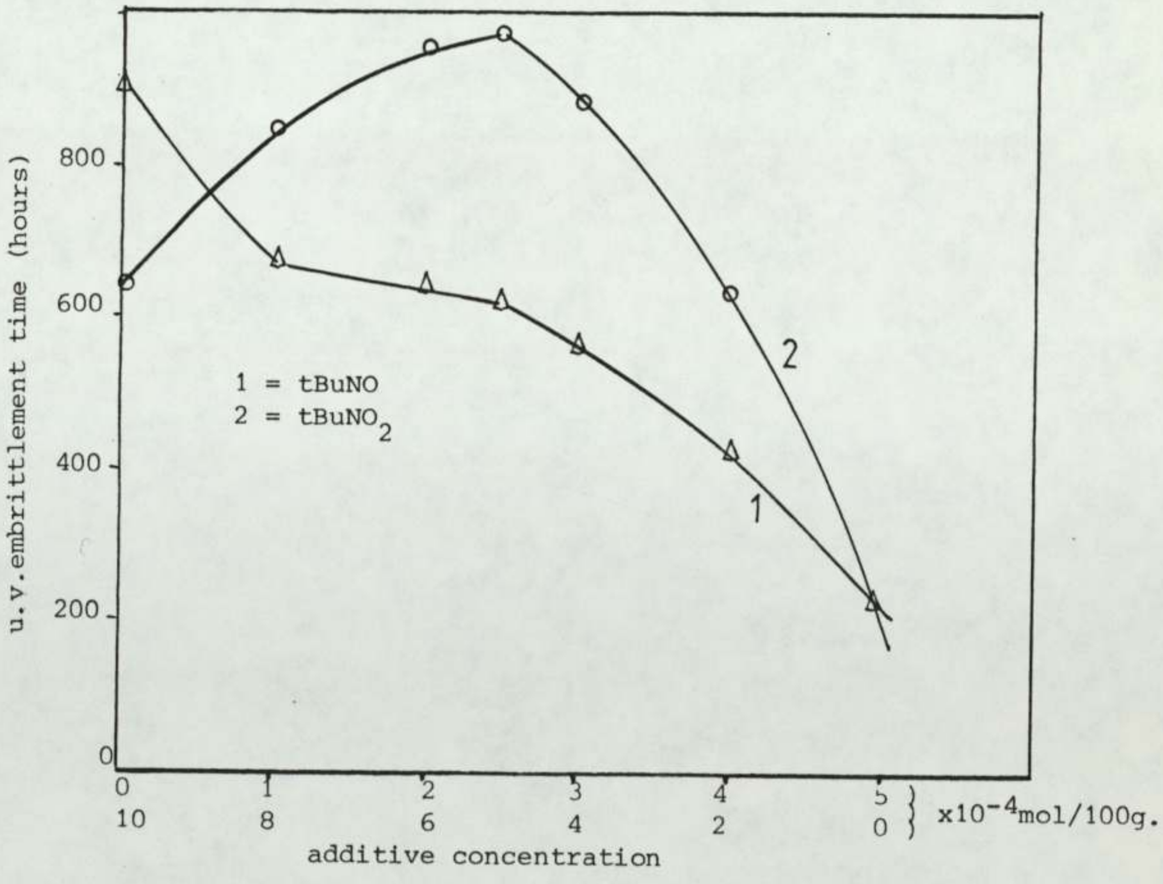


Fig. 4.58: Synergism of tBuNO and $tBuNO_2$ with Irganox 1010 processed in a closed mixer at 180°C for 10 minutes.

$tBuNO_2$ however, show a marked synergistic effect with both Irganox 1076 and 1010 but as Irganox concentration increases, photostability decreased. Again, synergism may be due to complimentary mutual protection or increased solubility of the components in the polymer matrix.

CHAPTER FIVE

ESTERS OF TRIMETHYLOL NITROMETHANE AS PHOTOSTABILISERS FOR POLYPROPYLENE

5.1 INTRODUCTION

Esters of nitro-alcohols have found some applications in industry for some time (particularly partially esterified nitro-alcohols). Some of their applications include uses as plasticisers for cellulose esters, natural resins, chlorinated rubber and moulding plastics.(133) They have also been used in the preparation of water-repellant textiles(151) and in rust inhibition formulations(132). However, the ability of this group of compounds as photostabilisation for polyoefins has not been investigated. Furthermore trimethylol nitromethane (TN)* itself was found (see Chapter 4) to stabilise PP against photo oxidation, albeit at high (weight percentage) concentrations. High molecular weight esters of trimethylol nitromethane (see Table 5.1) were therefore synthesised as described previously (Chapter 2, Section 2.2.6-2.2.9) and evaluated as photostabilisers for PP in comparison with trimethylol nitromethane, TN (which was used as a control).

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* Table of structures, code names and numbers of compounds used are on pages 36 and 37.

The concentrations used in this chapter are shown in Table 5.1.

Table 5.1: Molar concentrations and weight percentages of esters of trimethylol nitromethane $(RCOOCH_2)\ CNO_2$ used.

Alkyl gp $R^\cdot$	Code name	Mol. wt	Molar concentrations x 10^{-4} mol/100g.				
			1	5	10	15	20
					%		
C_2H_5	PTN	319	0.032	0.16	0.32	0.48	0.64
$C_{11}H_{23}$	LTN	697	0.07	0.35	0.70	1.05	1.4
$C_{17}H_{33}$	OTN	943	0.094	0.47	0.94	1.41	1.89
$C_{17}H_{35}$	STN	949	0.0985	0.47	0.95	1.42	1.90
$(HOCH_2)_3-C-NO_2$ *	TN	151	0.015	0.076	0.151	0.227	0.302

* Molecular structure.

5.2 RESULTS

Figs. 5.1 and 5.2 show the dependence of torque on processing time of PP containing (5×10^{-4} mol/100g) TN and its esters PTN, LTN, OTN and STN processed in both closed and open mixers respectively. In the closed mixer, some melt stabilising activity was observed as evidence by the constant level of the torque throughout processing. However, the maximum torque values in PP containing lauryl ester (LTN) and stearyl ester (STN) were higher than that of TN whereas those of propionyl ester (PTN) and oleiyl ester (OTN) were lower, although all esters gave higher torque values than the unstabilised PP. In the open mixer case however, all additives show a decreasing torque with increasing processing time, thus indicating chain scission, and the esters gave lower torque values (with processing time) when compared to the control (TN)- Fig. 5.2. All additives have lower maximum torque values compared to the unstabilised control.

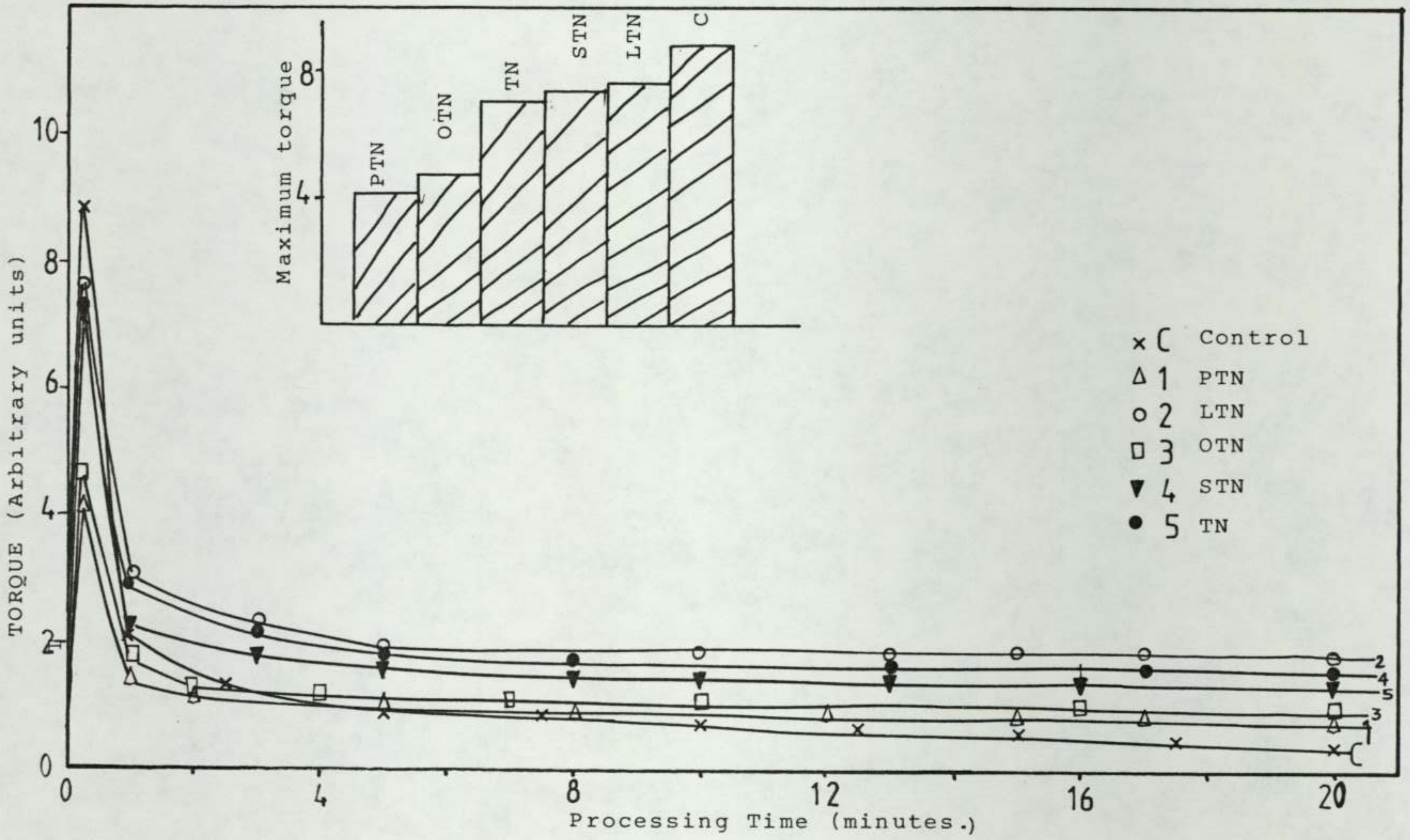
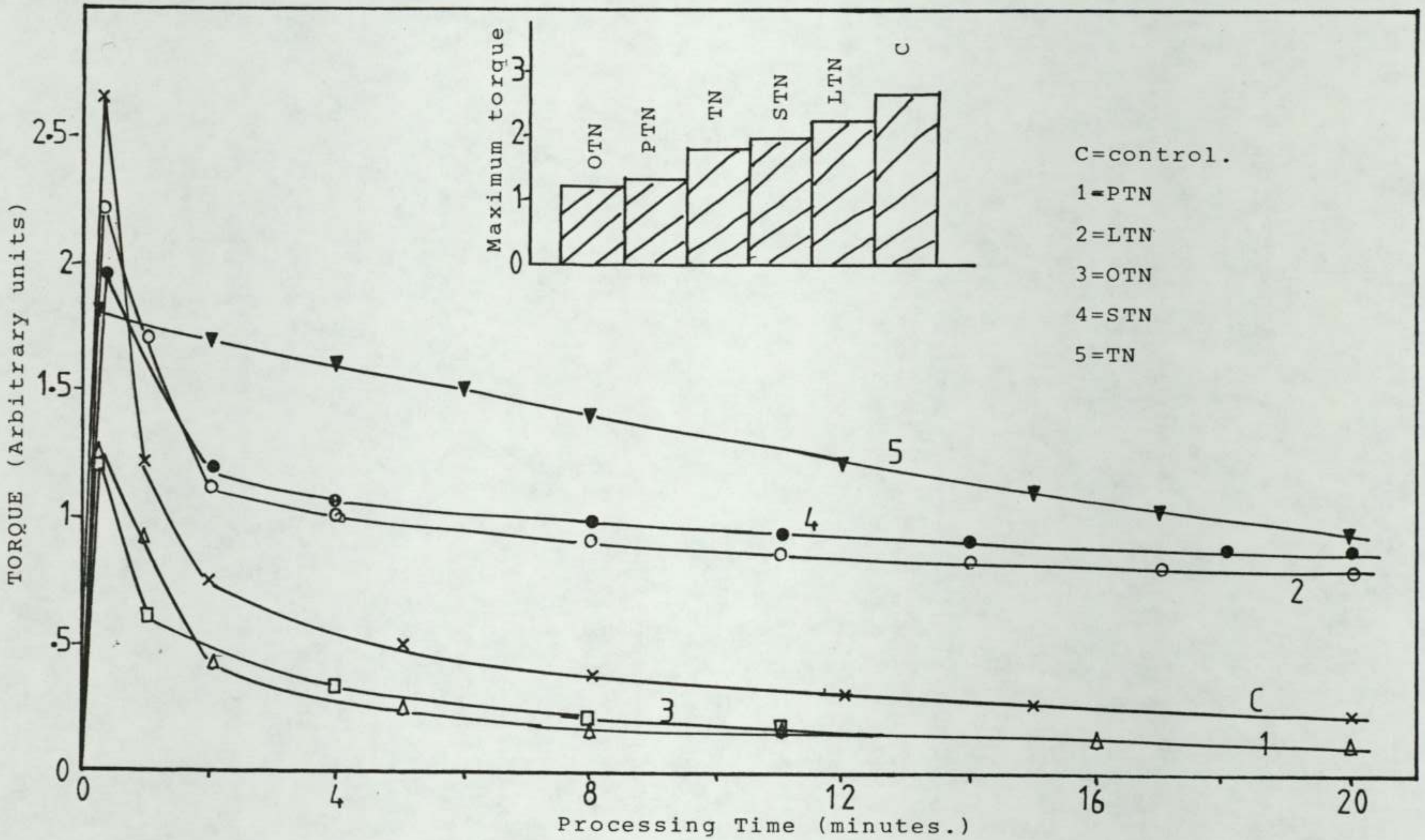


Fig.5.1: Dependence of torque on processing time of PP containing 5×10^{-4} mol/100g of TN and its esters processed in the closed mixer at 180°C.



<u>Fig.5.2.</u>: Dependence of torque on processing time of PP containing 5×10^{-4}mol/100g of TN and its esters processed in the open mixer at 180°C.

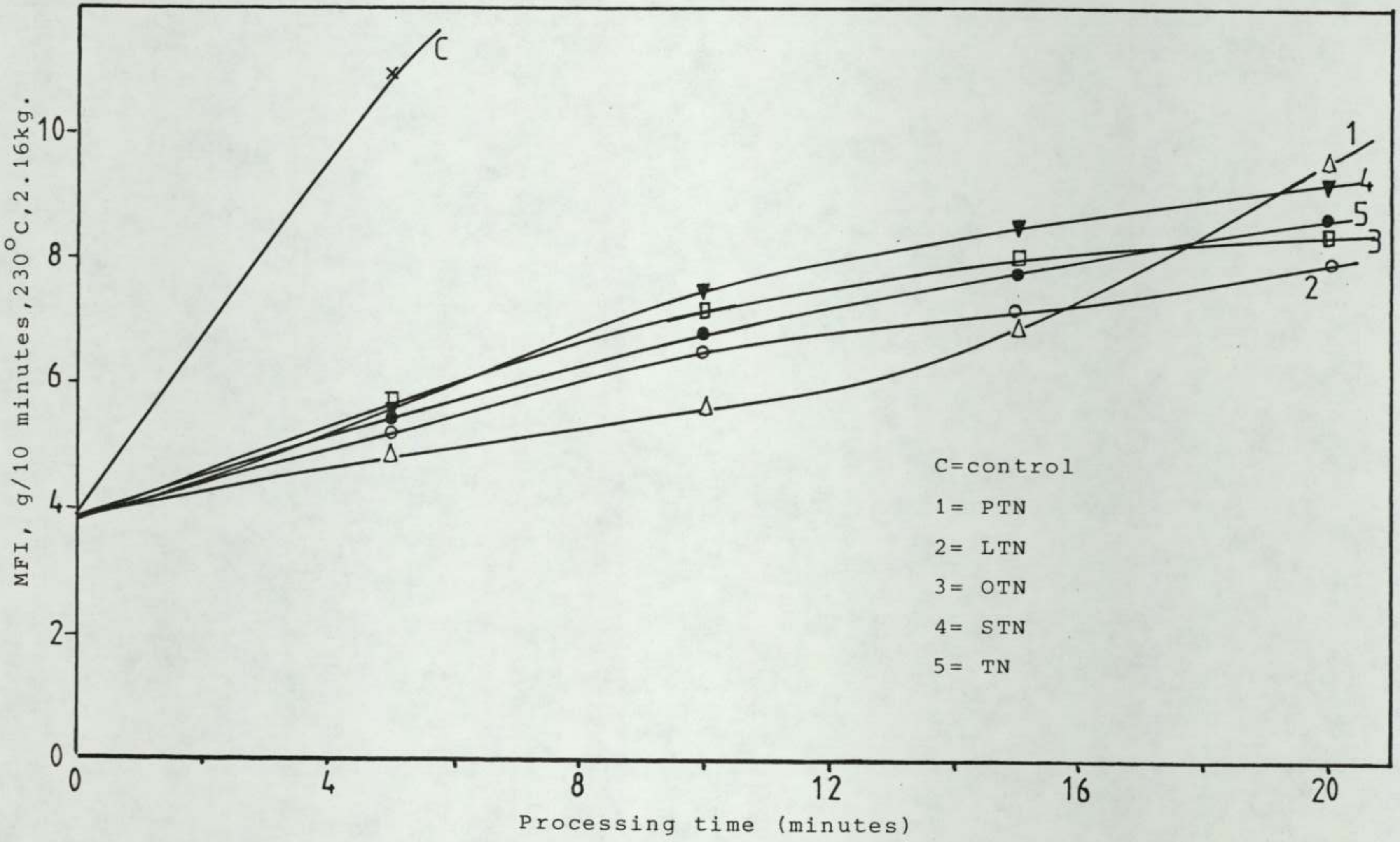


Fig. 5.3: Effect of processing time on the MFI of PP containing $5x10^{-4}$mol/100g of TN and its esters processed at 180°C in the closed mixer.

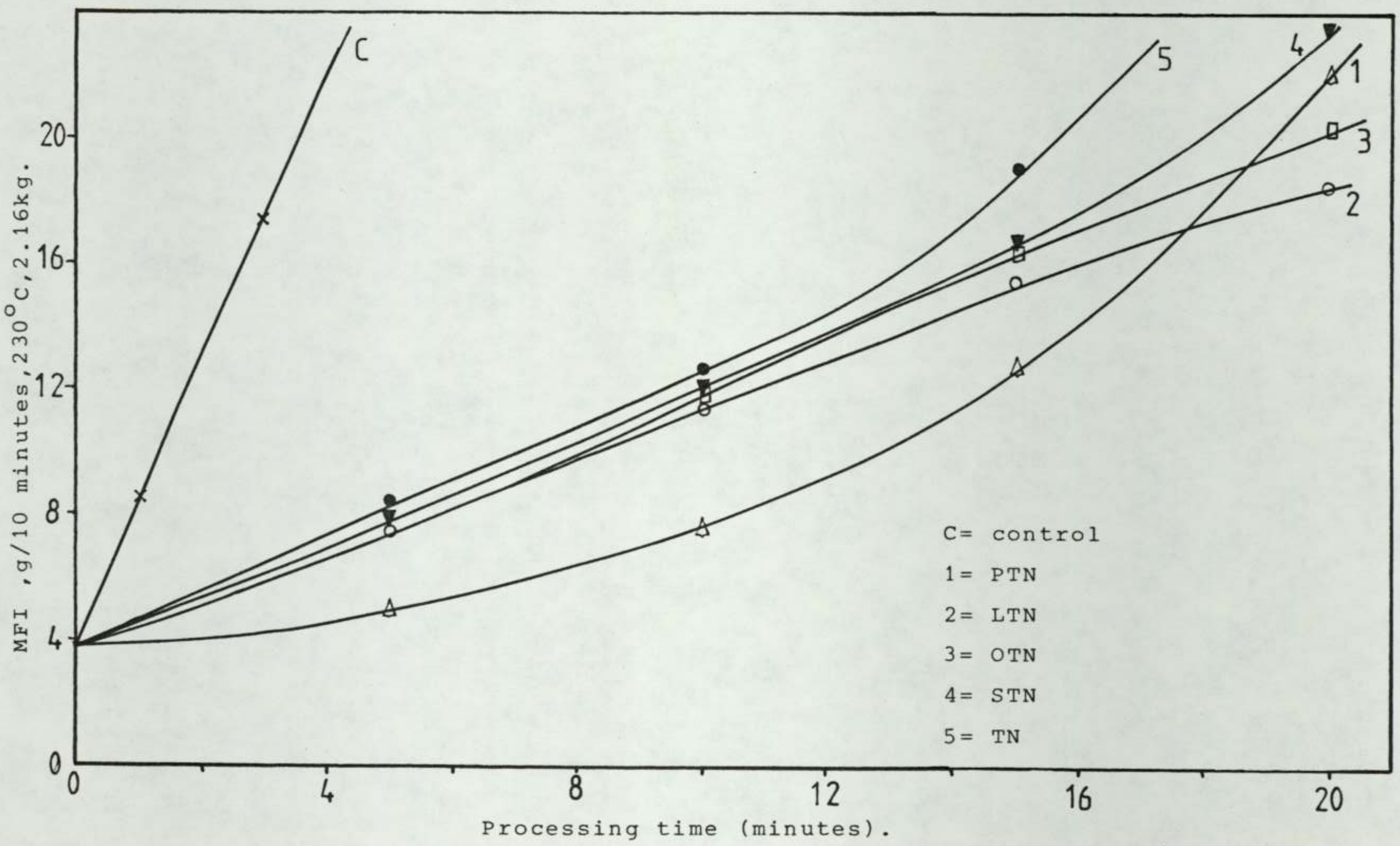


Fig. 5.4:Effect of processing time on the MFI of PP containing $5x10^{-4}$mol/100g of TN and its esters processed at 180°C in an open mixer.

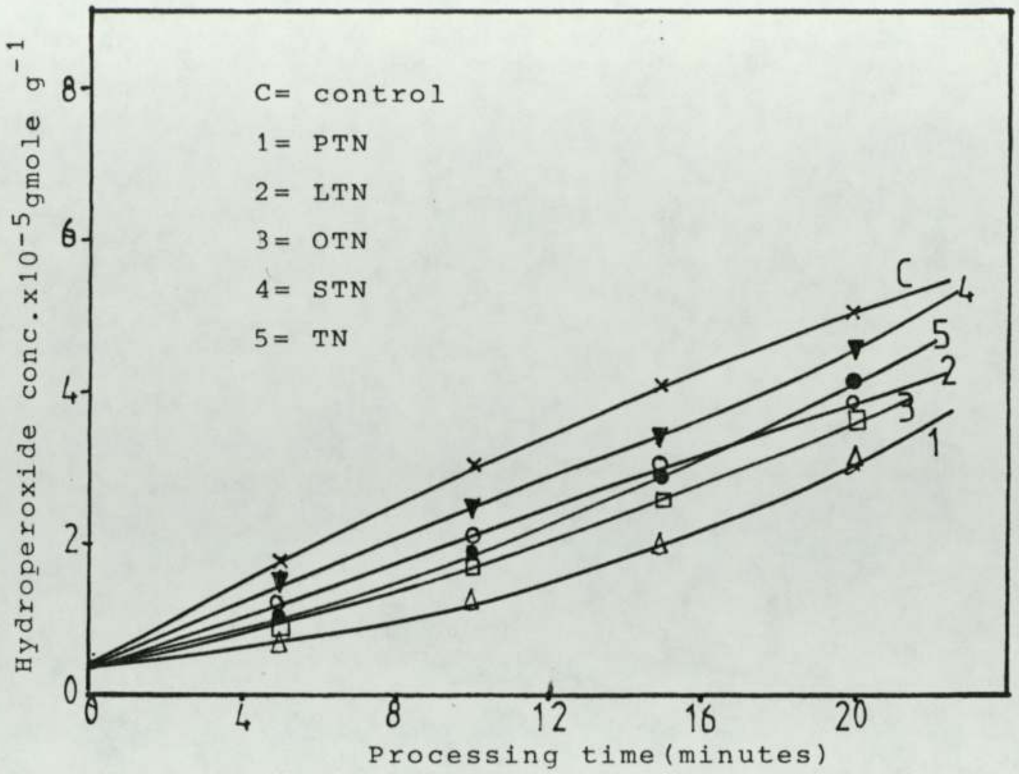


Fig 5.5: Effect of processing time on hydroperoxide formation in PP containing 5x10^{-4}mol/100g of (1)PTN (2)LTN (3)OTN (4)STN (5)TN processed in a closed mixer at 180°C.

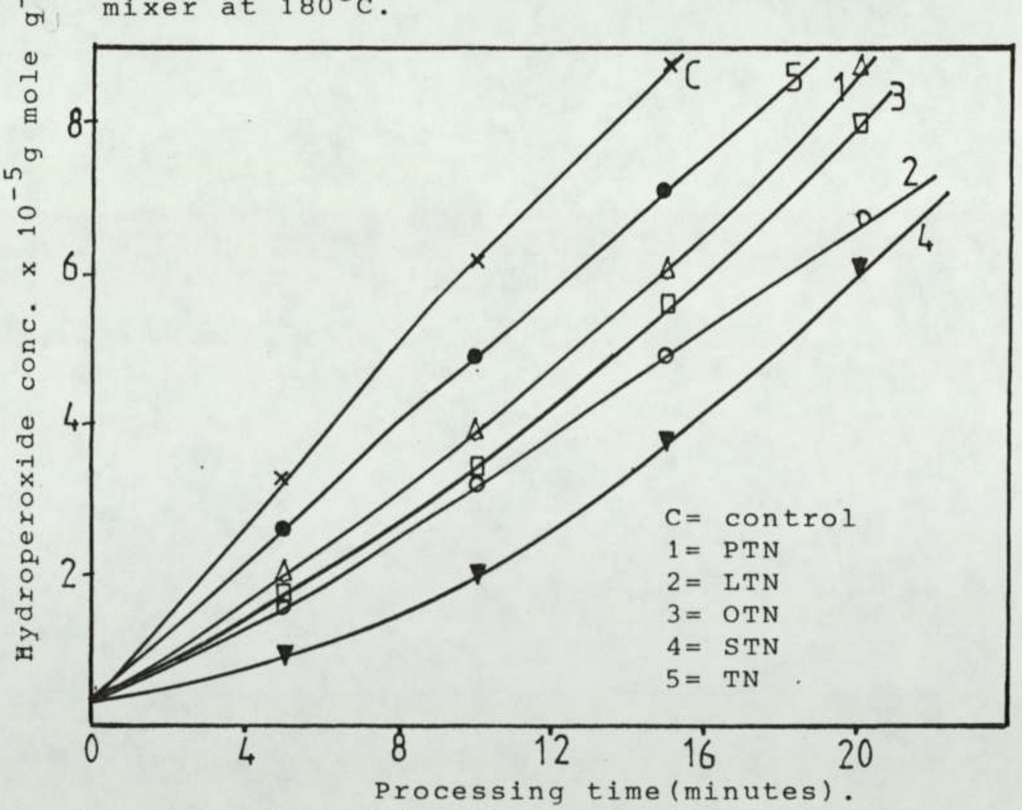


Fig.5.6: Effect of processing time on hydroperoxide formation in PP containing 5x10^{-4}mol/100g of (1)PTN (2)LTN (3)OTN (4)STN (5)TN processed in an open mixer at 180°C.

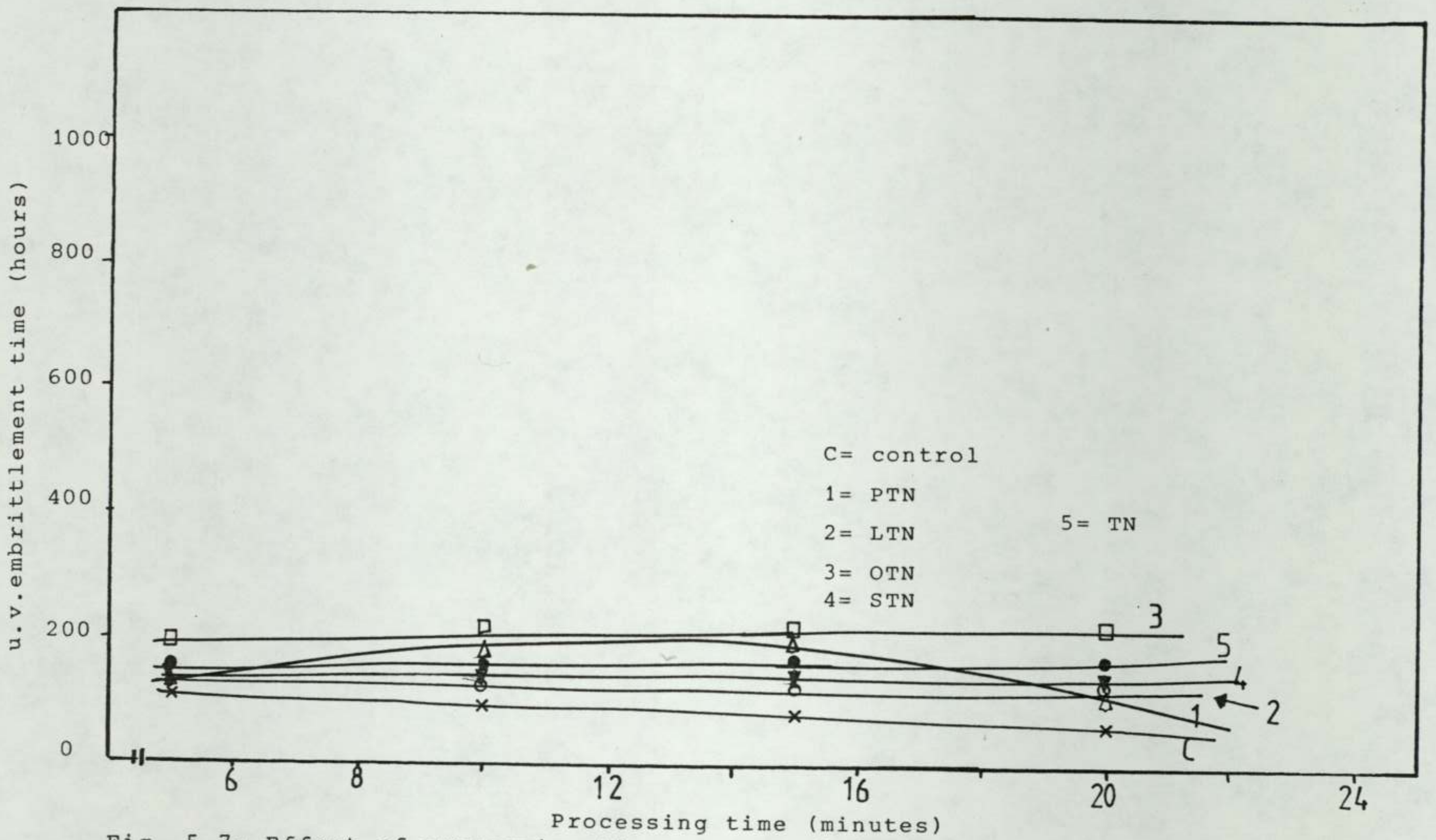


Fig. 5.7: Effect of processing time on u.v.embrittlement time of PP containing 5×10^{-4} mol/100g of (1)PTN (2)LTN (3)OTN (4)STN (5)TN processed in a closed mixer at 180°C.

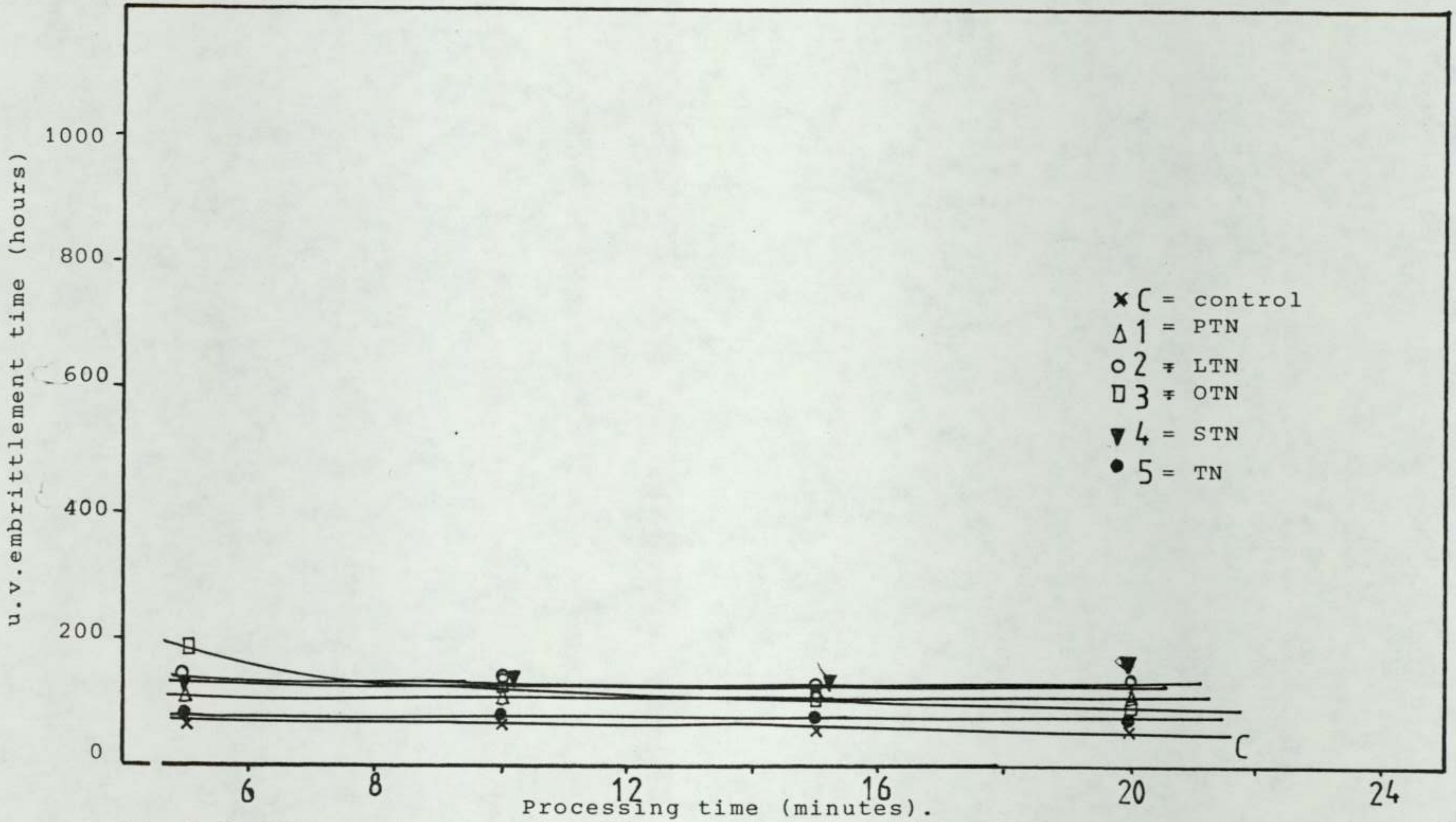


Fig.5.8: Effect of processing time on u.v.embrittlement time of PP containing 5x10^{-4} mol/100g of (1)PTN (2)LTN (3)OTN (4)STN (5)TN processed in an open mixer at 180°C.

The melt flow index (MFI) increases with processing time in all cases in both samples processed in a closed mixer (Fig. 5.3) and in open mixer (Fig. 5.4). The rates of increase however are larger in the case of open mixer. The melt flow index could be correlated with the dependence of hydroperoxide concentration with processing time in both closed and open mixer processed samples as indicated in Figs. 5.5 and 5.6 in which hydroperoxide formation increased with increasing processing time.

The effect of processing time on the subsequent photostability of PP containing 5×10^{-4}mol/100g of the additives is shown in Tables 5.2 and 5.3 and demonstrated in Figs. 5.7 and 5.8 for closed and open mixer processing respectively.

Table 5.2:**Effect of processing times on u.v. embrittlement time (EMT) of PP containing additives (5×10^{-4}mol/100g) processed in a closed mixer at 180°C.**

	UV EMT (hours)					
Proc. Time (minutes)	PP Control (no additive)	PTN	LTN	OTN	STN	TN
5	110	130	135	190	135	150
10	90	170	135	220	150	160
15	80	190	150	210	130	140
20	70	110	140	220	150	160

Table 5.3: **Effect of processing time on u.v. embrittlement time (EMT) of PP containing additives (5x10^{-4}mol/100g) processed in an open mixer at 180^{o}C.**

	UV EMT (hours)					
Proc. Time (minutes)	PP Control (no additive)	PTN	LTN	OTN	STN	TN
5	75	110	130	180	130	80
10	70	110	125	110	135	
15	60	110	130	120	135	
20	60	120	130	100	130	

Generally, in all cases (both in closed and open mixer processing) photostability was very low, with the maximum embrittlement time obtained as 220 hours despite the high (weight percentage) concentration. In films processed in the closed mixer (Fig. 5.7) increasing processing times do not have any significant effect on photostability in all additives except in the case of PTN in which an initial increase in photostability was observed with processing time followed by a decrease at longer processing times. Similarly, in films processed in the open mixer (Fig. 5.6) no significant changes occured with processing time.

Figs. 5.9-5.18 show the effect of processing time on the carbonyl formation (under the effect of u.v light) of PP containing PTN, LTN, OTN, STN and TN, processed in closed and in open mixers. In all cases, there is no induction period, and the rate of carbonyl formation is similar.

The effect of additive concentration on photostability of PP is shown in Tables 5.4 and 5.5 and in Figs. 5.19 and 5.20 for closed and open mixer processing respectively.

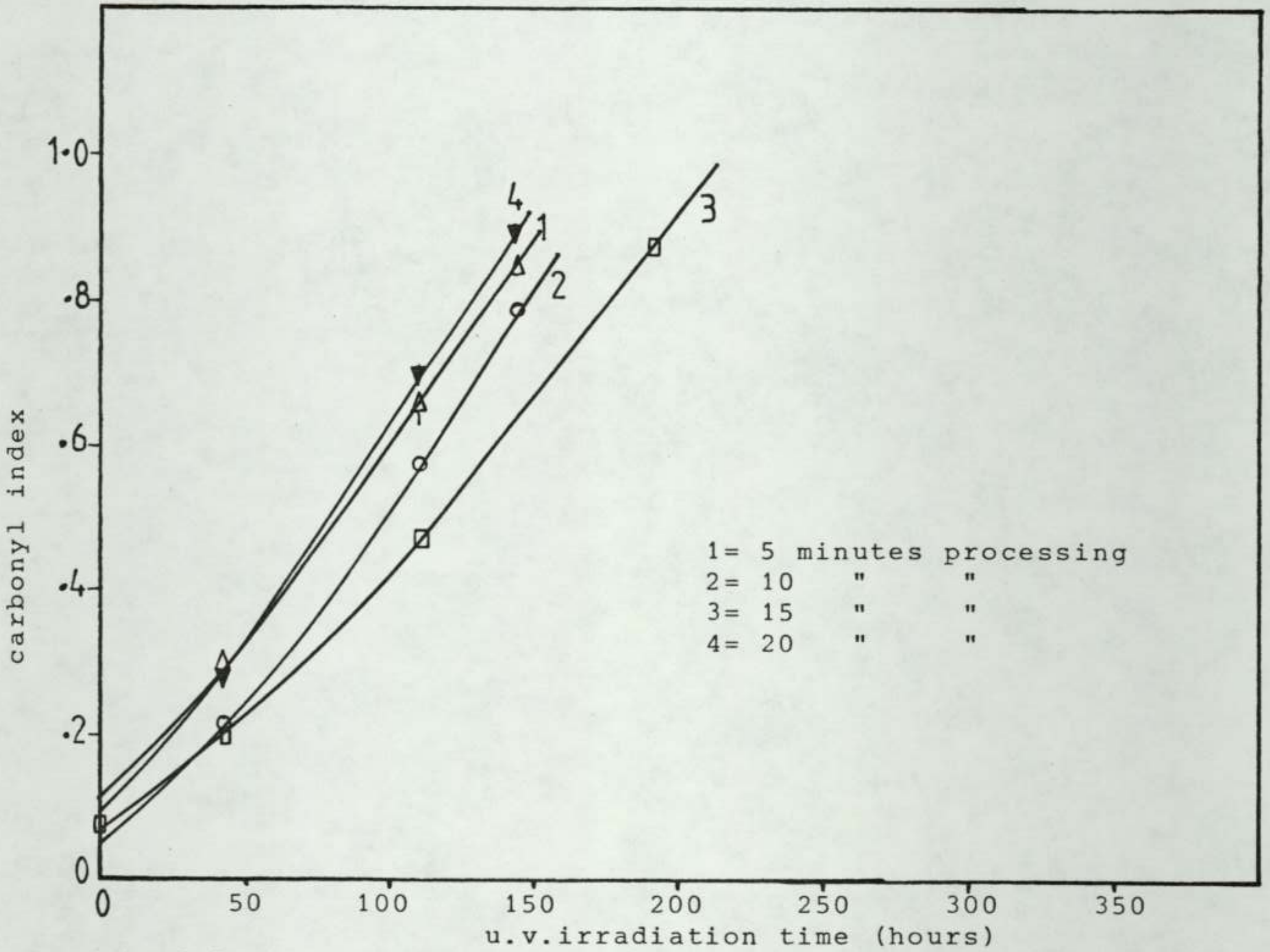


Fig 5.9: Effect of processing time on carbonyl formation(with u.v.irradiation) of PP containing 5x10-4mol/100g of PTN processed for (1)5 mins. (2)10 mins. (3) 15mins. (4) 20 mins. in a closed mixer at 180°C.

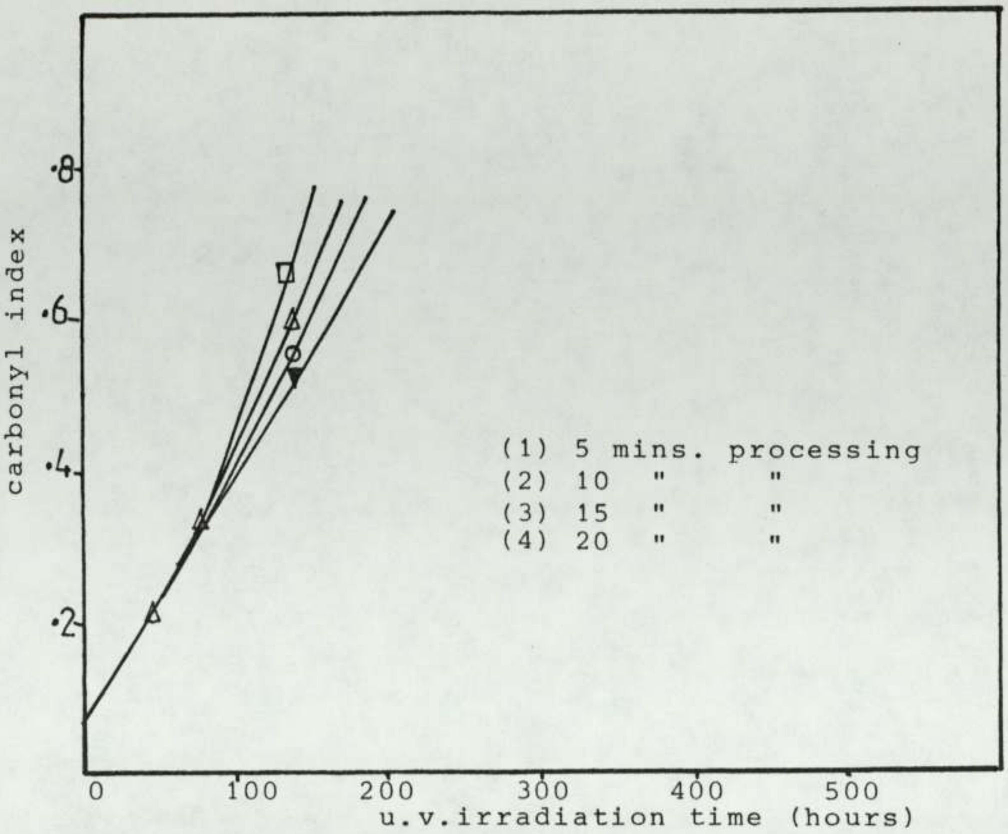


Fig. 5.10: Effect of processing time on carbonyl formation (during irradiation) of PP containing 5×10^{-4}mol/100g of LTN processed for (1)5mins. (2)10mins. (3)15mins. (4)20mins. in a closed mixer at 180°C.

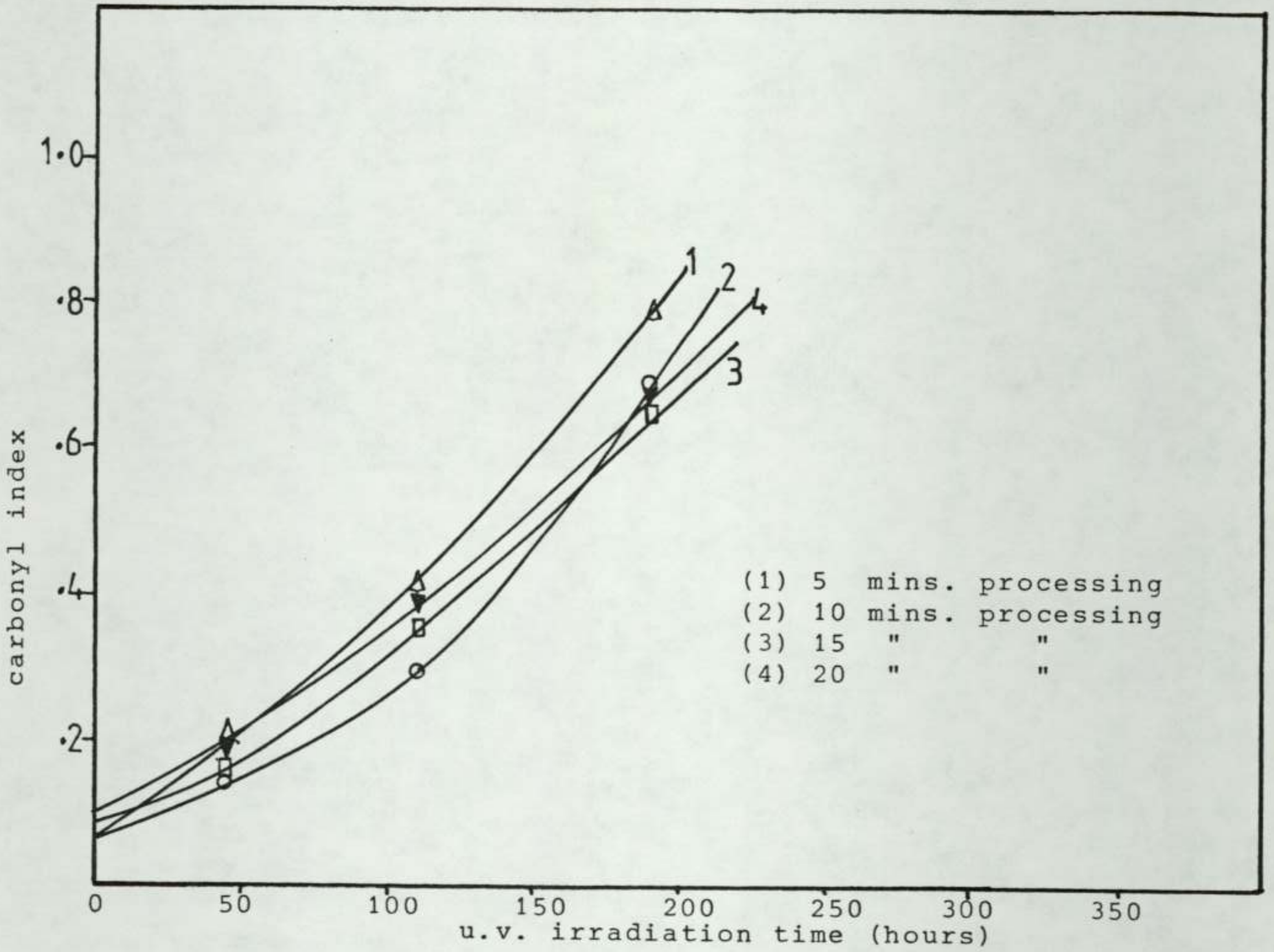


Fig. 5.11: Effect of processing time on carbonyl formation (during irradiation) of PP containing 5×10^{-4} mol/100g of OTN processed for (1) 5mins, (2) 10mins, (3) 15mins, (4) 20mins. in a closed mixer at 180°C.

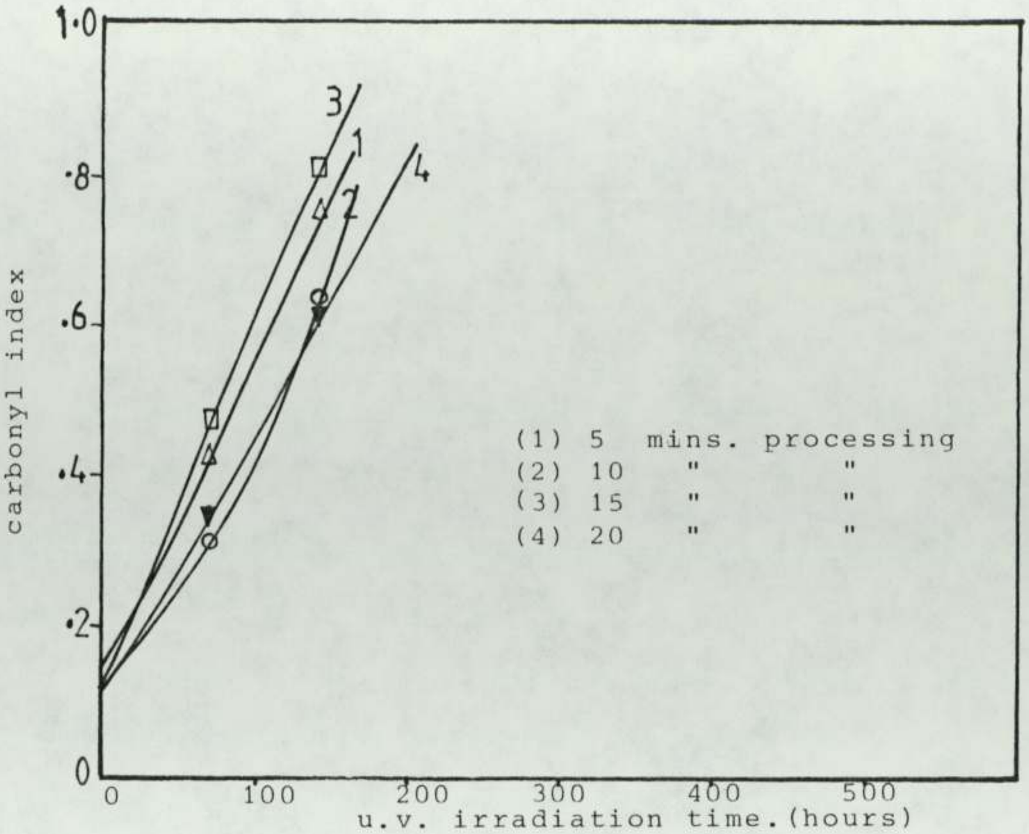


Fig. 5.12: Effect of processing time on carbonyl formation (during irradiation) of PP containing 5×10^{-4}mol/100g of STN processed for (1)5 mins, (2)10 mins, (3)15 mins, (4)20 mins. in a closed mixer at 180°C.

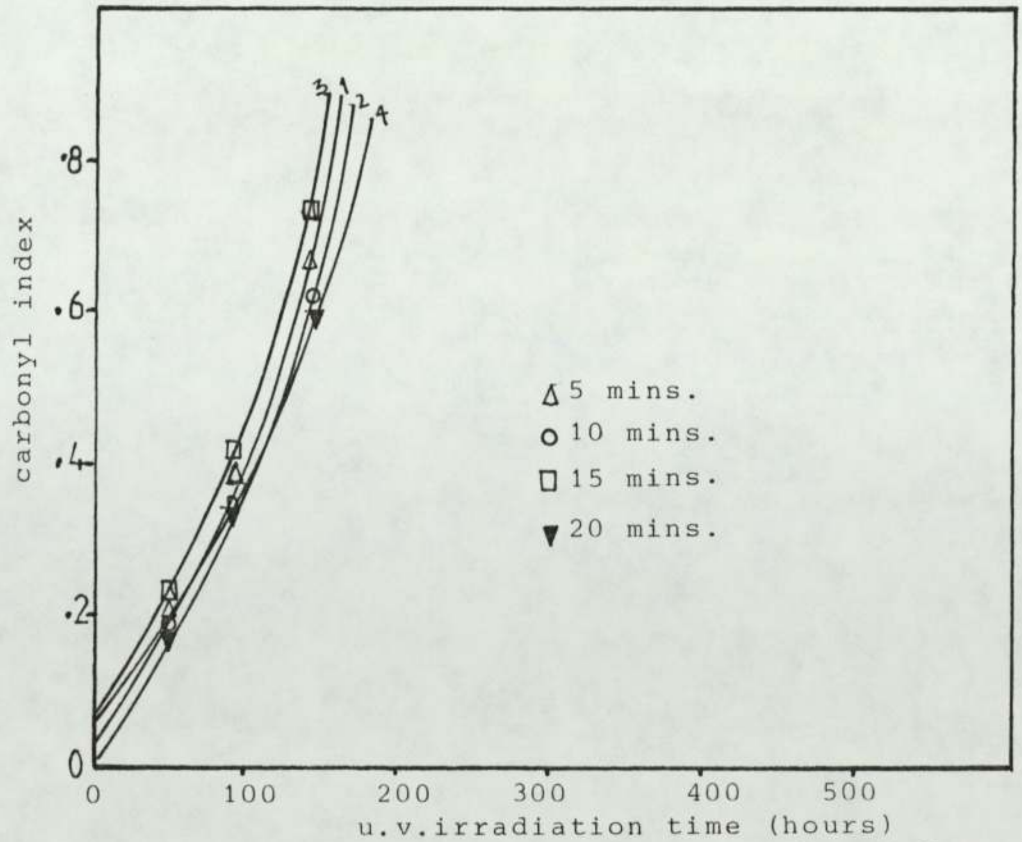


Fig.5.13: Effect of processing time on carbonyl formation of PP containing 5×10^{-4}mol/100g of TN processed for (1)5 mins, (2)10 mins, (3)15 mins, (4)20 mins. in a closed mixer at 180°C

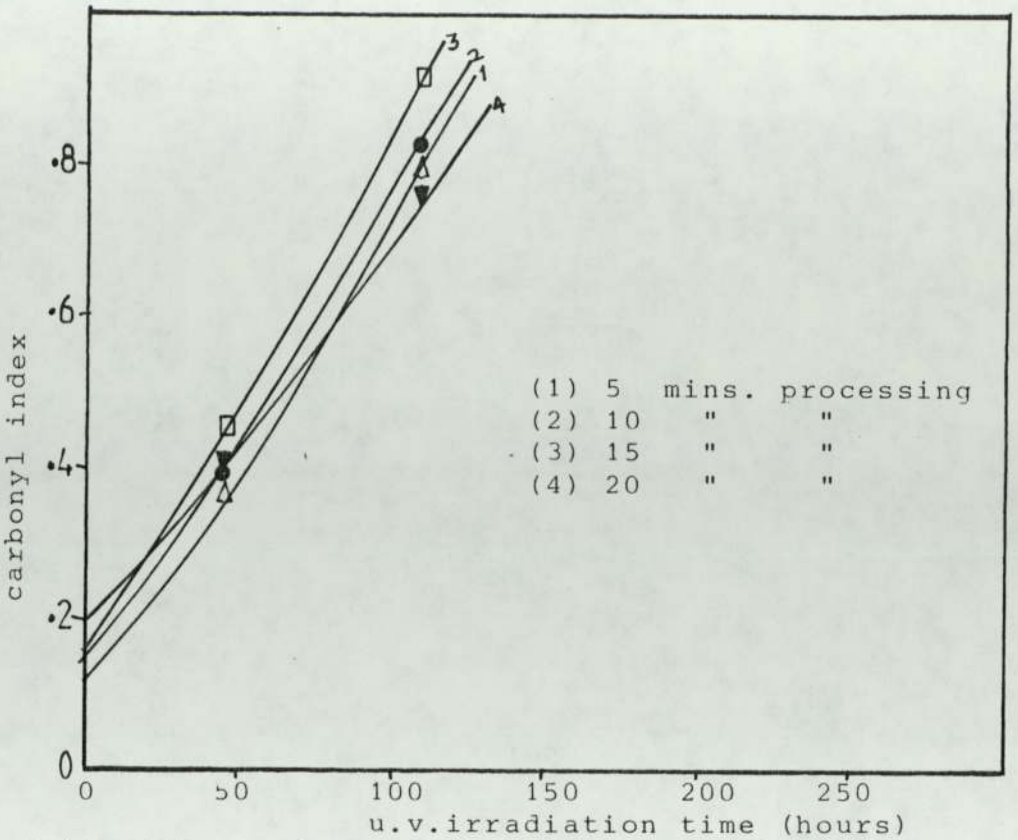


Fig.5.14: Effect of processing time on carbonyl formation (during irradiation) of PP containing 5×10^{-4} mol/100g of PTN processed for (1)5 mins, (2)10 mins, (3)15 mins, (4)20 mins. in an open mixer at 180°C.

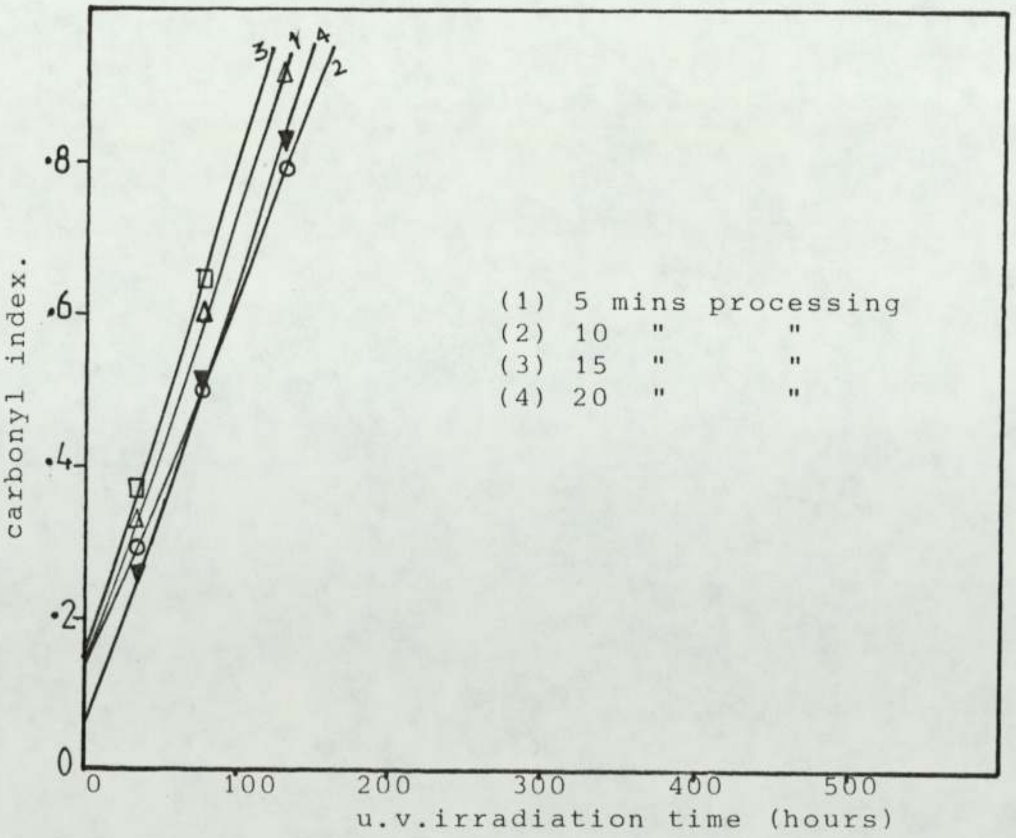


Fig.5.15: Effect of processing time on carbonyl formation (during irradiation) of PP containing 5×10^{-4} mol/100g of LTN processed for (1)5 mins, (2)10 mins, (3)15 mins, (4)20 mins. in an open mixer at 180°C.

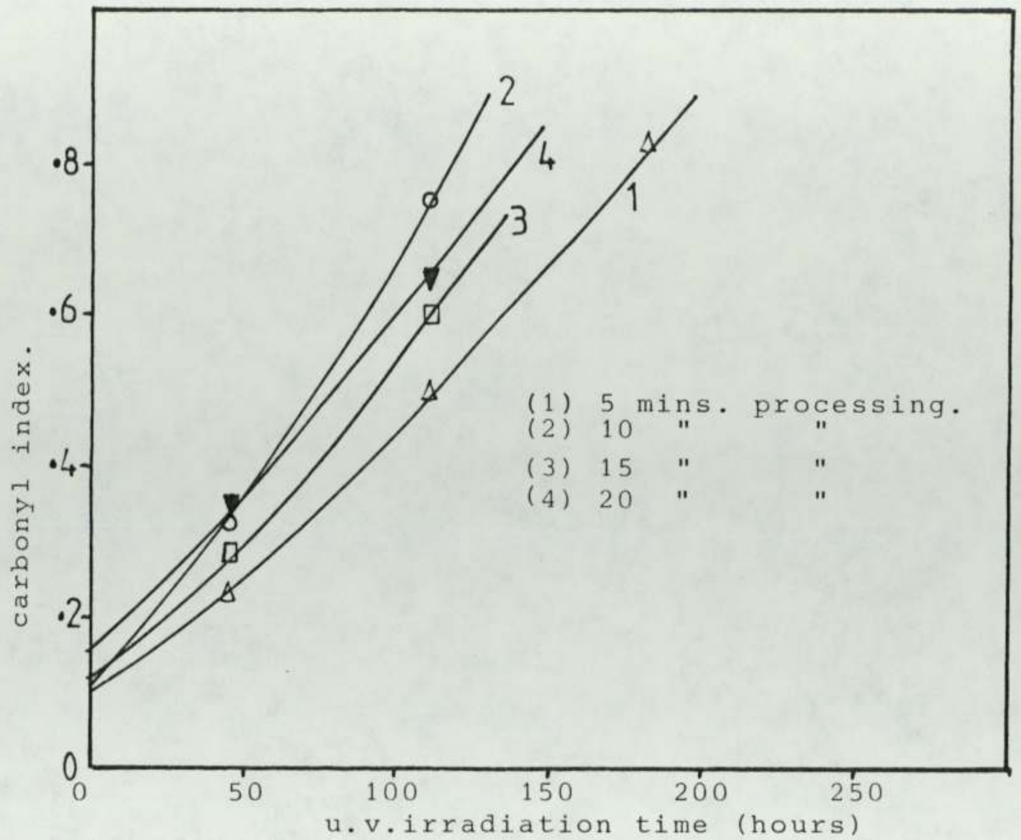


Fig.5.16: Effect of processing time on carbonyl formation (during irradiation) of PP containing $5x10^{-4}$mol/100g of OTN processed for (1)5 mins,(2)10 mins,(3)15 mins,(4)20 mins. in an open mixer at 180°C.

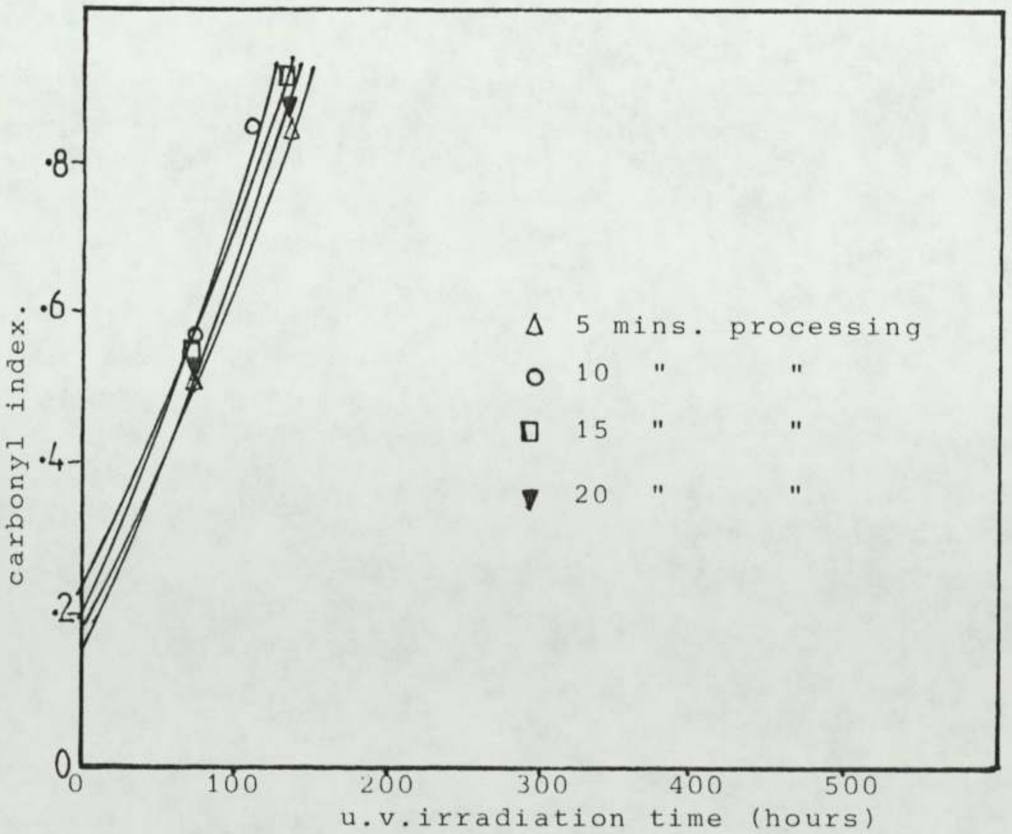


Fig.5.17: Effect of processing time on carbonyl formation (during irradiation) of PP containing $5x10^{-4}$mol/100g of STN processed for (1)5 mins,(2)10 mins,(3)15 mins,(4)20 mins. in an open mixer at 180°C.

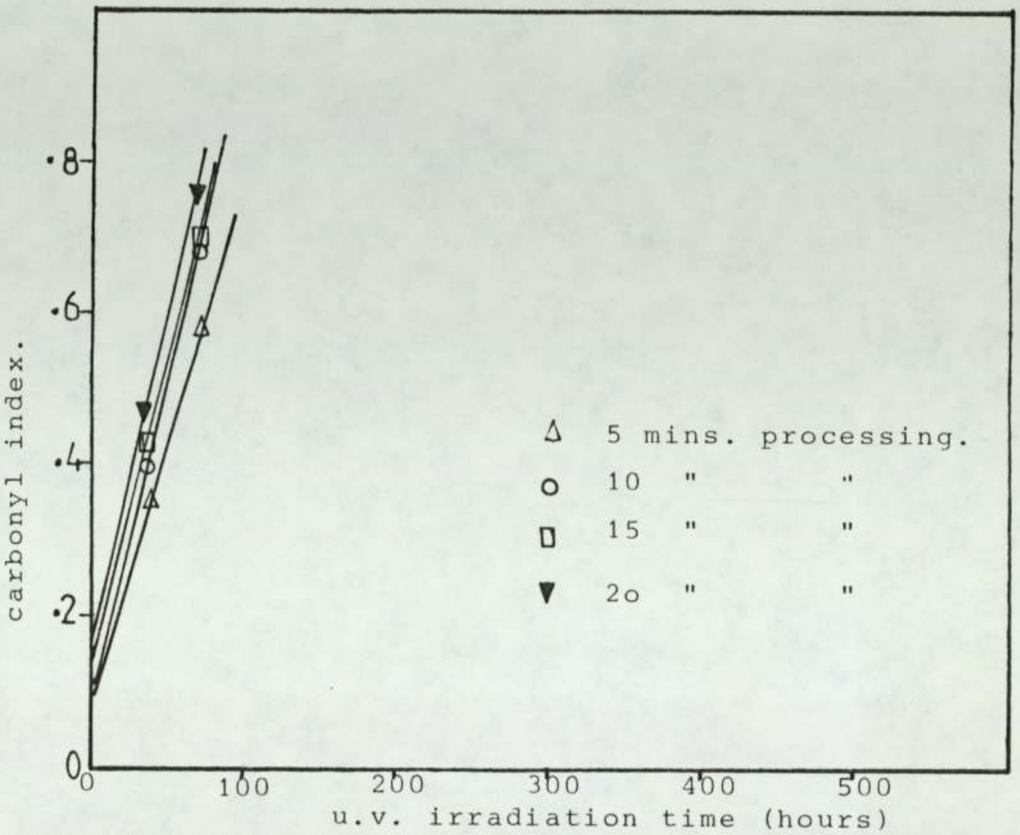


Fig 5.18: Effect of processing time on carbonyl formation (during irradiation) of PP containing 5×10^{-4}mol/100g of TN processed for (1)5 mins,(2)10 mins,(3)15 mins,(4)20 mins. in an open mixer at 180°C.

Table 5.4 Effect of additive concentration on u.v. embrittlement time (EMT) of PP containing the additives processed in a closed mixer at 180°C for 10 minutes.

	UV EMT (hours)				
Additive Con. ($\times 10^{-4}$mol/100g)	**PTN**	**LTN**	**OTN**	**STN**	**TN**
1	**130**	**130**	**180**	**135**	**150**
5	**170**	**135**	**220**	**150**	**160**
10	**180**	**180**	**280**	**190**	**180**
15	**295**	**240**	**350**	**230**	**230**
20	**620**	**290**	**740**	**320**	**280**

Table 5.5: Effect of additive concentration on u.v. embrittlement time (EMT) of PP containing the additives processed in an open mixer at 180°C for 10 minutes.

	u.v. Embrittlement times (hours)				
Additive Con. ($\times 10^{-4}$mol/100g)	PTN	LTN	OTN	STN	TN
1	90	73	100	72	↑
5	↑	125	110	125	│
10	110	↑	190	130	80
15	│	135	190	135	│
20	↓	↓	270	135	↓

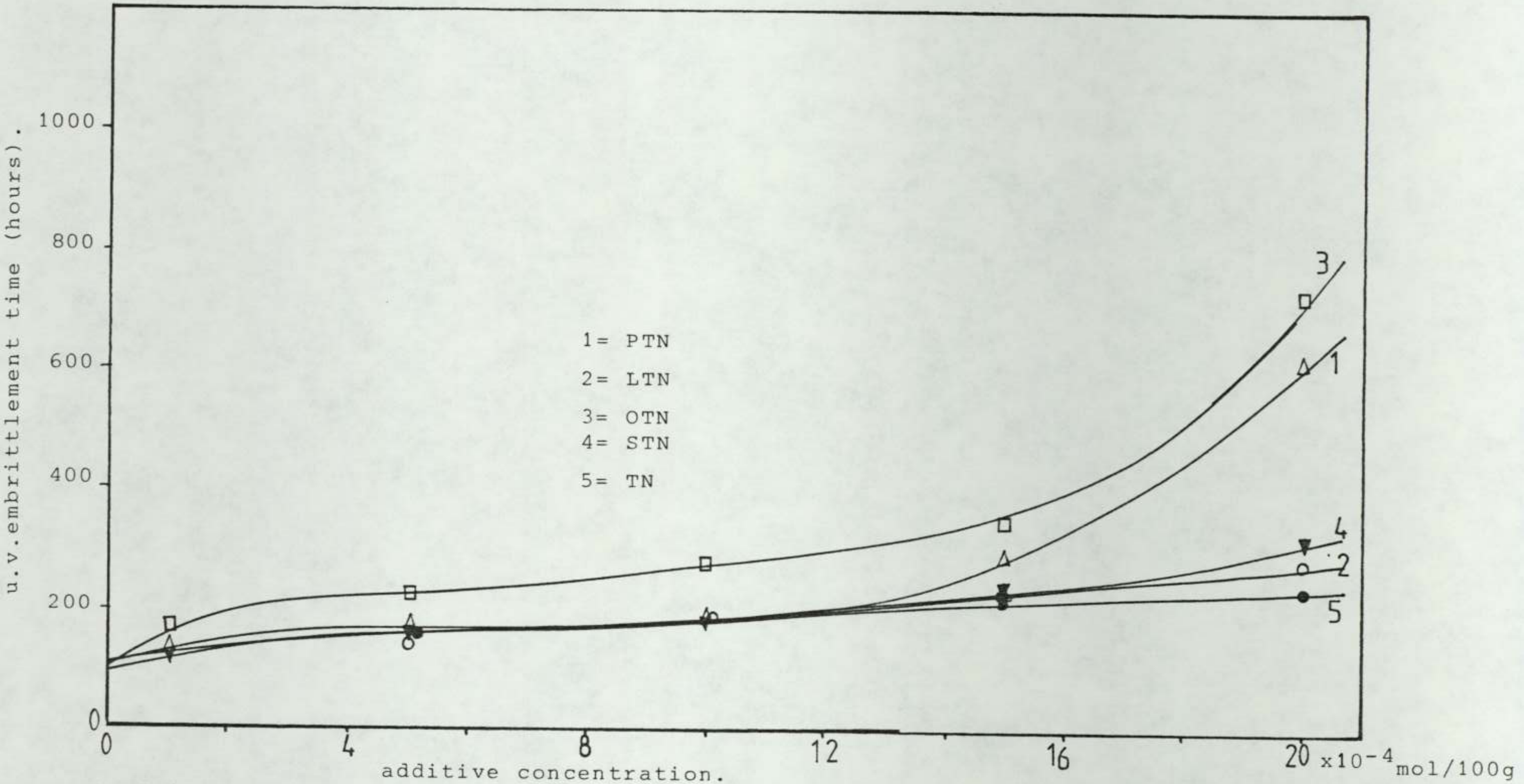


Fig.5.19: Effect of additive concentration on u.v.embrittlement time of PP processed with (1) PTN, (2)LTN, (3) OTN, (4) STN, (5) TN in a closed mixer at 180°C for 10 minutes.

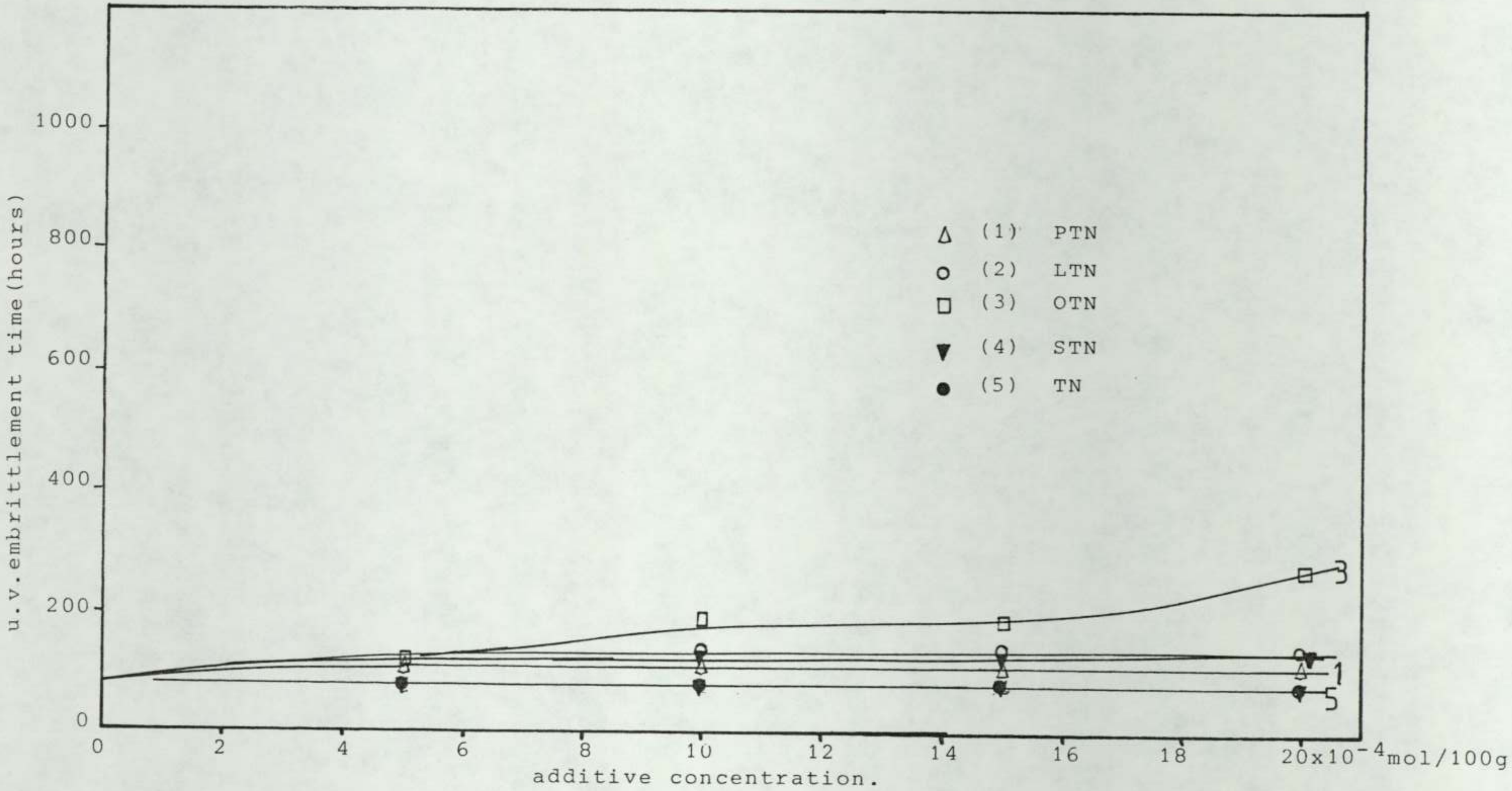


Fig.5.20: Effect of additive concentration on u.v.embrittlement times of PP processed with (1)PTN, (2)LTN, (3)OTN, (4)STN, (5)TN processed in an open mixer at 180^{o}C for 10 minutes.

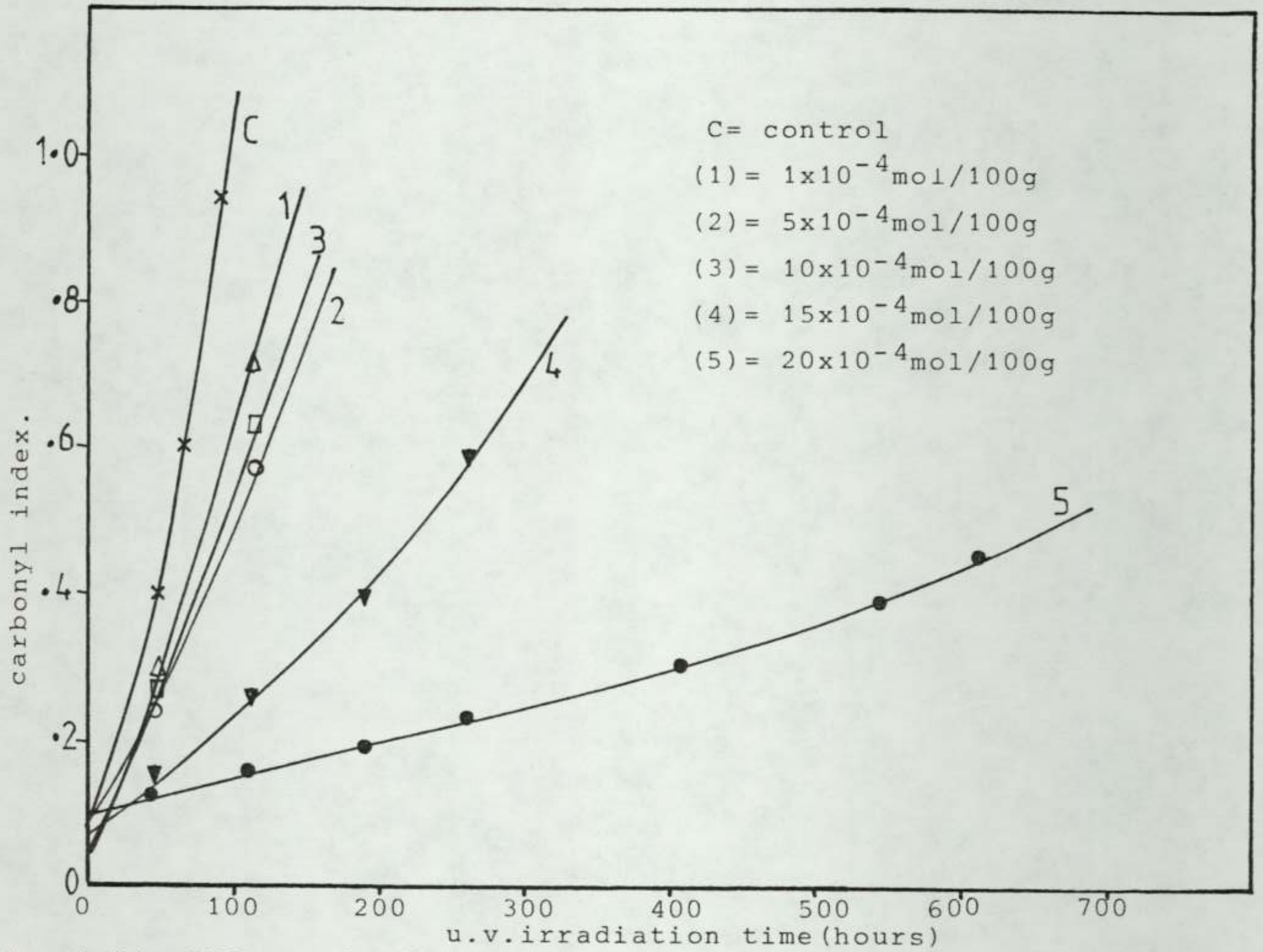


Fig. 5.21: Effect of additive concentration on carbonyl formation (during irradiation) of PP containing PTN processed in a closed mixer at 180°C for 10 minutes.

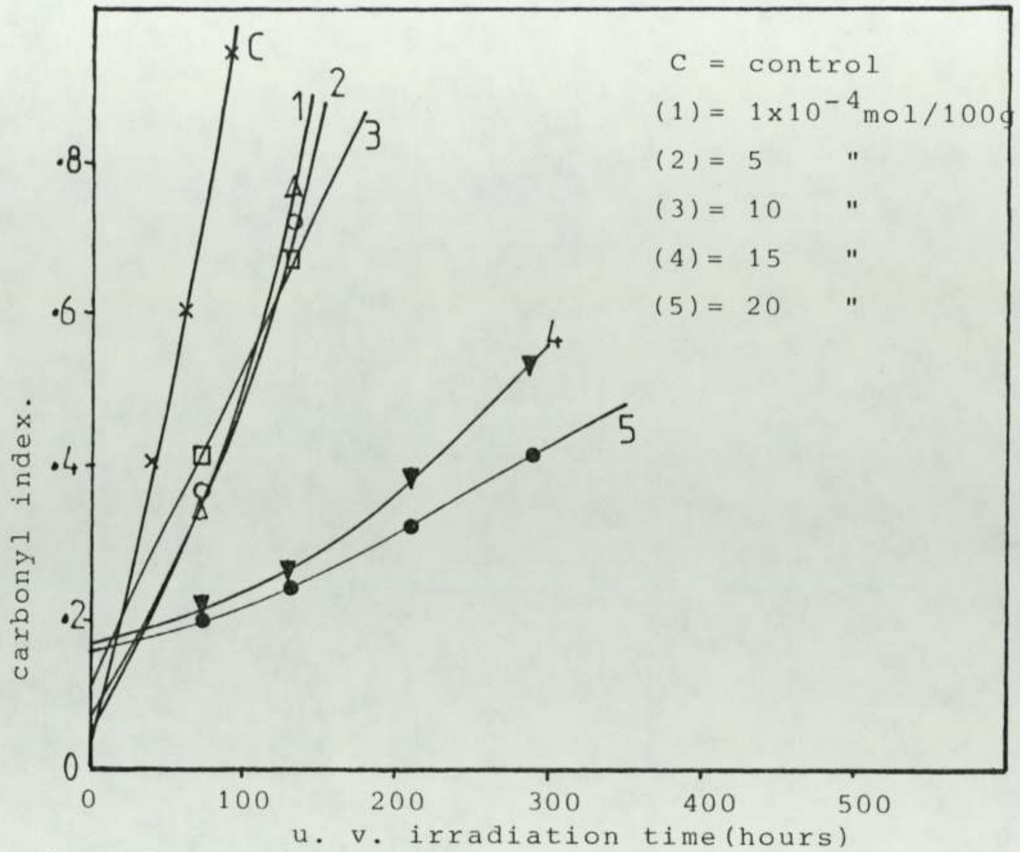


Fig.5.22: Effect of additive concentration on carbonyl formation (during irradiation) of PP containing LTN processed in a closed mixer at 180°C for 10 minutes.

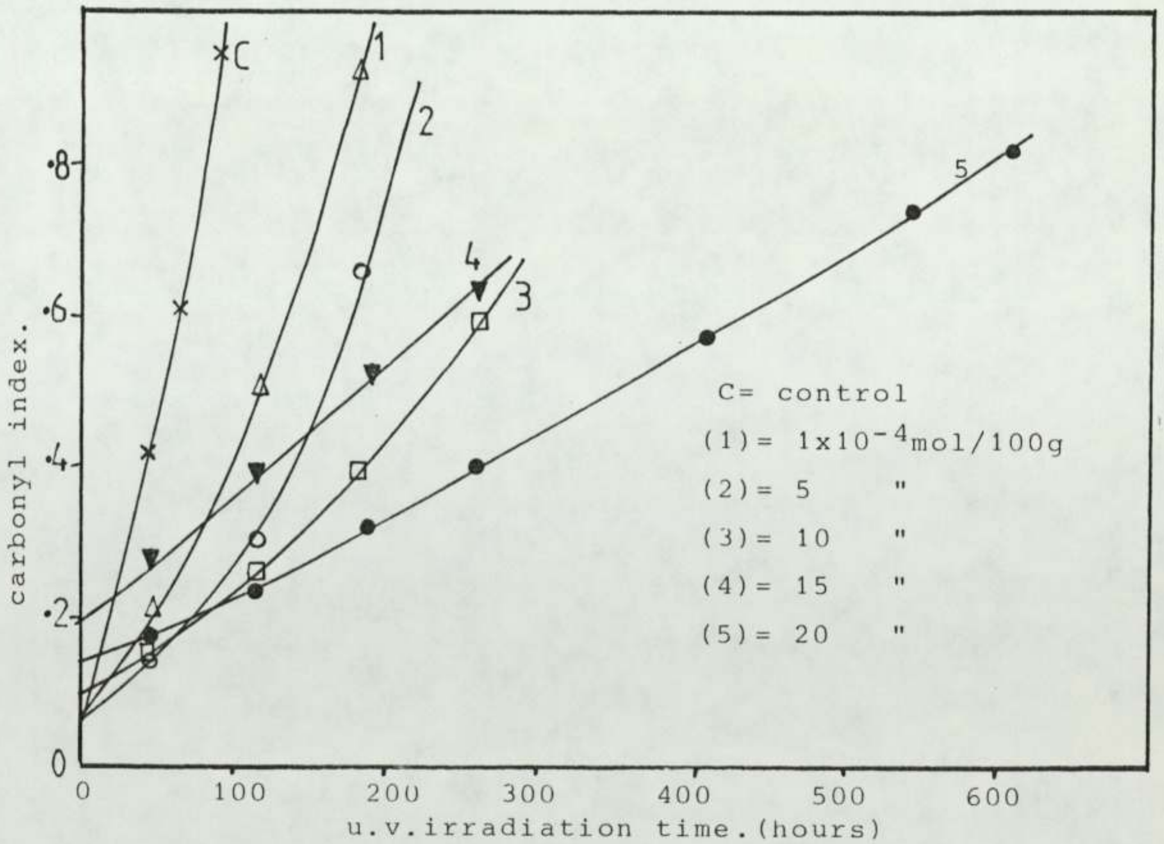


Fig. 5.23: Effect of additive concentration on carbonyl formation (during u.v.irradiation) of PP containing OTN processed in a closed mixer at 180°C for 10 minutes.

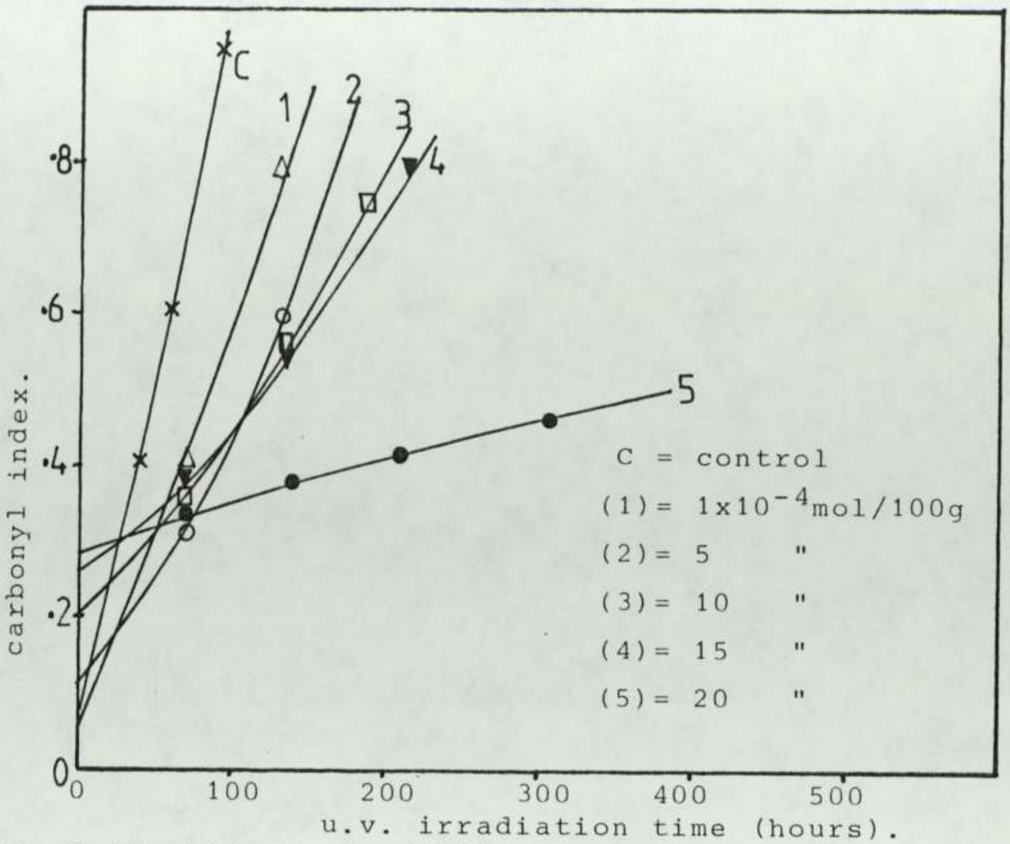


Fig. 5.24: Effect of additive concentration on carbonyl formation of PP containing STN processed in a closed mixer at 180°C for 10 minutes.

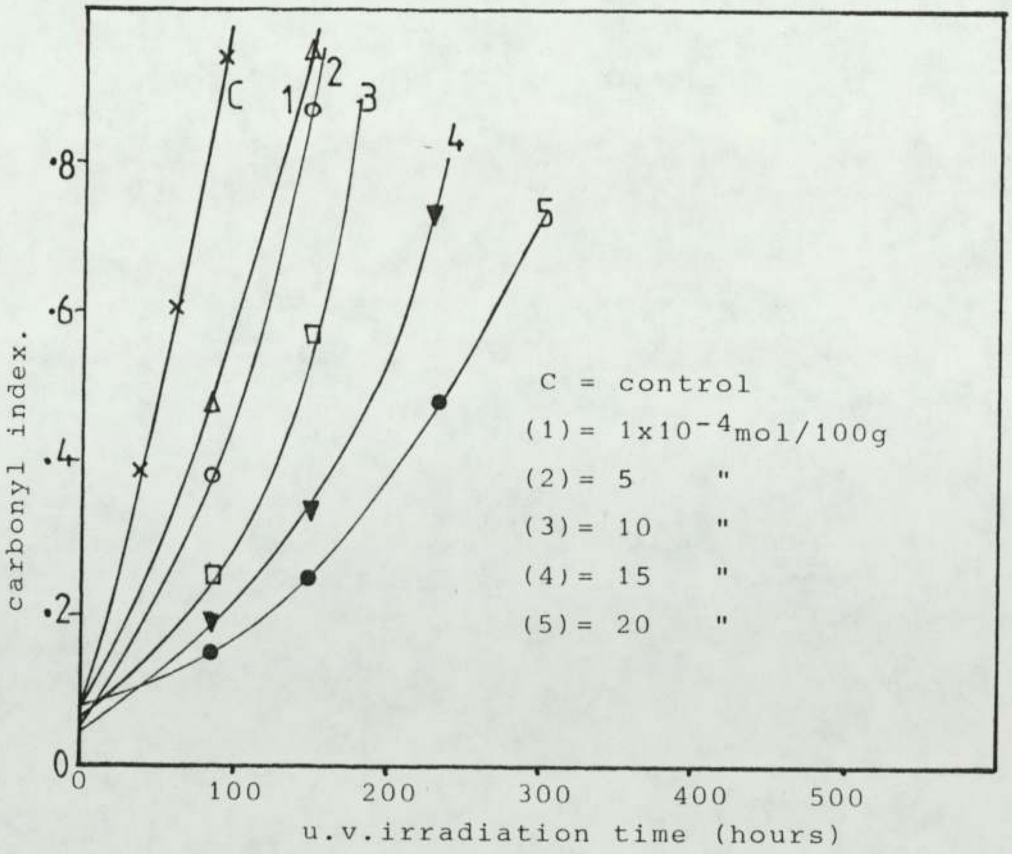


Fig. 5.25: Effect of additive concentration on carbonyl formation (during irradiation) of PP containing TN processed in a closed mixer at 180°C for 10 minutes.

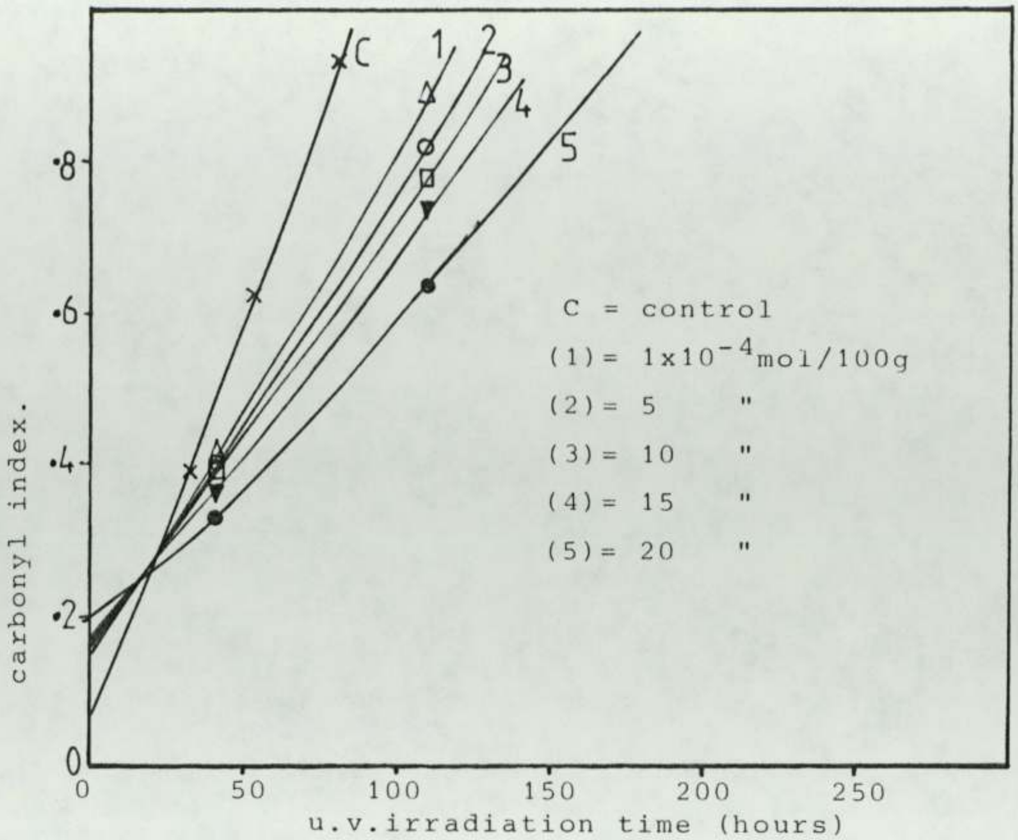


Fig. 5.26: Effect of additive concentration on carbonyl formation (during irradiation) of PP containing PTN processed in an open mixer for 10 minutes at 180°C.

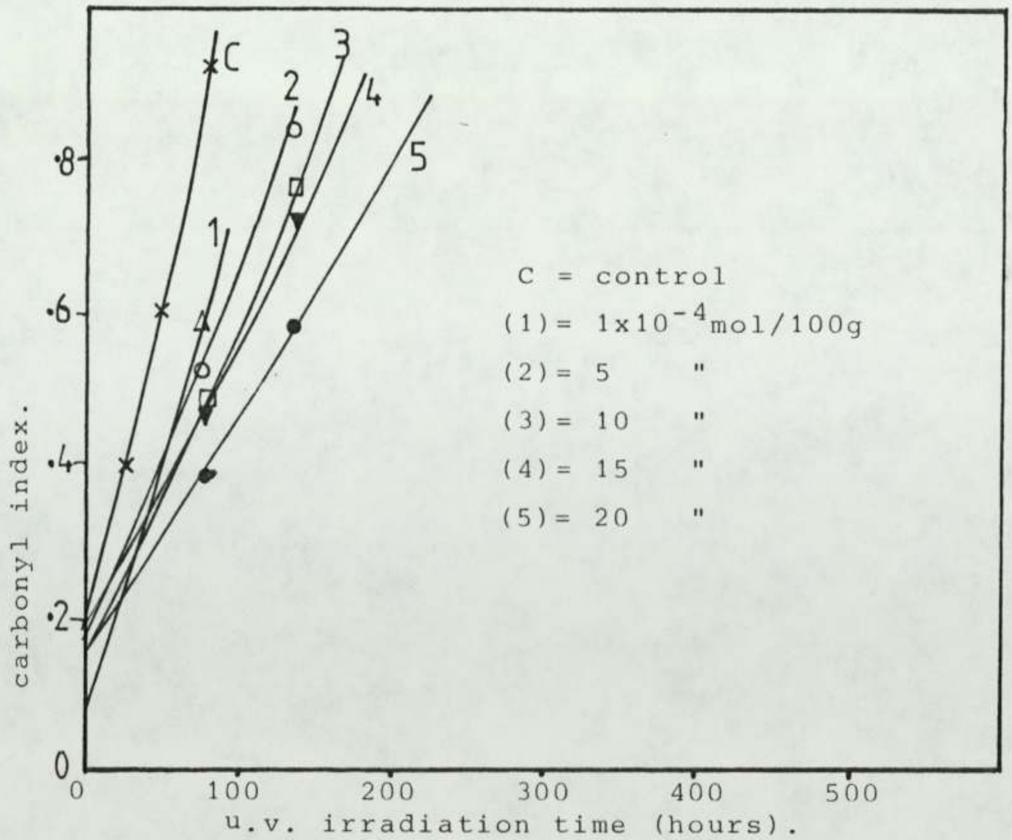


Fig. 5.27: Effect of additive concentration on carbonyl formation (during irradiation) of PP containing LTN processed in an open mixer for 10 minutes at 180°C.

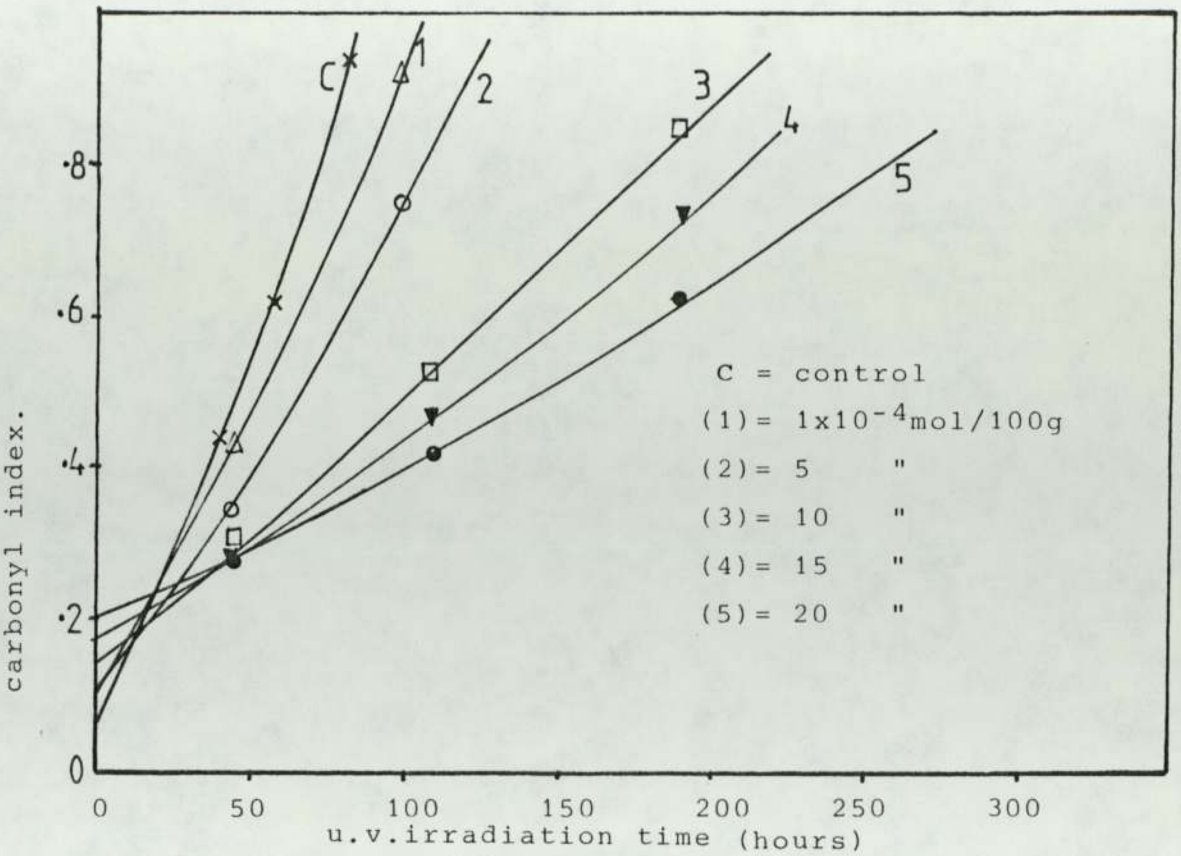


Fig. 5.28: Effect of additive concentration on carbonyl formation (during irradiation) of PP containing OTN processed in an open mixer for 10 minutes at 180°C.

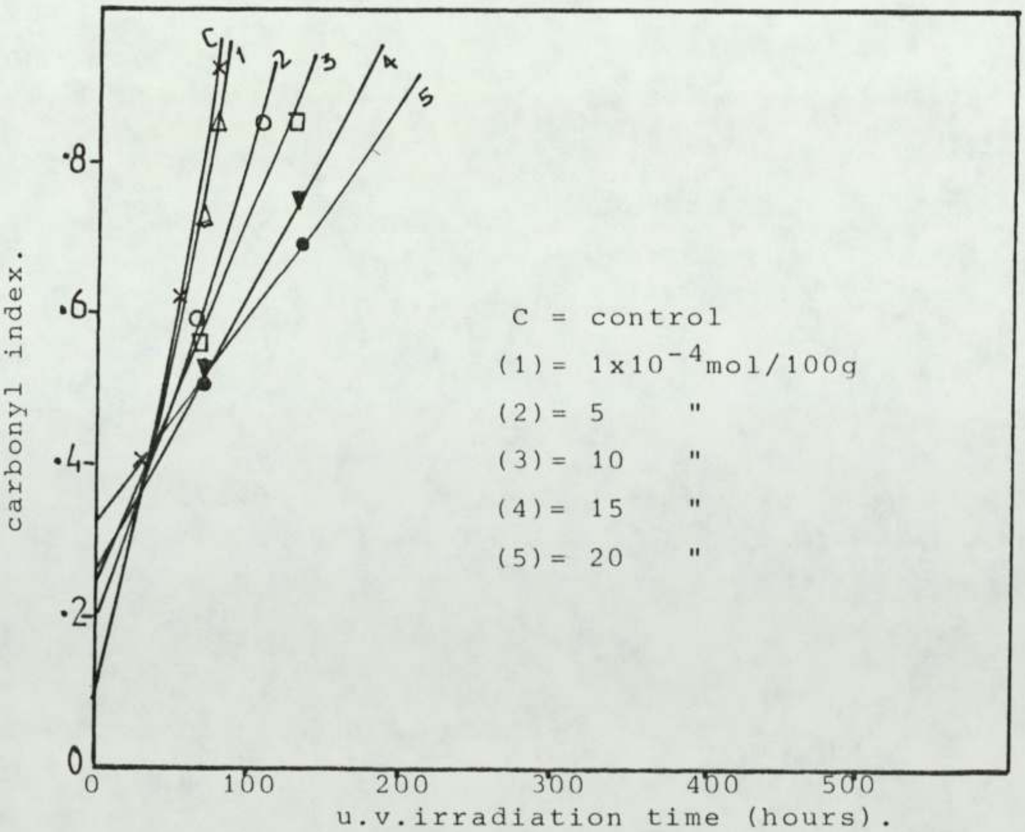


Fig. 5.29: Effect of additive concentration on carbonyl formation (during irradiation) of PP containing STN processed in an open mixer for 10 minutes at 180°C.

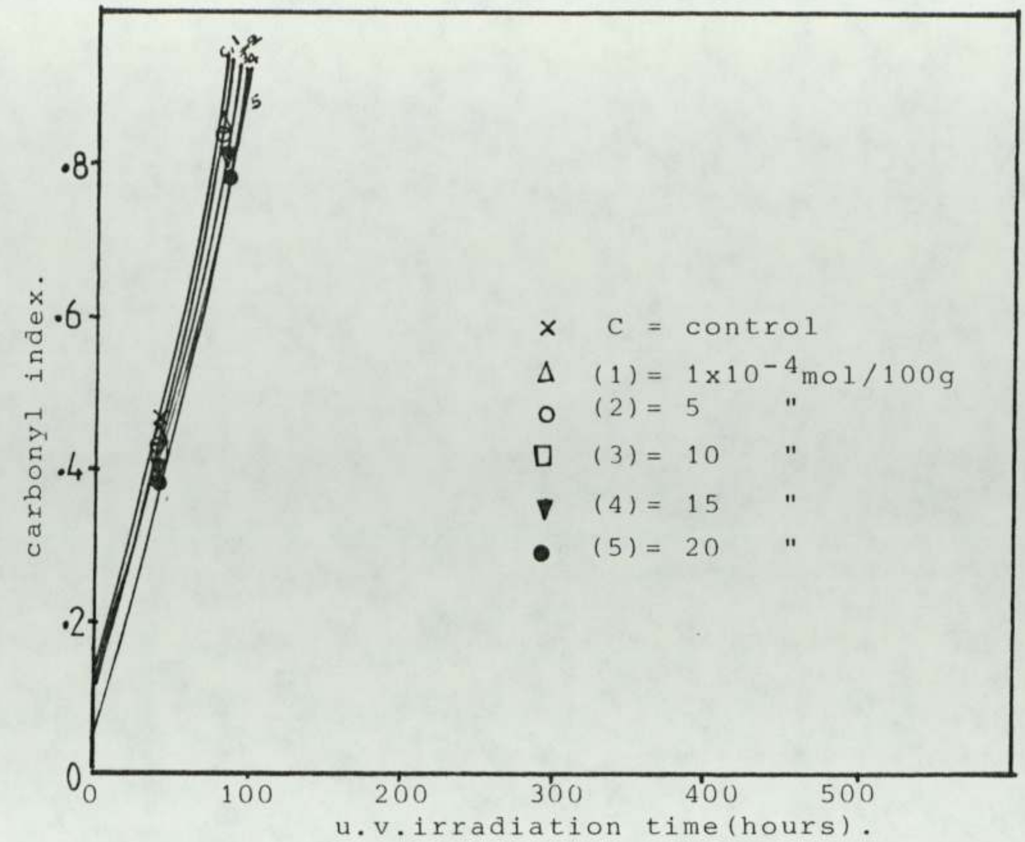


Fig. 5.30: Effect of additive concentration on carbonyl formation (during irradiation) of PP containing TN processed in an open mixer for 10 minutes at 180°C.

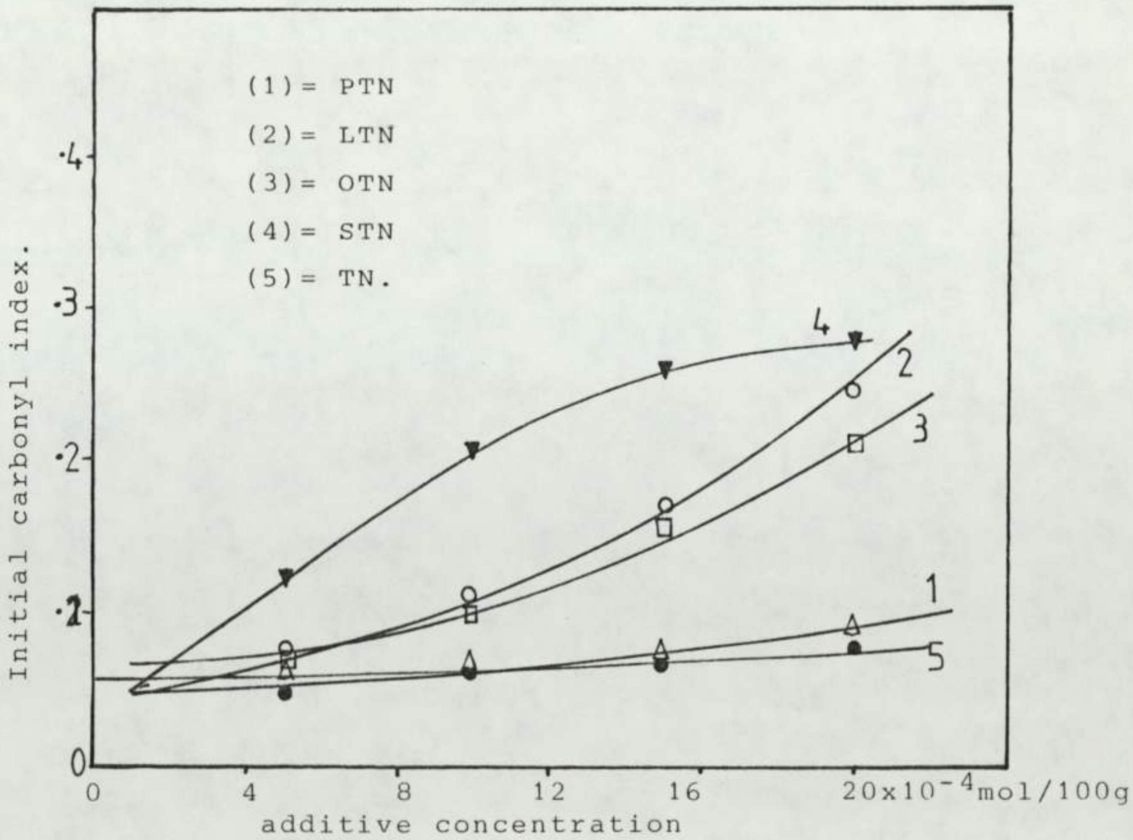


Fig. 5.31: Effect of additive concentration on initial carbonyl index of PP processed with (1)PTN,(2)LTN,(3)OTN,(4)STN,(5)TN in a closed mixer at 180°C for 10 minutes.

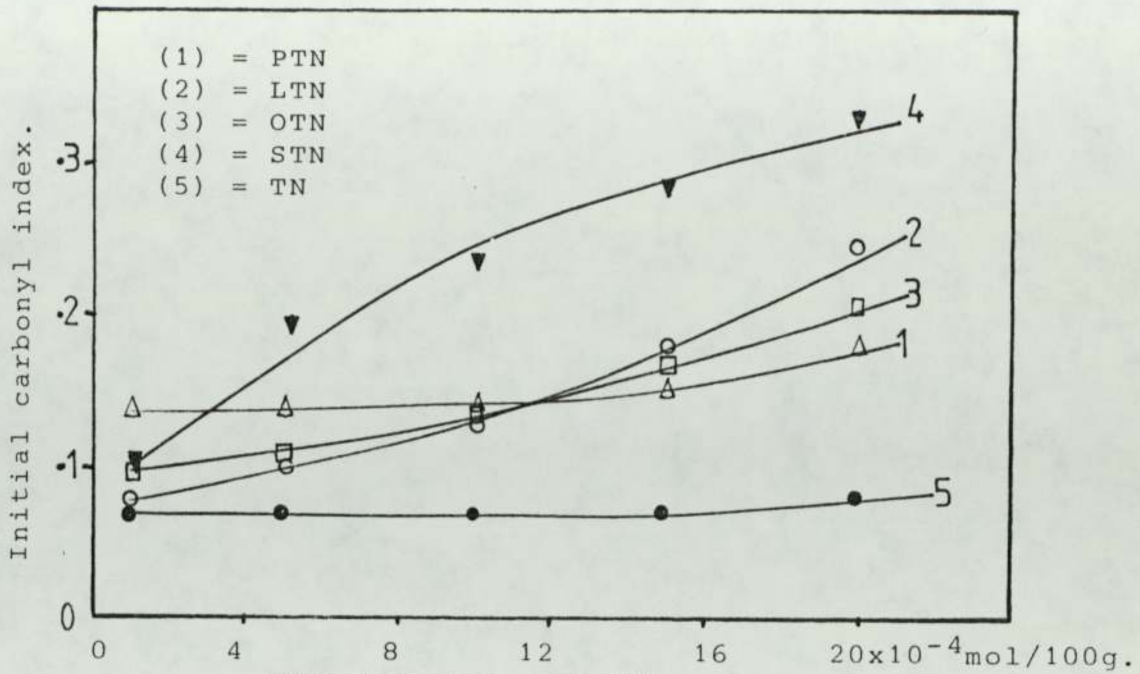


Fig. 5.32: Effect of additive concentration on initial carbonyl index of PP processed with (1) PTN, (2) LTN, (3) OTN, (4) STN, (5) TN in an open mixer at 180°C for 10 minutes.

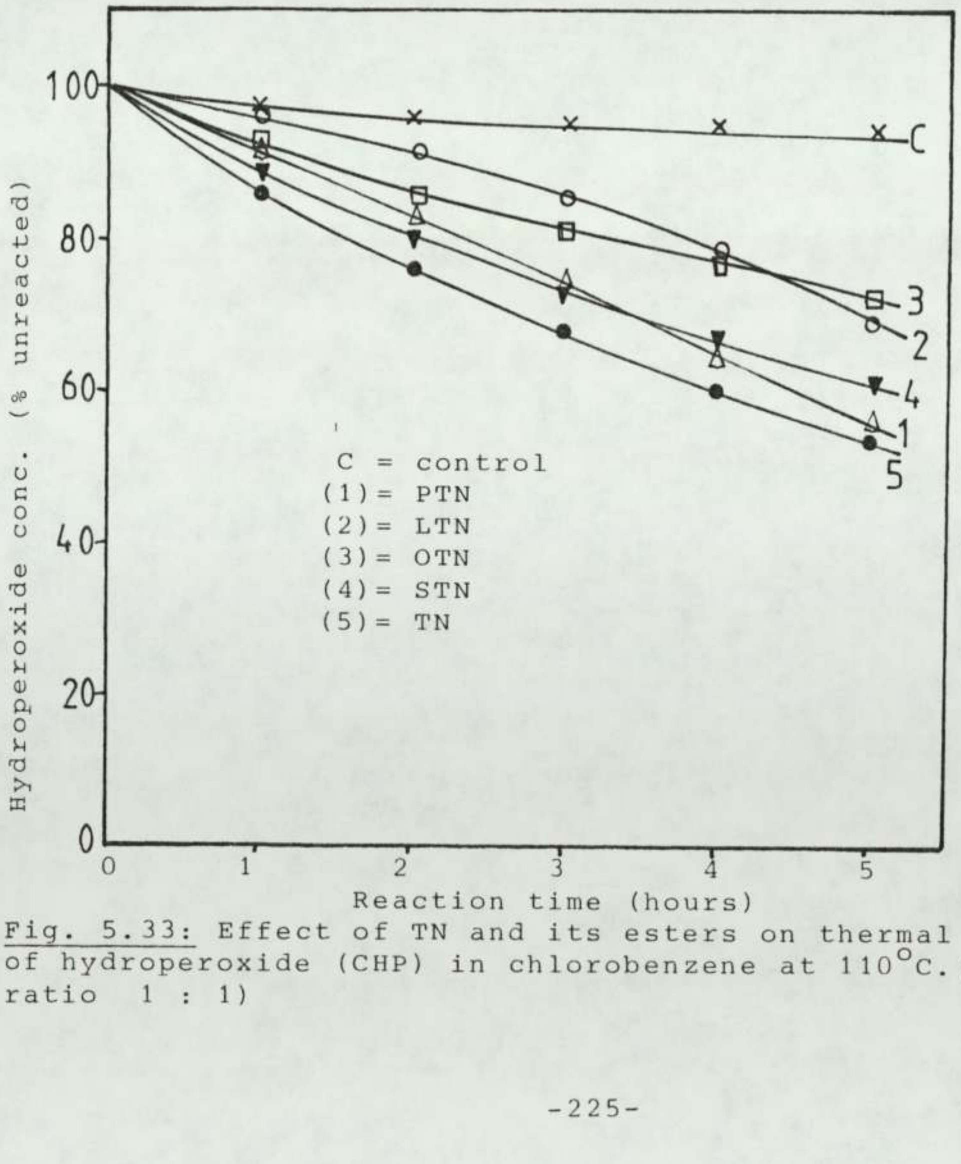


Fig. 5.33: Effect of TN and its esters on thermal decomposition of hydroperoxide (CHP) in chlorobenzene at 110°C. (reaction ratio 1 : 1)

Very little or no increases in photostability was obtained with increasing additive concentration in all films processed in the closed mixer (Fig. 5.19) except in the cases of both PTN and OTN in which significant improvements in photostability was obtained at high concentrations. In the open mixer, however (Fig 5.20), no improvement was obtained with increasing additive concentration except a slight improvement in the case of OTN at high concentration.

Figs. 5.21-5.30 show the effect of additive concentration on carbonyl formation of PP containing PTN, LTN, OTN, STN and TN processed in closed and open mixers. In all cases, no induction period was observed, although the rate of carbonyl formation varied with concentration; the higher the concentration, the slower the carbonyl build-up rate. However, it was observed that the higher the additive concentration, the higher the initial carbonyl index (before irradiation) as shown in Figs. 5.31 and 5.32 show (for closed and open mixers). In PP containing TN processed in an open mixer (Fig. 5.30) at all concentrations, the rate of carbonyl formation was very similar.

5.3 DISCUSSION

TN and its esters when processed with PP in a closed mixer did not show any signficant changes in torque (Fig. 5.1); this may indicate a melt stabilising action. This however may be a physical phenomenon rather than a chemical process as this melt stability is not reflected in either the melt flow index (Fig. 5.3) or in the increasing hydroperoxide concentrations with increasing processing time (Fig. 5.5). Indeed, the constant level of torque observed with increasing processing time may be due to a plasticising effect as esters of TN are known(133) to be good plasticisers for moulding plastics. The fact that both LTN and STN have higher torque values than TN while PTN and OTN have lower torque values than TN support this argument as both LTN and STN are solids while both PTN and OTN are liquids. Maximum torque valves at 0.25 minutes of processing (see Fig. 5.1 inset) shows that the liquid additives (PTN and OTN) have lower values while the solid esters (LTN and STN) and TN have relatively higher values. Similarly, in the open mixer processed samples, the same phenomenon was obtained except that TN has higher torque values with processing time than other additives while the liquid additives have relatively low values of maximum torque compared to those of the solid esters.

The increase in melt flow rate (MFI) with processing time as shown in Figs. 5.3 and 5.4 in PP containing TN and its esters processed in both closed and open mixers could be correlated to the build-up of hydroperoxides with processing time (Figs. 5.5 and 5.6). The higher the hydroperoxide concentration in the processed films, the higher the melt flow index. This indicates that mechano-chemical oxidative degradation must be taking place during processing. The fact that the additives would not inhibit hydroperoxide build-up during processing (Fig. 5.5 and 5.6) suggests that the additives cannot and do not deactivate the radical-chain propagating species- alkyl and alkylperoxyl radicals.

Results obtained in model compounds show that all the additives do not efficiently decompose hydroperoxides under the effect of heat, even at the stoichiometric ratio of additive to peroxide (Fig. 5.33). This results in the build-up of a reservoir of hydroperoxides with increasing processing time which then serve as the main initiators during subsquent photo-irradiation. This may be responsible for the absence of any induction period during irradiation. This may also account for the generally low of level photostabilisation of PP by the additives in both closed and open mixer processing conditions, as evidenced by the low embrittlement times obtained (Figs. 5.7 and 5.8) under the effect of u.v. light.

Electron spin resonance (e.s.r.) examination of all these films containing the additives showed no signal/resonance at all thus indicating that the additives do not take part in any reactions which give nitroxyl radicals as products or as intermediates.

With increasing additive concentrations (Figs. 5.19 and 5.20) the photostabilising activity of the additives is very comparable with that of TN at the same molar concentations except in the case of PTN and OTN in which photostabilisation increased at high concentrations (high weight percentage concentration- almost master- batch proportions, see Table 5.1). This indicates that the fatty acid substituents of esters have no significant stabilising activity on PP. Indeed they may be inert to radical-chain propagating species. The only stabilising function present in the esters and TN will therefore appear to be the nitro (NO_2) group but the concentration of this group becomes very insignificant as the molecular weight of the additives increase.

The slight improvement in photostabilisation of PP at high concentrations in the case of PTN and OTN (Fig. 5.19 and 5.20), may be due to the physical form of additives (both are liquids) which may have resulted in a better solubility hence substantivity of the two additives in PP. In the open mixer samples however (Fig. 5.20) all esters gave relatively low photo-stabilisation and the long substituent chains of the esters are of significance.

The absence of an induction period in these films must be due to the large concentration of hydroperoxides formed during processing which may be easily photo-cleaved to generate radical chain propagation species during photo irradiation.

5.4 SYNERGISM WITH ANTIOXIDANTS AND STABILISERS

Two esters LTN and OTN (a solid and a liquid) were both evaluated in two-component synergistic combinations with a commercial antioxidant Tinuvin 770 and a stabiliser, HOPB. The same performance tests were employed in the evaluation.

Tables 5.6 - 5.9 show the u.v embrittlement times at different additive combinations. These are summarised in Figs. 5.34. and 5.35 for combinations with HOBP and Tinuvin 770 respectively.

Table 5.6

LTN x10^{-4}mol/ 100g	HOBP x10^{-4}mol/ 100g	UV EMT HRS.	% * syner- gism.
10 (0.7)	0 -	180	-
5 (0.56)	2 (0.565)	390	25
6 (0.42)	4 (0.13)	420	- 30
5 (0.25)	5 (0.16)	540	- 17.4
4 (0.28)	6 (0.2)	560	- 26
2 (0.14	8 (0.26)	630	- 21.7
0 -	10 (0.23)	800	-

Table 5.7

LTN x10^{-4}mol/ 100g	Tin 770 x10^{-4}mol/ 100g	U.V. EMT. HRS.	% * syner gism.
10 (0.7)	0 -	180.	
8 (0.56)	2(0.1)	1510	
6 (0.42)	4 (0.19)	2870	
5 (0.35)	5 (4.24)	3180	58.06
4 (0.28)	6 (0.29)	3320	
2 (0.14)	8 (0.38)	3500	
0 -	10 (0.48)	3600	

Table 5.8

OTN$_4$ x10^{-4}mol/ 100g	HOBP x10^{-4}mol/ 100g	UV EMT (hrs)	% * Synergism
10 (0.843)	0 -	280	-
8 (0.75)	2 (0.065)	410	- 3.03
6 (0.57)	4 (0.13)	440	- 38.6
5 (0.47)	5 (0.16)	510	- 33.3
4 (0.38)	6 (0.20	570	- 31.4
2 (0.19)	8 (0.26)	620	- 28.86
0 -	10 (0.23)	800	-

Table 5.9

OTN$_4$ x10^{-4}mol/ 100g	Tin 770 x10^{-4}mol/ 100g	U.V. EMT. Hours.	% * synergism.
10 (0.943)	0 -	280	
8 (0.75)	2 (0.1)	2300	
6 (0.57)	4 (0.19)	2920	
5 (0.47)	5 (0.24)	3100	51.96
4 (0.38)	6 (0.29)	3240	
2 (0.19)	8 (0.38)	3390	
0 -	10 (0.48)	3600	

Figures in brackets are weight percentages.

$$\text{Synergism}^{(95)}\% = \frac{(Es-Ec) - [(E_1-Ec) + (E_2-Ec)]}{(E_1 - Ec) + (E_2 - Ec)} \times 100$$

Es = embrittlement time of synergist

Ec = embrittlement time of control

E_1= embrittlement time of component 1

E_2= embrittlement time of component 2

From Fig. 5.34, it could be seen that no combination of either LTN or OTN with HOBP gave better photostability of PP than the HOPB control itself. It is clear from Tables 5.6 and 5.8 that both LTN an OTN show antagonism with HOBP in PP. HOBP is known(150) to be decomposd in the presence of peroxides under the effect of u.v. light and since both LTN and OTN do not prevent the formation of hydroperoxides, antogonism may have been due to high concentration of hydroperoxides present in the system. Additionally it may be that both components in the synergistic system form complexes which are inactive to both alkyl and/or

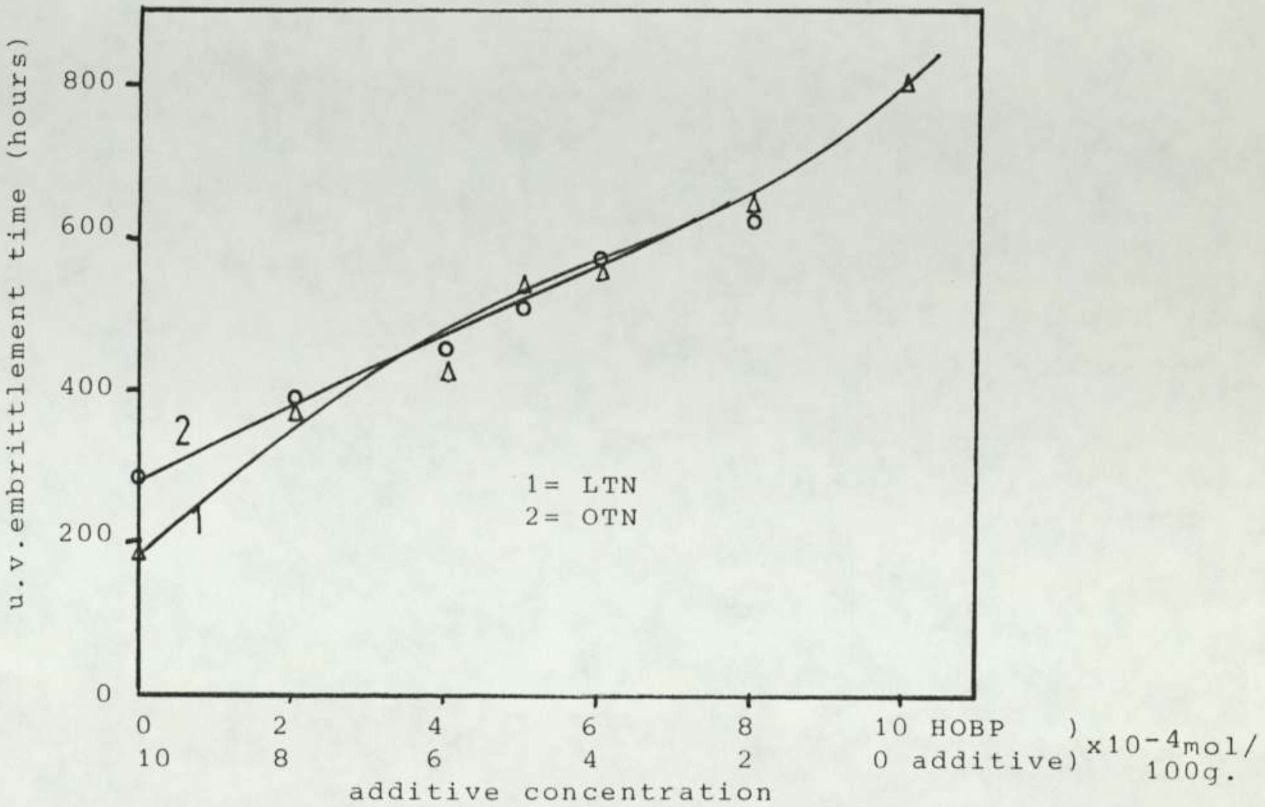


Fig. 5.34: Synergism between LTN, OTN with HOBP processed in a closed mixer for 10 minutes at 180°C.

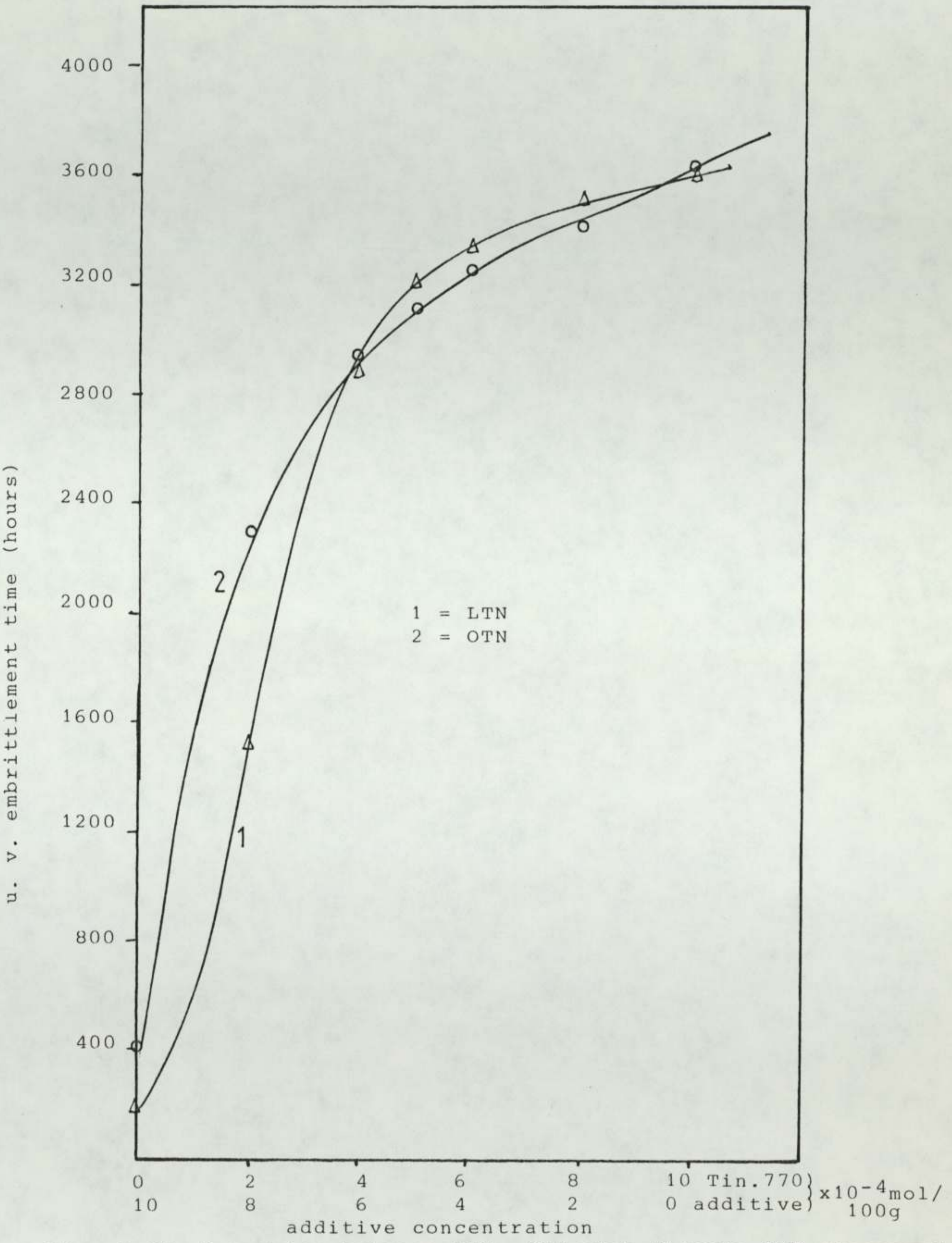


Fig. 5.35: Synergism between LTN, OTN with Tinuvin 770 processed in a closed mixer for 10 minutes at 180°C.

alkylperoxyl radicals, thus not interfering in the radical chain propagation reactions of degradation.

On the other hand although no combination with Tinuvin 770 gave better photostability activity than the Tinuvin 770 itself, at equal molar concentration, synergism was obtained in excess of 50%. As both LTN and OTN do not prevent hydroperoxide formation, the conversion of Tinuvin 770 to its corresponding nitroxyl radicals by the hydroperoxides enhances the scavenging of alkyl radicals by the nitroxyl radicals formed.

Additionally, it may be that both LTN and OTN enhance the solubility of Tinuvin 770 in PP thus enhancing the antioxidant function.

CHAPTER SIX

CONCLUSIONS AND SUGGESTIONS FOR FURTHER WORK

6.1 CONCLUSIONS

From results obtained in this work, the following conclusions could be made.

(1) 4-hydroxyl,2,2,6,6 tetrametheyl piperidinyl-1-oxyl (4OHTMPNO$^\bullet$) stabilised Polypropylene effectively (in restricted oxygen) during thermal processing by alkyl radical deactivation. Although substituted (alkyl) hydroxylamine and other non-extractable products were formed, their concentration was low relative to other species in the system. Olefinic unsaturation was found to increase with increasing processing time indicating the conversion of the nitroxyl radical to its corresponding free hydroxyl-amine. The free hydroxylamine was estimated by deduction from the nitroxyl radical concentration in processed films and the total nitroxyl radical concentration upon extraction and oxidation of the extract. The nitroxyl radical however continued to regenerate with processing time (in films), though the overall concentration decreased with increasing processing time. This confirms that the redox reactions between nitroxyl radicals and free hydroxylamines occured.

The regeneration must be by oxidation of the free hydroxylamine by alkyl peroxyl radicals. This will depend on the amount of oxygen as well as the alkyl radical concentration present in the system, at any given time.

(2) 4-hydroxyl 2,2,6,6, tetramethyl piperidinyl-1-oxyl (4OHTMPNOH) offered photostabilisation to Polypropylene. There was a fair correlation between the total nitroxyl concentration in films (nitroxyl radicals and that due to hydroxylamines) and photostabilisation indicating that both nitroxyl radicals, and hydroxylamines took part in the photo-stabilisation process. Regeneration of nitroxyl radicals may have occured during photo oxidation by reaction of either free or alkyl hydroxylamines with alkylperoxyl radicals but evidence here (infra-red spectroscopy) is not enough to draw a more definite conclusion.

(3) Free hydroxylamine, 4-hydroxyl,2,2,6,6 tetramethyl piperidinyl-1-ol (4OHTMPNOH) offered good melt stabilising effect to Polypropylene during thermal processing. This again must be mainly due to alkyl radical deactivation as hydroperoxides concentrations did not increase substantially with increasing procesing time. Nitroxyl radicals were increasingly furnished from the hydroxylamine until a maximum was reached and then starts to decrease. Again, there was a fair correlation between the total nitroxyl radical concentrations (upon extraction and oxidation) and photostability of the processed films. Thus photostabilisation must be by the same mechanism as in the case of 4-hydroxyl 2,2,6,6, tetramethyl piperidinyl-1-oxyl above.

(4) Both compounds above the nitroxyl radical and its free hydroxylamine (4OHTMPNO$^\bullet$and OHTMPNOH) have comparable phostostabilising activity in Poly-propylene at the same concentration and under the same processing condition. This depends on the amount of oxygen present in the system which is essential in the stabilisation process. In the complete absence of oxygen (e.g. under argon atmosphere) stabilisation was relatively low and this must be due to the

lack of regenerating capability.

(5) Both 2-methyl-2-nitroso propane (tBuNO) and N-nitroso diphenylamine stabilised Polypropylene during thermal processing by mechanism which involved nitroxyl radical formation. In both cases, the nitroxyl radicals must be bound to the polymer chain as exhaustive extraction did not remove the radicals completely. The radicals are therefore responsible for photo-stabilisation of the polymer (radical concentration decreased with increasing photo-irradiation time). There was no evidence to suggest regeneration of the nitroxyl radicals during thermal processing (or during photo-oxidation). In the case of the N-nitroso compound, the nitroxyl radical formation was due to the nitric oxide radical initially formed by thermal breakdown of the parent compound.

(6) 2-methyl-2-nitro-propane ($tBuNO_2$) and Trimethylol nitromethane (TN) are not nitroxyl radical precursor, either during thermal processing or during photo-oxidation. They also do not deactivate alkyl or alkyl peroxyl radicals and are not efficient peroxide decomposers under heat. Thus they are not very good melt stabilisers for Polypropylene. Both are however, good photostabilisers (particularly Trimethylol nitromethane). The mechanism of their photostabilisation of Polypropylene is not clear at this stage but results indicate that in the case of 2-methyl-2-nitro propane, the mechanism involves the formation of unsaturation by hydrogen abstraction from the polymer resulting in a reduced product of the additive. In the case of Trimethylol nitromethane however, during thermal processing, decomposition occurs resulting in an aldehyde and a nitroalkane. The contribution of these products to the overall stabilisation is presently

not clear but the mechanism appears to be through a u.v. absorbing/ screening mechanism or through photo-induced non-radical hydroperoxide decomposition.

(7) Trimethylol aminomethane did not offer any significant melt or photo stabilisation to PP. It neither deactivated alkyl or alkylperoxyl radicals nor decomposed the formed hydroperoxides under heat.

(8) Like trimethylol aminomethane, esters of the nitromethane did not offer any improved photostabilisation to PP than the nitromethane. The longer alkyl chains are inert and were of no significance. High concentrations of hydroperoxides formed during processing of PP with the esters must have been the major initiators of photo-oxidation.

(9) All additives (except esters of trimethylol nitromethane) showed synergism with HOBP while synergism with Tinuvin 770 was modest. No synergistic combination offered better photostabilisation than Tinuvin 770 alone. Esters of the nitromethane however, antagonised HOBP in PP.

6.2 SUGGESTIONS FOR FURTHER WORK

(1) In this work, the concentrations of the hydroxylamines were deduced by the difference between the total nitroxyl radical concentration (upon extraction and oxidation), the observed concentration in the processed films and the initially added concentration. In order to confirm the mechanism in the processing operations in detail, quantitative determination of the three different species is necessary. So also is the identification and estimation of other products formed (if any). These may explain the termination

reactions involved in the system. Although the concentration of alkyl hydroxylamine deduced was low, it is suggested that photo-stabilisation due to alkyl hydroxylamines be quantified by oxidation of the extracted films back to the nitroxyl radical and measuring the nitroxyl concentration.

(2) Products of thermal decomposition of trimethylol nitromethane include an aldehyde and nitroalkane. The role of these products in the overall stabilisation of PP and the extent of the decomposition with processing time may be investigated. It is also suggested that attempts be made to synthesise trimethylol nitroso methane and it be examined as a photostabiliser for PP.

(3) Nitro compounds (e.g. 2-methyl-2-nitro propane) under photo-oxidative conditions may form nitrites and nitrates. The effectiveness of these compounds as photostabilisers for PP may be investigated. This may provide some understanding of the mechanism of photostabilisation of PP by nitro compounds.

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