THE ROLE OF THE PROCESSING OPERATION ON THE UV DEGRADATION OF PVC

by

Joseph Vyvoda

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SUMMARY

In this work the thermal degradation of a commercial poly (vinyl chloride) has been studied during the mixing in a processing machine which simulates a commercial operation (Rapra Torque Rheometer). Processing was carried out without additives and also with dibutyltin maleate-based stabilizer Irgastab T290 and lubricants Ca-stearate and Wax E. Photodegradation of PVC processed with both additives and without additives has been also studied.

Apart from thermal energy, the factors which influenced the thermal degradation of unstabilized PVC were found to be the presence of air and mechanical work (shear forces). ~~The~~ Peroxide was formed in the initial stage of processing. The concentration of peroxide rapidly decreased due to the occurrence of hydrogen chloride-induced decomposition. The presence of a lubricant decreased the shear forces and the contribution of a pure mechanical process to the overall thermomechanical degradation was smaller. On prolonged processing crosslinking and chain scission occurred and chemical analysis showed an increase in peroxide concentration. Infrared spectroscopy showed the formation of carbonyl and conjugated carbonyl groups. The chain scission was shown to be of an oxidative character. The lower molecular weight species were formed as a result of rearrangement of intermediate alkoxy radicals formed by the decomposition of both peroxide and peroxy-crosslinks. The exact mechanism of the crosslinking reaction is not yet clear but the ~~presence~~ occurence of

oxidation suggested the participation of intermediate alkoxy, hydroxy~~l~~ and alkylperoxy radicals.

The study of the processing of PVC with dibutyltin maleate-based stabilizer (Irgastab T290) ha~~ve~~s shown the occurrence of the exchange reaction between the carboxylate moiety of the stabilizer and the labile chlorine atoms (probably allylic). The formation of anhydride, dibutyltin chloride and the occurrence of Diels-Alder type reaction was demonstrated. The role of Ca-stearate in the presence of dibutyltin maleate stabilizer was shown to be predominantly that of a lubricant.

Photodegradation of processed unstabilized PVC in the presence of air by the ultraviolet radiation of wavelength greater than 280nm ha~~ve~~s resulted in an extensive photo-oxidation. The photo-oxidation proceeded in two stages viz an initial fast-rate stage followed by the second slower-rate stage. Initiation of photo-oxidation by the peroxide formed during processing has been demonstrated. The unsaturation generated by the thermomechanical treatment was considered to be important as sensitizer of photo-oxidation. The formation of polymeric ketone and polymeric alcohol have been shown and it was suggested that they were the products of photolysis of intermediate hydroperoxide. Retardation of photo-oxidation was shown to be the result of a slower diffusion rate of air through the crosslinked structure.

It has been demonstrated that during photodegradation the thermal stabilizer dibutyltin maleate, which remained in the polymer after processing, acted as an UV-stabilizer.

The work described herein was carried out at The University of Aston in Birmingham between April 1973 and April 1976.

It has been done independently and submitted for no other degree.

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CONTENTS

CHAPTER 1. Introduction

PVC when subjected to forms of energy such as heat or light liberates hydrogen chloride and becomes increasingly discoloured. Dehydrochlorination is accompanied by crosslinking, chain scission and also changes in mechanical properties are observed.

This thesis is concerned with the investigation of changes which occur in PVC during mixing at higher temperature in a processing machine which simulates a commercial operation (Rapra Torque Rheometer)[38,105,106]; the role of a thermal stabilizer and lubricants during processing and with the effect of the processing operation on the ultraviolet degradation of processed PVC. The aim of this work is to elucidate the chemical and physical changes in the polymer during processing, the factors which influence these changes and the role of these changes during the ultraviolet degradation of the polymer in the presence of oxygen.

Poly (vinyl chloride) is essentially[107] a polymer with head-to-tail structure ~~and~~ which when heated somewhat above 100°C degrades[18,32] with evolution of hydrogen chloride and discolouration. The relatively low thermal stability of PVC as compared to low molecular weight alkyl chlorides is generally attributed to abnormal structures in the polymer chains[15,18,19]. They include[18,19] a) chain ends groups with initiator residues or unsaturated end groups, b) head-to-head units, c) oxidation structures, d) extraneous impurities, e) branching sites with tertiary chlorine atoms, f) random unsaturation with allylic chlorine atoms. The tertiary and allylic chloride structures are often favoured[24] as ~~an~~ initial sites for dehydrochlorination.

The study of PVC thermal dehydrochlorination reaction is often conducted under an inert atmosphere. However, in practice conditions are likely to be more complicated and for example oxygen is considered[18] to be present to a certain extent during processing and this factor should be taken into consideration. The presence of oxygen increases the rate of dehydrochlorination[14,31,102,103] and accelerated evolution of hydrogen chloride is observed. The influence of hydrogen chloride on thermal dehydrochlorination of PVC was noticed by many workers[14,23,24,31,32,90,112] and the catalytic acceleration of the degradation by HCl is now an accepted feature of thermal degradation of PVC[15,19]. The catalytic action of HCl is for example explained in the radical-chain mechanism in terms of the catalytic influence of hydrogen chloride on the decomposition of peroxide[25,18].

For the thermal dehydrochlorination of PVC three distinct mechanisms have been proposed[15,18,19], radical, ionic and unimolecular elimination mechanisms. Because of the use of different experimental conditions, different polymer samples with varied history, a clear decision in favour of any one mechanism is not yet possible. However, under more controlled conditions and especially in the presence of oxygen it is very probable that the reaction follows a radical mechanism[4,15,19,30].

During processing the polymer is effected not only by the thermal energy and by the presence of oxygen but is also subjected to a mechanical shearing. The decrease of molecular weight during mastication of solvent-plasticized PVC has been attributed[16] to a chain scission mechanism and it was concluded[16] that free radicals were formed on the polymer chain by bond scission. It has been previously pointed out[18] that the radicals so created are capable of initiating radical chain dehydrochlorination. However, only a few studies[7,16,109] on the thermomechanical degradation of PVC could be found in the literature.

Because of the elimination of hydrogen chloride during thermal degradation, polyenes are formed and polymer becomes discoloured. Average polyene sequence length was calculated[110] and value of 13 to 15 was obtained. Similar short average polyene sequence length was reported[32]. Other author reported value of 5 to 20[19]. Despite the different data obtained concerning the estimates of polyene sequence length, it is clear[15,18] that some mechanism exists which prevents dehydrochlorination from extending the whole length of a polymer chain. In the radical chain mechanism the termination of polyene sequences is explained[18,110] for example by the kinetic chain transfer or termination. Crosslinking is an established feature of thermal degradation of PVC[18,31,103,111] and for example two polymer radicals could combine to form a crosslink[33] and termination of the kinetic chain will occur. Crosslinked structure may also be formed by addition of a macroradical to a conjugated polyene sequence, a reaction which Winkler[33] compared to butadiene polymerization. In the presence of oxygen, ~~an~~ alkylperoxy, alkoxy and hydroxyl radicals are present. Addition of these radicals to conjugated unsaturation will lead to crosslinking with peroxy and/or ether and carbon-carbon linkages[33,30].

Chain scission is also a characteristic feature of polymer oxidation. It has been demonstrated[34] that molecular weight distribution of PVC degraded in oxygen has shifted to lower molecular weights due to chain scission and both chain scission and crosslinking have been observed[34] when degradation was carried out in air. Chain scission is considered[30,33,18] to be a result of rearrangement of alkoxy radicals formed by the decomposition of peroxide which is responsible for the reduction in molecular weight.

The common feature of all PVC stabilizers is an ability to react with hydrogen chloride. This ability alleviates harmful hydrogen chloride catalysis but does not in itself prevent the fundamental uncatalyzed dehydrochlorination[18]. The most efficient commonly used[15,87,113] single component systems are the autosynergestic[113] dialkyl tin salts (general formula R_2SnY_2) of carboxylic acids (e.g. maleic acid) and of mercaptans including alkylthioglycollates. The stabilizing properties of the organotins derive from one or more of the following features[15]: a) capacity for hydrogen chloride absorption, b) an ability to replace labile chloride in the polymer to give more thermally stable group, c) ability to react with conjugated unsaturation, d) hydroperoxide deactivation and the possibility of disrupting free radical chain processes.

Frye and co-workers[48] suggested, using radiotagging technique, that the Y groups replace labile chlorine atoms by more stable ester group and this replacement is the part of stabilizing action of organotin stabilizers. Infra-red spectroscopy results in this work support this theory. Dienophilic properties of organotin maleates have been previously demonstrated[51,112] and this property is ~~being regarded~~ considered[15,18,113] to be responsible for the inhibition of colour formation. The Importance of inhibition of oxidative reaction by hindered phenols was previously emphasized[97,114] and superior stabilization exhibited by organotin compounds containing sulphur may be the result of a peroxide deactivation[15,114,115]. In this work the formation of peroxide especially in the initial stage of processing was demonstrated. The induced decomposition of tert.-butyl hydroperoxide by cobalt octoate was retarded by dibutyltin dilaurate[33] which suggested an ability to modify radical chain reactions.

Apart from chemical factors, ~~a~~ physical factors may be important when considering stabilization of PVC. A degree of dispersion of a stabilizer in PVC powder blends was considered[18,52,110] to be important and the influence of other additives, namely lubricants on fusion rate during processing has been previously demonstrated[52,63].

Most studies of PVC degradation of a fundamental nature have been directed towards the studies of degradation at processing temperatures and less attention has been given in the literature to the photo-oxidation of PVC. Recent expansion in the application of rigid PVC in the building industry substantiates the importance of the photodegradation studies of PVC.

When poly (vinyl chloride) is irradiated with light of wavelength greater than 280nm it undergoes a photodegradation reactions and in the presence of oxygen photo-oxidation occurs. Radical chain mechanism in photodegradation has almost universal support[9,11,31,33,18,89].

The oxidative degradation of polymers follows the mechanism proposed for the auto-oxidation of low molecular weight hydrocarbons[116] and olefins[17]:

initiation $RH \longrightarrow R^\bullet$

$R^\bullet + O_2 \rightarrow ROO^\bullet$

$2\ ROOH \rightarrow ROO^\bullet + RO^\bullet + H_2O$

propagation $ROO^\bullet + RH \rightarrow ROOH + R^\bullet$

$ROO^\bullet + C{=}C \rightarrow ROOC - C^\bullet$

chain branching $ROOH \longrightarrow RO^\bullet + OH^\bullet$

$RO^\bullet + RH \rightarrow ROH + R^\bullet$

termination

$$\left.\begin{array}{l} 2R^\bullet \\ ROO^\bullet + R^\bullet \\ 2ROO^\bullet \end{array}\right\} \text{ inert products}$$

The fact that PVC shows substantial degradation upon exposure to ultraviolet radiation above 280nm appears to be in contradiction[117] with the fact that PVC is essentially transparent to ultraviolet radiation in that wavelength range. Most likely explanation for this[118] is the absorption of UV light by impurities present in the polymer. Small traces of a solvent (THF) were reported[117] to ~~have~~ cause decreased resistance of PVC to UV-irradiation. Carbonyl species were suggested[89] as possible initiators of photodegradation and the initiation of dehydrochlorination by benzophenone has been previously demonstrated[98]. However, a conjugated unsaturation formed during processing of PVC may also act as sensitizer~~s~~[11,18,30]. Alkyl hydroperoxides photolyse very efficiently at ambient temperature[84,95] and it is likely that peroxide formed during processing is an initiator of UV degradation. In the present work the evidence is provided to suggest the initiation by peroxide formed during processing.

Gibbs and MacCallum[92,93] have reported that degradation takes place in a thin surface layer when PVC films are irradiated by ultraviolet light in nitrogen. The HCl evolved was directly proportional to the surface area and independent of the film thickness. The photodegradation proceeded in two stages viz initial fast-rate stage followed by a slower-rate stage. The slow rate reaction was shown[93] to be independent of radiation intensity and temperature. Martin and Tilley[9] have shown formation of carbonyl during photo-oxidation of PVC films but no unsaturated carbonyl was found. They concluded that dehydrochlorination did not precede oxidation. Mack stated[87] that oxidation is the main mechanism in light degradation and that oxidative attack depends on an initial dehydrochlorination. A maximum in polyene concentration was found[83] when PVC pre-irradiated in nitrogen was subsequently photo-oxidized. It was suggested[83] that photo-oxidation is controlled by the diffusion of oxygen through the layer of polyenes formed by the pre-irradiation in nitrogen. Kwei[10] has also suggested that the photo-oxidation of PVC film is diffusion-controlled. Results in this work provide the evidence for the above suggestions.

For most applications of polymers it is necessary to stabilize the polymer against the adverse effects of oxidative degradation. Although PVC differs from hydrocarbon polymers in that its degradation is not only an auto-oxidation process, there can be little doubt[119] that oxygen is an important factor in practice. At least six mechanistic types of PVC stabilizers have been distinguished[113]: a) conventional chain-breaking antioxidants (which is probably most important for plasticized formulations), b) UV-absorbers, c) non-radical hydroperoxide decomposers, d) hydrogen chloride scavengers, e) labile chlorine reagents, f) dienophilic reagents.

CHAPTER 2 Experimental

In this chapter materials and experimental methods are described which were used throughout the course of this work. Other experimental methods used are also described in the following chapters. These include peroxide and unsaturation measurements (chapter 3, sections 3.1.1., 3.1.2.), dynamic mechanical and impact strength measurements (chapter 5, sections 5.1.1. and 5.1.2.). Ultraviolet irradiation apparatus and radiation source is described in chapter 6, section 6.1.

1.1. Materials

Commercial PVC, suspension type polymer Solvic 223 was kindly donated by Borg-Wagner Chemicals, Amsterdam, Netherlands. Information on molecular weight was obtained from Polymer Supply and Characterization Centre of RAPRA, Shawbury, Shrewsbury, U.K.:

$M_n = 32032 \qquad M_w = 65\ 198$

Processing additives:

a) Commercial dibutyltin maleate-based stabilizer (Irgastab T290), manufactured by Ciba-Geigy (UK) Ltd., Industrial Chemicals Division, Manchester was donated by ICI Ltd., Plastics Division, PVC Technical Service, Welwyn Garden City, Herts., U.K. Infrared spectroscopy analysis suggested that this stabilizer may contain "hindered" phenol component.

b) Calcium stearate, BDH Chemicals Ltd., (Analar grade)

c) Lubricant Wax E (Trade name of Hoechst A.G.) was obtained from RAPRA, Shawbury, Shrewsbury. Wax E was obtained in the form of flakes and prior to use was powdered in a mortar.

1.2. Processing in Rapra Variable Torque Rheometer

1.2.1. Description of the Torque Rheometer

The torque rheometer is essentially[38] a small internal mixer in which the torque of the rotors is measured by a dynamometer. A thermocouple can be fitted in the chamber and both torque and temperature can be recorded. The mixer is fitted with a heated jacket so that its temperature may be controlled. The rotor speed may be varied and the chamber is loaded by means of a ram. Two rotor speeds are available ("high" and "low" speed). In this work high speed was used which corresponded to 60 rev/min.

1.2.2. Evaluation of torque versus time curve

Idealized torque vs processing time curve[38] is illustrated in Fig. 2-1. When the powder blend is introduced into the rheometer the torque rises sharply. The polymer is heated and when it reaches its Tg (glass transition temperature) ~~and~~ it becomes rubbery. Torque then decreases and reaches a minimum which gives rise to a peak 'a' (see Fig. 2-1). This stage is followed by the gelation of the material. The polymer starts to melt causing the torque to increase. When the melting (or gelation) is completed the torque decreases again giving rise to a peak 'b' (see Fig. 2-1). The time to reach the peak 'b' is called fusion or flux time[38]. An example of the torque vs time for different temperatures is shown in Fig. 2-2. PVC powder blend contained 2.5 parts of Irgastab T290, 0.8 parts of Ca-stearate, 0.65 parts of Wax E and 100 parts of

Solvic 223. This formulation was also used during processing as it will be described in chapter 4. It should be noted (see Fig. 2-2) that time between the beginning of processing and the fusion peak 'b' is less than 1min and decreases with increased temperature.

1.2.3. Powder blend preparation and mixing procedure in torque rheometer.

The additives were mixed with PVC (in the powder form) at room temperature by ~~t~~humble-mixing for 1 hour with each individual additive~~s~~. The mixing in an order similar to that used in the Henschel cycle, i.e. the polymer, the stabilizer, the internal lubricant Wax E and finally Ca-stearate, was used.

The powder blend (48 g) was then introduced into the torque rheometer and the mixing chamber was closed during the mixing by the ram. Two processing temperatures were used (170°C and 210°) and processing was carried for various times at high rotor speed (60rev/min). The hot polymer melt was chilled in water on removal from rheometer to avoid uncontrolled thermal oxidation. The processed polymer was then powdered and kept at room temperature in closed sample containers until required.

1.3. Determination of gel content

When poly (vinyl chloride) is degraded it becomes eventually insoluble in organic solvents. Insolubility of polymers often arises from a crosslinked network structure. Crosslinking of PVC has been previously followed[32,111] by the time to reach the gel point, i.e. the time when the degraded polymer solution becomes immobile. Another approach is to measure gel content. Gel fractions of the irradiated PVC film were determined[120] by

[redacted]

General shape of the torque vs time curve

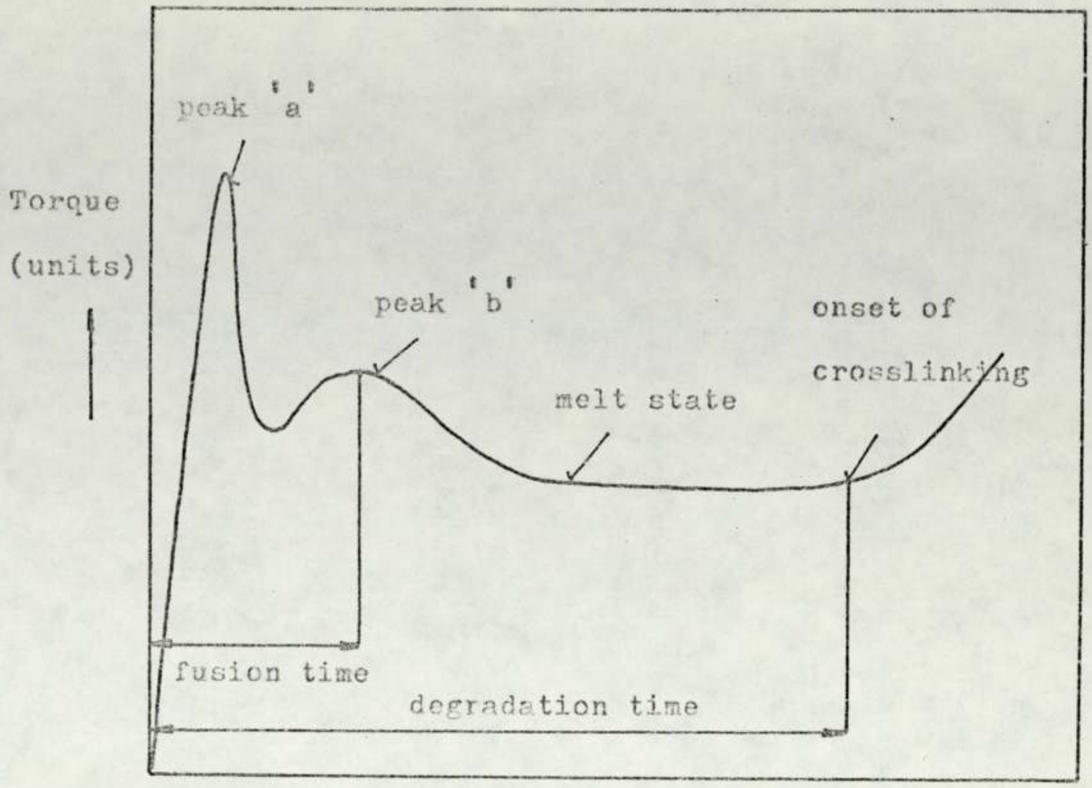


Fig.2-1 t(time) of processing

Torque vs time of PVC with 2.5phr of Irgastab T290, 0.8phr of Ca-stearate and 0.65phr of Wax E

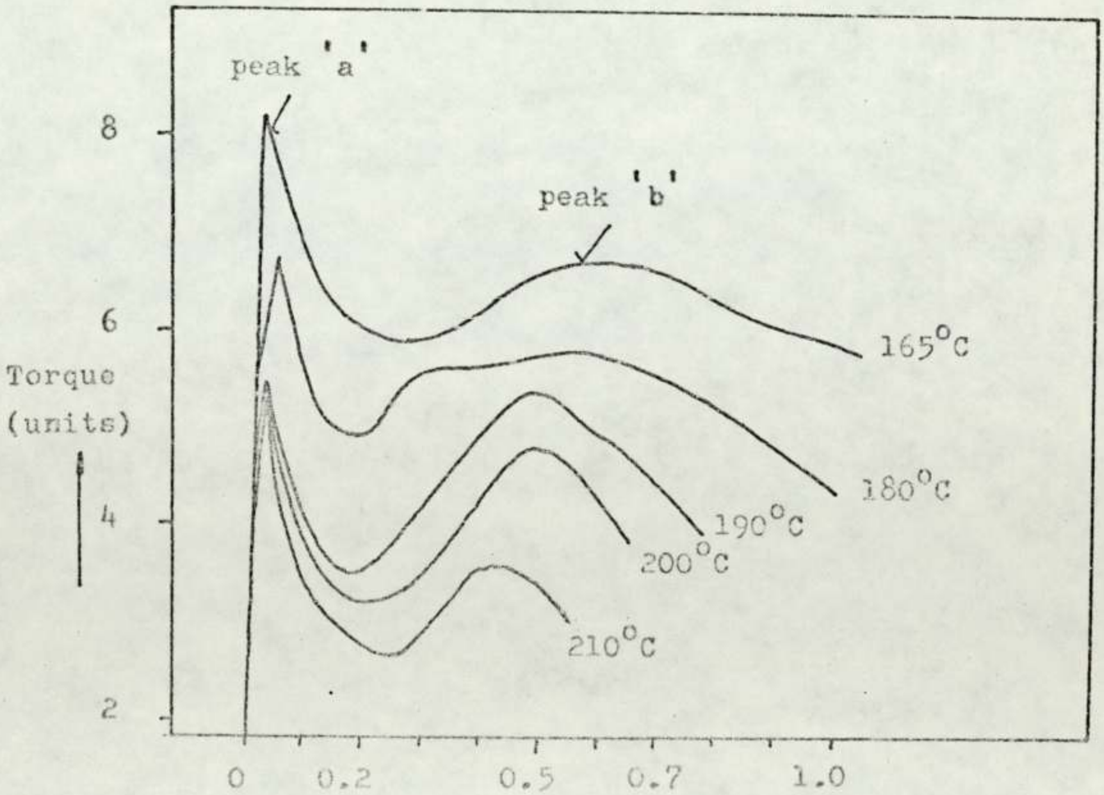


Fig.2-2 t(min) of processing

weighing films which had been extracted with tetrahydrofuran and vacuum-dried. The amount of the crosslinked PVC was also estimated[100] as the gel remaining insoluble after standing for one week in cyclohexanone at 30°C or 50°C. A method based on separation of the gel phase by centrifugation with subsequent repeated centrifugation of the gel with fresh portion of solvent was reported[121] for the determination of the gel content of vinylchloride polymers and copolymers.

In this work the gel content was determined by the centrifugation separation technique. 0.5g of polymer powder was placed in the Erlenmeyer flask and 50ml of methylene dichloride (AR grade) was added. After refluxing for 10min (boiling point of CH_2Cl_2 is 39.5°C - 40°C) 25ml of 'dissolved' polymer solution was placed in the polypropylene centrifuge tubes. The tubes were capped securely to prevent spillage or volatilisation and centrifuged for 30min at 15,000 rpm using MSE ultra centrifuge. After removing the caps a clear solution of uncrosslinked material (sol) was carefully removed from the tubes without disturbing separated gel which was left at the bottom of the tubes. In order to wash the gel free of soluble polymer fresh portion of solvent was added and centrifugation operation was repeated. Three such washing operations proved sufficient. The remaining gel in the tubes was allowed to dry at ambient temperature overnight. After removing the gels from the tubes (facilitated by the use of polypropylene tubes) the gels were further vacuum-dried to constant weight and after weighing stored in sample bottles. Soluble (uncrosslinked) material was used for the preparation of 'soluble phase' films by casting on mercury.

1.4. IR-spectroscopy measurement

1.4.1. Polymer films

Polymer films for IR spectroscopy examination were prepared by compression moulding. The appropriate weight of polymer powder was compression moulded (using glaze steel plates with steel backing-plates) to obtain films of desired thickness between 0.025mm and 0.050mm. The temperature of the hydraulic press was set at 170°C and maximum pressure was maintained for 1min before water-cooling the mould to room temperature.

Polymer films were then placed in a specimen holders suitable for Perkin-Elmer, Model 257 and 457 IR spectrometers. Films of 0.05mm thickness were found suitable to give measurable absorption peaks with no interference. The spectra from 4000 cm^{-1} to 625 cm^{-1} were recorded (Model 257) at medium scan speed. Some spectra were also recorded from 4000 cm^{-1} to 250 cm^{-1} (Model 457). The peak at 2915 cm^{-1} was taken[11] as the reference peak. The growth or decay of observed absorption peaks were expressed as indices. The indices were defined as the ratio of the absorbance of growing or decaying peaks to that of the reference peak.

1.4.2. Polymer solutions

For this work a pair of sodium chloride variable path cells were used. 7% solutions of the polymer in methylene dichloride gave measurable peaks at a path length of approximately 1mm. Solutions in methylene dichloride were prepared using samples in the form of films. They were prepared prior to spectroscopic examination by casting the soluble phase (see 1.3.) on mercury with subsequent room temperature and vacuum-drying. By adjustment of the cell containing undegraded sample in the reference beam, all peaks including those corresponding to methylene dichloride were compensated for, leaving only those of the thermal degradation products. Other types of spectra were obtained with only the solvent used in the reference beam. These spectra were used for the calculation of indices of appropriate absorption peaks.

1.5. UV spectroscopy of polymer solutions

UV-spectra could not be obtained using total sample because of the presence of the gel phase. Hence the spectra were obtained using soluble phase (see 1.3.) of processed samples. Appropriate solutions were prepared by dissolution of 'soluble phase' films (see 1.3. and 1.4.2.) in methylene dichloride. The spectra were recorded using Perkin-Elmer, Model 137 spectrophotometer employing silica glass cells of 10mm and/or 1mm path length with the solvent in the reference beam.

1.6. Colour change measurement

In practice discolouration is normally the first and important manifestation of degradation of PVC. During the thermal treatment in an inert atmosphere[18] the pink-red-brown-black sequence is observed and with certain additives a yellow-orange-brown-black sequence is obtained. Most tests are comparative and measurement of colour is attempted by comparison with standard colours. The Garner Colour Scale standard ASTM D 1544-58T) was used[41] to compare the colours of samples aged with metal laurates. Colour formation (yellowing) is essentially the difference between the absorption at 400nm and 700nm wavelength and some authors have attempted to make use of the ultraviolet and visible absorption spectra as a measurement of colour[91,97].

Colour change of PVC during ultraviolet degradation has been followed[86] using M.E.E.C.O. Colormaster colorimeter, Model V. In this work the colour change after processing and also during UV-exposure was measured by the same instrument (Manufacturers Engineering & Equipment Corp., Warrington, PA., USA). The samples used were in the form of the films and were prepared by the compression moulding (see 1.4.1.). Thickness of the samples was 0.05mm. Since the specimens were transparent, transmittance measurement procedure[122] was used. The readings are obtained[122] using red, green and blue filters and total colour difference was obtained using a computer programme[123], (see Appendix I). The Colormaster data of unprocessed cast film of PVC without additives were used as a reference.

1.7. Air permeability measurement with Davenport Gas Permeability Apparatus.

1.7.1. Description of the Apparatus

The Davenport Gas Permeability Apparatus is used commercially to measure gas permeability of a plastics film~~s~~ (or a rubber sheet) in gas/gas condition. The apparatus consists of a stainless steel permeability cell connected through a capillary tube (1.5mm bore) to a manometer and a vacuum system and is fitted to a vertical mounting. (See fig. 2-3.)

The permeation cell unit has two parts which contain a rubber '0' ring to form a seal when they are clamped together by vertical studs with the nuts. The lower part of the cell is fitted with a changeable insert so that the volume of the free space in this part of the cell can be 20,15,10 or 5 mls. The manometer unit consists of a manometer connected to the

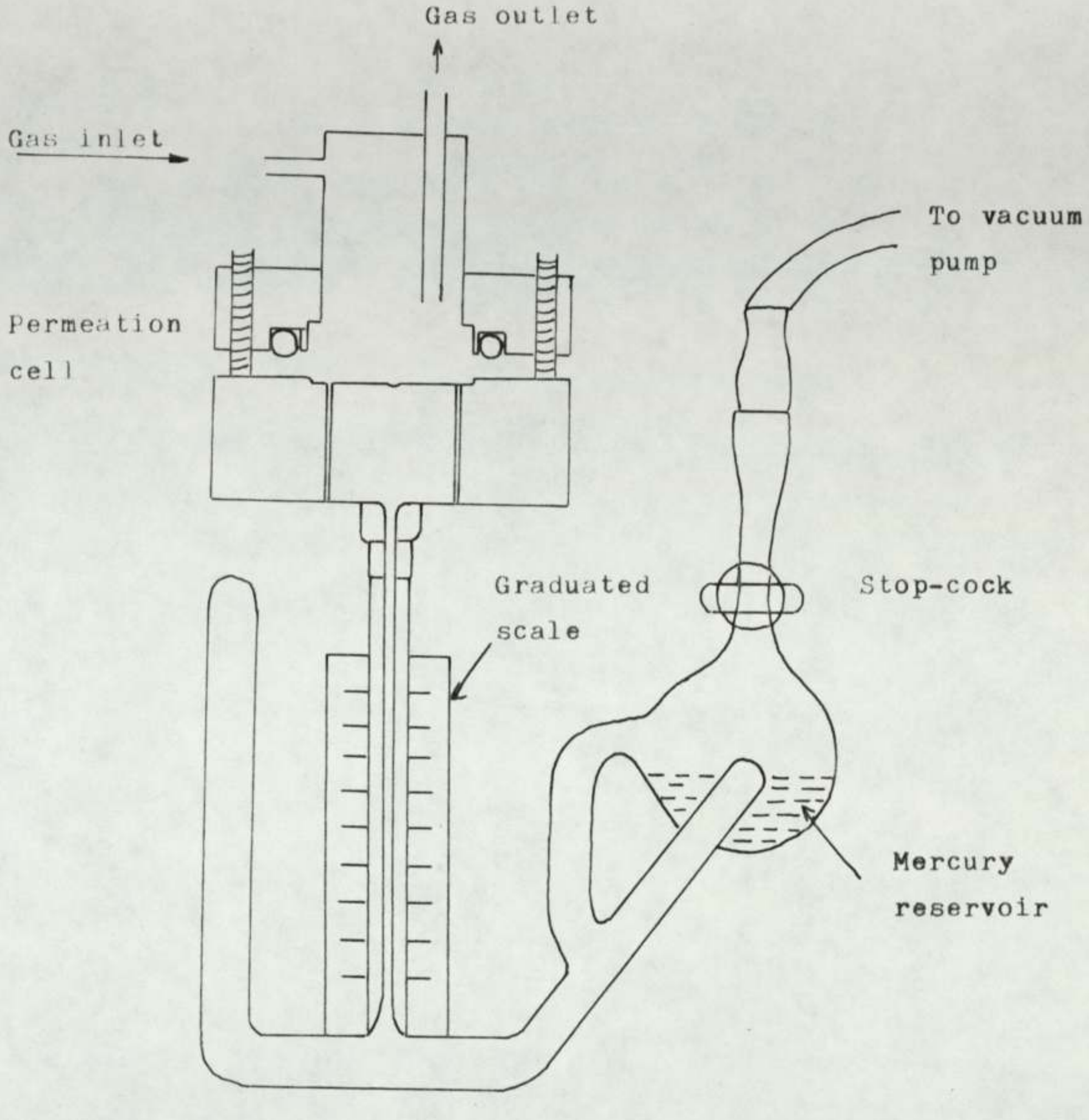


Fig.2-3 The Davenport Gas Permeability Apparatus

lower part of the permeation cell through a capillary. On the other end of the manometer is a mercury reservoir which can be connected to a vacuum system. Behind the capillary there is a scale mounted vertically. The length of the scale is 10cm and is graduated in divisions of 1cm and sub-divisions of 1mm.

1.7.2. Testing procedure

A suitable insert was chosen (15ml~~s~~)and placed in the lower part of the permeation cell. A pre-dried No.1 Whatman filter paper (5.5cm in diameter) was placed centrally on the top surface of the insert and than a test sample (6cm diameter pressed film). The two parts of the cell were closed and tightened with six nuts. With mercury in the reservoir, the lower cell unit and the manometer were evacuated (1 hr) with the pump attached with a Vacustat pressure gauge, the vacuum pump was disconnected and the whole apparatus was tilted to get mercury from the reservoir into the manometer tubes. The mercury level in the capillary tube was read on the scale. Air was passed into the top chamber of the cell and a stop-watch was immediately started. The mercury level inthe capillary tube fell due to air transmission through the test sample and the readings were taken at time intervals. The height of the mercury was plotted against time and the measurement was continued until six consecutive readings showed a linear correlation.

1.7.3. Evaluation of results

From the experimental data permeability coefficient of processed PVC was calculated using following equation:

$$P_g = \left(\frac{273}{273+T} \times \frac{\Delta p_2}{\Delta t} \times \frac{1}{76} \times V_2\right) \times \frac{1}{A} \times \frac{1}{p_1 - p_2} \times t$$

where T = test temperature in °C (room temperature was used)

$\Delta p_2/\Delta t$ = rate of pressure change in the capillary in cm Hg/sec

A = area of the specimen under the test (23.77 cm^2)

p_1-p_2 = pressure difference across the sample at the time when $\Delta p_2/\Delta t$ was taken, in cm Hg

V_2 = total volume (cc) of vacuum between the test specimen and the mercury level in the capillary tube. It is the sum of volume (V) of the cavity, the volume of the capillary above the mercury level half-way through the test (0.018 x y) and the free-space volume (0.24) in the filter paper.

So V_2 = (V+ 0.018y + 0.24) where y is the length (cm) of the capillary above the mercury half-way through the test

t = thickness of the specimen (average value was 0.025cm)

1.8. Gel Permeation Chromatography (GPC)

The molecular weight changes during thermal degradation of PVC have usually been explained[34] by chain scission or crosslinking, the latter leading to branching or network structures. The study of a competitive crosslinking and chain scission reactions is facilitated by the use of GPC and this technique has been used in the thermal[34,35], thermomechanical[7] and photo-oxidative degradation[11] studies of PVC.

A chain scission process shifts the molecular weight distribution (MWD) to lower molecular weight. A molecular enlargement will be observed as an increase of the high molecular weight tail[34]. Molecular weight and molecular weight distribution in this work were obtained using GPC and were kindly carried out by the Polymer Supply and Characterization Centre of RAPRA. Because of the presence of insoluble gel in the processed samples the measurement was carried out using soluble part after removal of the gel by centrifugation (see section 1.3. of this chapter). Experimental conditions used[11] were as follows: solvent tetrahydrofuran with 0.1% of 2,6 di-tert-butyl-p-cresol as inhibitor; temperature, ambient; columns, $5 \times 10^6 - 10^7$ Å, $7 \times 10^5 - 5 \times 10^6$ Å, $1.5 \times 10^4 - 5 \times 10^4$ Å, $0.7 \times 10^3 - 2 \times 10^3$ Å; sample concentration, 0.2%; flow rate, 1ml/min; injection time, 2min. Polystyrene was used for calibration and Mark-Houwink constants ($[\eta] = K M^a$) used for conversion of calibration were $K = 1.5 \times 10^{-4}$, $a = 0.77$. Molecular weight distribution curves were obtained by the plot of dW/d log M versus log M.

CHAPTER 3. Processing of PVC in Rapra torque rheometer without additives

3.1. Experimental

Most of the methods used here are described in the experimental chapter 2. Additional methods were employed for specific investigations namely peroxide and unsaturation determinations which are described in the following sections.

3.1.1. Peroxide determination

Iodometric method based on the oxidation of potassium iodide was used[1,2]. Liberated molecular iodine was determined by spectrophotometric method using Perkin-Elmer 137 spectrophotometer. Observed absorption maximum centred at 360nm was used for the determination. This maximum corresponds to the triiodide anion which is formed in excess of potassium iodide[1,3]:

$$I_2 + I^- \rightleftharpoons I_3^-$$

Detection of peroxide in ozonized degraded PVC based on Uri[1] and Banerjee[2] methods was described by Geddes[4]. This procedure was adopted for the peroxide determination. Polymer after processing was immediately cooled in water, dried and powdered. Because of only partial solubility, the reaction with potassium iodide was carried out with the polymer in swollen state after 12 hours swelling in chloroform using 1g of the polymer sample in the form of the powder. The glacial acetic acid was added followed by freshly prepared 5% solution of potassium iodide. All solvents were deaerated in bulk prior to use with nitrogen gas flow through capillary and the procedure using rubber seals was employed. The reaction was carried out in dark at room temperature for 4 hours. This reaction time was found to be necessary for the complete reaction between iodide and peroxide. After the reaction was completed swollen polymer was removed by centrifugation and absorbance of the solutions was immediately measured at 360nm using silica glass cells against reference solutions. Peroxide content was then determined using calibration plot relating absorbance at 360nm of solutions with varying iodine concentrations.

3.1.2. Determination of unsaturation

The method used was based on the unsaturation determination of isoprene-isobutylene copolymers by Gallo, Wiese and Nelson[5]. This method is based on the addition of iodine to double bonds catalyzed by mercuric acetate in the presence of trichloroacetic acid. The iodine monochloride method was shown by Lee, Kolthoff and Johnson[6] to be in good agreement with iodine-mercuric acetate method. It was also noted that the method is convenient for the determination of relative unsaturation.

PVC in powder form was used as in the peroxide determination. Polymer was swollen in chloroform for 12 hours. Longer swelling time did not have a significant effect on the results. In order to obviate possible substitution by iodine, the optimum time was determined first. Results for a 0,1 and 5 min processed samples are shown in Fig. 3-1. From these results 1 hour reaction time was adopted and the value of 0.4ml 0.1N $Na_2S_2O_3$ for unprocessed polymer was subtracted from each titration reading of processed samples. After swelling for 12 hours in chloroform 5ml of 20% trichloroacetic acid in chloroform was added, 25ml of 0.1N iodine solution in $CHCl_3$ and 25ml of mercuric acetate in glacial acetic acid. The content of the flask was gently shaken and after 1 hour reaction time in dark 75ml of 7.5% potassium iodide solution was added. The excess iodine was then titrated with standard 0.1N $Na_2S_2O_3$ and the starch end point was observed in the aqueous layer. For each series separate blank titrations were carried out.

3.2. Results

3.2.1. Processing in Rapra torque rheometer and the gel content measurements.

The change of torque with processing time for two temperatures (170°C and 210°C) is shown in Fig. 3-2. The part insoluble in methylene dichloride (the gel) formed during processing is plotted together with the torque as a function of processing time. The amount of gel (0.45%) which was found in the original polymer was subtracted from the gel found after each processing time. Initially the torque increased and after reaching a maximum, (usually called fusion point) decreased due to melting of the polymer and the measured torque corresponds to the melt viscosity of the polymer. It should be noted that the fusion of the polymer takes place within the first minute of processing. The level of the torque and therefore mechanical work (or shear stresses) in the initial period is higher at 170°C than at 210°C. With further processing the torque reaches a minimum but starts to increase after 10min at 170°C and more rapidly at 210°C after 4-5min indicating a crosslinking reaction. After 10min the rate of torque increase is slower.

A small amount of gel (between 3-8%) is formed initially and with further processing this gel decreases slightly until the point where there is a further increase. For 210°C the fast increase in the gel content starts after 4-5min and reaches 89%

at 20min. For 170°C the gel formation is slower and 21.1% is reached at 20min. It should be noted that the formation of the gel parallels the increase in torque, but at 210°C the torque after 10min increases more slowly than the gel. A Brabender plastograph, which is similar in design to Rapra torque rheometer, has previously been used to study the thermomechanical degradation of PVC[7]. Shorter processing times and lower temperatures were employed and no data on gel formation were presented.

3.2.2. Colour change

Discolouration during processing expressed as total colour difference, viz experimental chapter 2, is shown in Fig. 3-3. The colour initially increased linearly for both temperatures with a higher rate at 210°C. After 10min the rate at this temperature decreased.

3.2.3. Unsaturation

During thermal degradation of PVC hydrogen chloride is evolved and the dehydrochlorination reaction is usually the focus of attention[18,19,21,24,32]. It was not feasible, however, to measure HCl evolved during processing in the torque rheometer. Therefore an attempt was made to measure the unsaturation formed as a result of HCl evolution using the method described in section 3.1.2. The result for both temperatures is presented on Fig. 3-4. For 170°C there is initial fast increase of unsaturation within the first 1-2min after which the rate is slower and constant up to 20min. The initial increase for 210°C is smaller but after 2-3min the rate increases reaching the same value at 5min for both temperatures (crossover point). With further processing the rate continues to increase indicating auto-accelerating character of dehydrochlorination reaction. It is interesting to note (Fig. 3-2) that the level of torque during fusion and immediately after fusion up to 5min for 170°C is higher probably because corresponding melt viscosity is higher at this temperature. At 5min, however, the torque is equal and a crossover point can also be seen as in the case of the unsaturation plot.

3.2.4. IR-spectroscopy results.

IR-spectra were obtained of processed PVC using pressed films and also as solutions in methylene dichloride. The changes in the carbonyl absorption at 1720 cm^{-1}- 25 cm^{-1} of the soluble phase were observed. 7% solutions were used and two types of spectra were obtained. First, uncompensated spectra in which the adjustable cell in the reference beam of the spectrophotometer contained only the solvent methylene dichloride and second, compensated spectra in which a 7% solution of undegraded PVC was used in the reference beam. The compensated method was found to be useful in i~~n~~dentification of the growth of 2850 cm^{-1}- 55 cm^{-1} absorption. Uncompensated spectra were used for the calculation of the carbonyl index $I_{1720\ cm^{-1} - 25\ cm^{-1}}$ and C-H stretching absorption index $I_{2850\ cm^{-1} - 55\ cm^{-1}}$. An example of a compensated spectrum for the sample processed for 20min at 210°C is shown in Fig. 3-5. Apart from the absorption peaks at 2850 cm^{-1} - 55 cm^{-1},1720 cm^{-1} - 25cm^{-1} and 1600 cm^{-1} which were also seen for the samples processed for less than 20min, an additional absorption peak at 1675 cm^{-1} - 85 cm^{-1} was observed at 20mins.

It is known[8] that the C-H stretching of olefins is in the region of 3125 cm^{-1} -2855 cm^{-1} and overlaps in part the C-H stretching modes of saturated alkyl groups[8]. The growing peak at

$2850\ cm^{-1} - 55\ cm^{-1}$ on Fig. 3-5 can be assigned to the C-H stretching of unsaturated -HC= CH- bond as a result of dehydrochlorination.

Carbonyl absorptions at $1725\ cm^{-1} - 45\ cm^{-1}$ present in PVC after thermal and UV-irradiation treatment have been suggested[9] to be mainly due to a α-halogen substituted ketone. Another author[10] assigned the $1725\ cm^{-1}$ absorption to β-chloro ketone but the treatment with triethylamine affects this region and it was suggested[11] that it may also contain α-chlorocarboxylic group. Chloroacetone was shown[12] to have two absorptions at $1722\ cm^{-1}$ and $1745\ cm^{-1}$ due to the existence of two rotational isomers. The absorption at $1675\ cm^{-1} - 85\ cm^{-1}$ could be attributed to the C-O stretching vibration of a conjugated carbonyl[13] and the $1600\ cm^{-1}$ peak to olefinic bond stretching vibration[13].

The plot of the index $I_{2850\ cm^{-1} - 55\ cm^{-1}}$ vs processing time for two temperatures is shown in Fig. 3-6. In the first 5min the index for 210°C is smaller than for 170°C but after 5min (crossover point) there is a rapid increase. For 170°C the index increases linearly up to 20min. It is interesting to compare the unsaturation on Fig. 3-4 with the unsaturation on Fig. 3-6 as measured by IR-spectroscopy using absorption at $2850\ cm^{-1} - 55 cm^{-1}$. It appears that the shape of unsaturation curves and other features viz the crossover point at 5min, are similar for both types of measurements. The carbonyl absorption at $1720\ cm^{-1} - 25\ cm^{-1}$ plotted as an index $I_{CO}\ 1720\ cm^{-1} - 25\ cm^{-1}$ vs processing time is shown in Fig. 3-7. Also on the same figure there is a plot of peroxide content as determined by iodine-liberation method described earlier in the section 3.1.1. The carbonyl at 210°C is smaller in the first 5min than for 170°C. After 5min it increases sharply up to 20min. For 170°C after small initial increase the index remains constant for the whole processing period. The peroxide curves show initial increase with small maxima for both temperatures. For the lower temperature peroxide was again detected after 15min. For the higher temperature peroxide increased sharply again after 5-10min. It should be noted that the increase of carbonyl at 210°C follows the peroxide curve but is slightly shifted along the time axis. This observation suggests that the carbonyl is formed by the decomposition of peroxide formed during processing. The increase of carbonyl and parallel decrease of hydroperoxide in the initial stage of processing may suggest a similar type of reaction.

Using an ultracentrifugation separation technique described in the experimental chapter 2, it was found that the original polymer contained 0.45% of insoluble material in methylene dichloride. IR-spectra of this material revealed two absorption peaks at 1735 cm^{-1} and 3360 cm^{-1} and is shown in Fig. 3-8. The CO stretching vibration at 1735 cm^{-1} may come from an aliphatic ester[13] and 3360 cm^{-1} from OH-stretching of H-bonded alcoholic hydroxyl group. Sharp absorption peak at 1720 cm^{-1} - 35 cm^{-1} was reported[21] to be present in the methanol extract of suspension PVC and it was suggested that this carbonyl function may arise from an initiator residues, emulsifiers or suspension stabilizers used during polymerization. Poly (vinyl alcohol), cellulosic derivatives, etc. are known to be used as a dispersing agents[36] during polymerization and therefore observed absorption peaks in the gel of the unprocessed PVC at 1735 cm^{-1} and 3360 cm^{-1} may arise from these materials.

IR-spectral examination of the gel phase of the processed PVC showed the presence of a broad absorption centred at 3400 cm^{-1}. This absorption was especially pronounced for the initially processed samples. The plot of the index $I_{3400\ cm^{-1}}$ is shown in Fig. 3-8a. For 210°C there is a maximum at 2min and for 170°C at 1min. After 5min (210°C) the index decreased and for 170°C the index had already started to decrease after 1min. The position of this absorption suggests the presence of H-bonded hydroxyl group[13] but it is known[8] that OH-stretching frequency of cumene hydroperoxide is at 3450 cm^{-1} and for a n-alkyl hydroperoxides is at 3360 cm^{-1} - 3450 cm^{-1}. Therefore it is probable that these samples contain a peroxidic moiety because it was also found that they are very unstable when they were exposed to UV-irradiation. (This will be discussed in a later chapter on UV-degradation). Also the gel curves on Fig. 3-2 have a small initial maxima which may suggest the presence of thermally unstable crosslinks and could be explained by the presence of peroxy-linkages.

3.2.5. UV-spectroscopy measurements

Because of the difficulty of carrying out UV-spectra of samples containing gel (viz experimental section), the UV-spectra were measured on soluble phase. Absorption spectra of 0.2% solutions in methylene dichloride after the removal of the gel phase by centrifugation were recorded employing Perkin-Elmer 137 spectrophotometer with the solvent in the reference beam. The major absorbance was centred at 225-35nm with the smaller absorptions at 265nm and 270nm-280nm and a small ill-defined absorption at 300nm-315nm. Above 315nm the absorbance became progressively smaller with no distinct absorptions up to 750nm. Absorbance vs processing time for the observed absorptions are shown in

Figs. 3-9 and 3-10 for 210°C and 170°C, respectively. For 210°C the increase within the first 5min is slower but after 5min the rate sharply increased and had autoaccelerated character. For 170°C the initial fast increase within 1-2min was followed by a constant rate. The comparison of the absorbance at 310nm vs processing time for both temperatures is shown in Fig. 3-11. For 170°C after the initial increase the absorbance increased linearly up to 20min. For 210°C the absorbance sharply increased after 5min. It could be noted that the plot of absorbance on Fig. 3-11 is similar to the unsaturation plot on Fig. 3-4 and also to the unsaturation on Fig. 3-6 as measured by IR-spectroscopy.

It was shown on Fig. 3-2 that the gel content increased sharply after 5min (210°C) and therefore it is clear that the increase of absorbance on Fig. 3-10 and 3-11 comes from progressively smaller portion of the total sample (93% at 5min down to 11.1% at 20min). This observation may suggest the existence of chain scission reaction. The presence of peroxide and increased concentration of carbonyl on Fig. 3-7 and also the presence of conjugated carbonyl on Fig. 3-5 suggests that this chain scission reaction is of oxidative character.

3.2.6. Molecular weight measurement

Molecular weights and molecular weight distribution (MWD) were measured using gel permeation chromatography as described in the experimental chapter 2. Here again the measurements were possible only on the soluble phase of processed samples. MWD for 170°C is illustrated in Fig. 3-12 and for 210°C in Fig. 3-13, respectively. Soluble phase for 170°C represents between 97%-79% of the total sample (1-20min) but for 210°C this is 93%-97% for

1-5min processed samples which then progressively decreases to 11.1% at 20min. As can be seen a distinct increase in the high molecular weight end is observed for the lower processing temperature up to 20min and 5min for higher temperature. The presence of high molecular weight material suggests the existence of crosslinking reaction. For 210°C MWD was shifted after 5min towards the lower molecular weight region which is a result of chain scission reaction. This result is in good agreement with the observed increase in UV-absorbance, peroxide and carbonyl content as shown in the previous section.

3.3. Discussion

Although the access of air was restricted in the torque rheometer it is believed that oxygen is always present. It has previously been suggested[14,15] that the effect of oxygen during processing may be significant. The results presented here shows that oxidation takes place during processing and therefore the effect of oxygen on thermal degradation must be considered to be important. In the torque rheometer the polymer as in any commercial extruder is subjected to mechanical work as well as thermal energy and this factor may be also of importance.

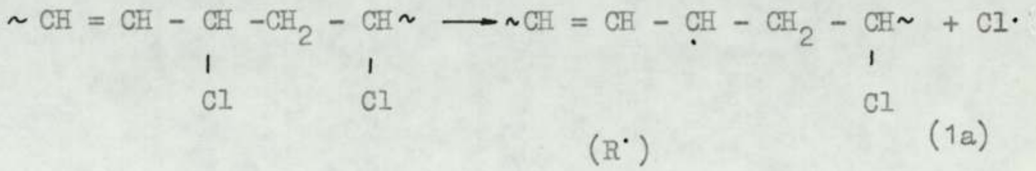
The level of torque during the fusion and immediately after the fusion is higher for 170°C temperature (Fig. 3-2) than for 210°C. This suggests that mechanical work at 170°C is higher in the initial period of processing. It was previously shown by Ceresa[16] that the molecular weight, measured by limited viscosity number (LVN), decreased during mastication of the solvent (THF) - plasticized PVC from 160 to 50 after 3 hours as a result of mechanical degradation. Also ~~e.g.~~ LVN decreased for temperature-plasticized polystyrene at 130°C and was shown to be shear rate dependent. The decrease in LVN was attributed to a chain scission mechanism and was concluded that the free radicals are produced on the polymer chain by bond scission. The mechanical degradation is temperature dependent and it has a negative temperature coefficient[16]. At higher temperature the melt viscoelasticity (and also torque) is lower and therefore the contribution of the pure mechanical process to the thermo-mechanical degradation is lower at higher temperature. If the degradation in torque rheometer is shear rate dependent the higher torque for 170°C on Fig. 3-2 suggests that the contribution of the mechanical degradation to the overall degradation process is higher than at 210°C.

The unsaturation formed by the dehydrochlorination reaction is shown in Fig. 3-4. At 170°C there is rapid increase within 1-2min and is followed by the constant rate reaction. The peroxide concentration on Fig. 3-7 has small maxima within the initial period after which the peroxide content decreases. The initial unsaturation for 210°C is smaller but increases with the higher rate. It was demonstrated ~~e.g.~~ by Geddes[4] that the addition of benzoylperoxide, dicumyl peroxide and also peroxide formed by the ozonisation of pre-degraded PVC increased the rate of dehydrochlorination which was proportional to the concentration of peroxides. Because of the formation of peroxide (Fig. 3-7) the rapid initial dehydrochlorination is the result of the catalysis by the peroxidic intermediates during the initial stage of processing. The formation of peroxide requires the presence of a radical R: In the presence of oxygen, R. is rapidly oxidized with formation of an alkyl peroxy radical ROO·[17]:

$$PVC \longrightarrow R^\bullet \quad \text{or} \quad \underset{(PVC)}{R\text{-}R} \longrightarrow 2R^\bullet \tag{1}$$

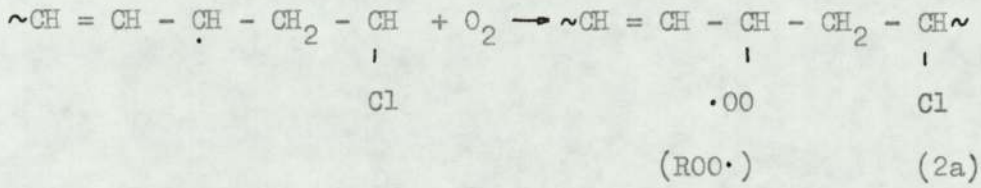
$$R^\bullet + O_2 \longrightarrow ROO^\bullet \tag{2}$$

The alkyl radical $R^\bullet$ could be formed by bond scission as a result of the mechanical degradation[16,18] as discussed above. The presence of structural irregularities in the polymer extensively discussed in the literature[15,17,18,19] are considered as initial sites for the dehydrochlorination and the allylic chlorine structure is often favoured:



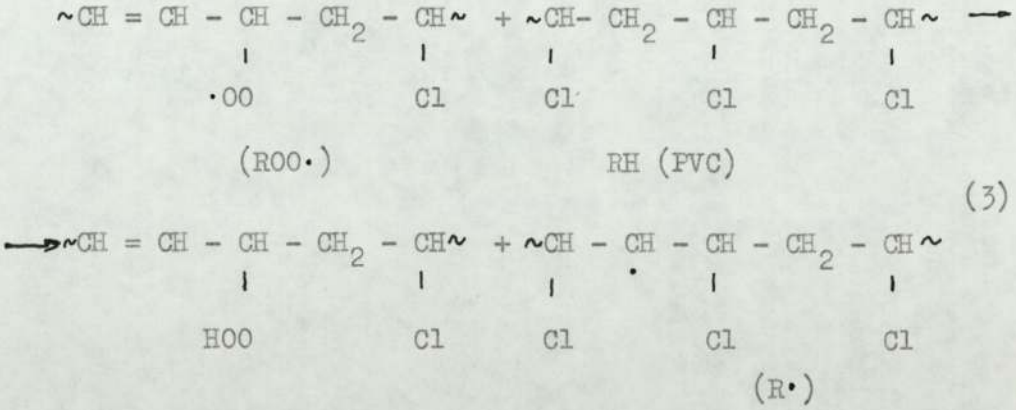
$$\sim CH = CH - \underset{Cl}{CH} - CH_2 - \underset{Cl}{CH}\sim \longrightarrow \underset{(R^\cdot)}{\sim CH = CH - \underset{\cdot}{C}H - CH_2 - \underset{Cl}{CH}\sim} + Cl\cdot \tag{1a}$$

In the presence of oxygen an alkyl peroxy radical is formed:



$$\sim CH = CH - \underset{\cdot}{C}H - CH_2 - \underset{Cl}{CH} + O_2 \longrightarrow \underset{(ROO\cdot)}{\sim CH = CH - \underset{\cdot OO}{CH} - CH_2 - \underset{Cl}{CH}\sim} \tag{2a}$$

The alkylperoxy radical $ROO^\bullet$ is capable of H-atom abstraction with formation of hydroperoxide[17]:

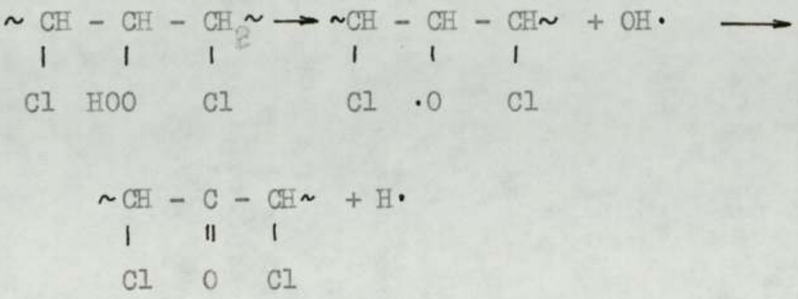


$$\underset{(ROO\cdot)}{\sim CH = CH - \underset{\cdot OO}{CH} - CH_2 - \underset{Cl}{CH}\sim} + \underset{RH\ (PVC)}{\sim \underset{Cl}{CH} - CH_2 - \underset{Cl}{CH} - CH_2 - \underset{Cl}{CH}\sim} \longrightarrow$$

$$\longrightarrow \sim CH = CH - \underset{HOO}{CH} - CH_2 - \underset{Cl}{CH}\sim + \underset{(R\cdot)}{\sim \underset{Cl}{CH} - \underset{\cdot}{C}H - \underset{Cl}{CH} - CH_2 - \underset{Cl}{CH}\sim} \tag{3}$$

The macroradical $R^\bullet$ thus produced is capable of continuing the dehydrochlorination chain and therefore reaction 3 constitutes a transfer step which does not disrupt the kinetic chain.

Peroxide initially formed decreases and there is a small increase of carbonyl absorption band as could be seen on Fig. 3-7. The presence of carbonyl band indicates the formation of an in-chain ketone as a result of oxidation:

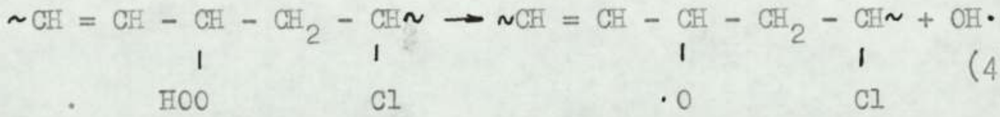


$$\sim\underset{\mathrm{Cl}}{\mathrm{CH}}-\underset{\mathrm{HOO}}{\mathrm{CH}}-\underset{\mathrm{Cl}}{\mathrm{CH}_2}\sim\;\longrightarrow\;\sim\underset{\mathrm{Cl}}{\mathrm{CH}}-\underset{\cdot\mathrm{O}}{\mathrm{CH}}-\underset{\mathrm{Cl}}{\mathrm{CH}}\sim+\mathrm{OH}\cdot\;\longrightarrow$$

$$\sim\underset{\mathrm{Cl}}{\mathrm{CH}}-\underset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}-\underset{\mathrm{Cl}}{\mathrm{CH}}\sim+\mathrm{H}\cdot$$

However, the increase of carbonyl index is small for both temperatures until 5min and for 170°C is constant for the whole duration of processing (20min). Therefore the extent of the ketone formation is insignificant. For 210°C after 5min, however, the ketone increases. This result together with other findings will be discussed later.

Known unimolecular radical decomposition of hydroperoxide[20] will result in the formation of highly reactive alkoxy and hydroxyl radicals:



$$\sim\mathrm{CH}=\mathrm{CH}-\underset{\mathrm{HOO}}{\mathrm{CH}}-\mathrm{CH}_2-\underset{\mathrm{Cl}}{\mathrm{CH}}\sim\;\longrightarrow\;\sim\mathrm{CH}=\mathrm{CH}-\underset{\cdot\mathrm{O}}{\mathrm{CH}}-\mathrm{CH}_2-\underset{\mathrm{Cl}}{\mathrm{CH}}\sim+\mathrm{OH}\cdot \qquad (4)$$

These radicals by suitable H-atom abstraction (e.g. methylenic or tertiary) are initiators for further dehydrochlorination and therefore the rapid initial dehydrochlorination (Fig. 3-4) is the result of the catalytic action of alkylperoxy, alkoxy and $\mathrm{OH}^{\bullet}$ radicals formed in the initial phase of processing.

HCl evolved by the dehydrochlorination reaction has been shown[21-24] to increase the rate of dehydrochlorination and the HCl catalysis is an accepted feature of thermal degradation[15,18]. It is therefore necessary to consider the role of HCl. HCl is not likely to decompose into free radicals at temperatures below 200°C[19.21] to provide the necessary radical source for the increased dehydrochlorination. On the other hand it has been shown that HCl catalyses the thermal decomposition of peroxides[25] (di-t-butylperoxide, di-t-amylperoxide at 136.7°C):

$\text{ROOR} \longrightarrow 2\ \text{RO}\cdot$

$\text{RO}\cdot + \text{HCl} \longrightarrow \text{ROH} + \text{Cl}\cdot$

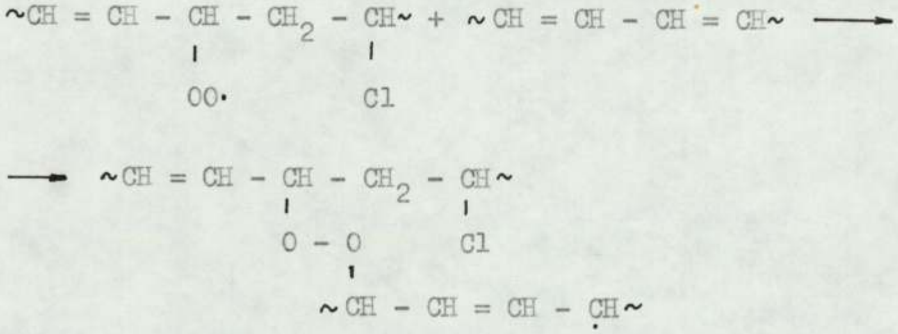
and this reaction was referred to [21] as a possible explanation of the HCl- autocatalysis in the presence of peroxides acting as initiators.

In the oxidation of e.g. atactic polypropylene it was shown by Manasek et al[26] that the ROOH concentration-time curve passes through a maximum. Similar maxima were found for polyethylene processed in torque rheometer[27,28]. The presence of the maxima was explained[29] on the basis of the observed carboxyl group catalytic effect. In the first stage of oxidation the rate of ROOH formation predominates over the rate of decomposition. When a certain quantity of acid has formed, the rate of decomposition increases as a result of the reaction of ROOH with the acid until it becomes greater than the rate of formation. The possible reaction was given as follows:

$\text{ROOH} + \text{HX} \longrightarrow \text{RO}\cdot + H_2O + \text{X}\cdot$

The initial decrease of peroxide on Fig. 3-7 could be explained by the decomposition of ROOH catalysed by HCl. The small difference between the position of the initial peroxide maxima could be then accounted for by the difference in the initial unsaturation concentration (Fig. 3-4) and consequently by the difference in the HCl concentration initially evolved. It is also possible that the alkylperoxy radicals will undergo other reactions than the hydrogen atom abstraction and this possibility is discussed further.

It is known[30] that conjugated polyolefins are able to copolymerise readily with oxygen in the presence of a source of free radicals with formation of polyperoxides. During PVC degradation the concentration of conjugated double bonds builds up and crosslinking reaction involving the addition of alkylperoxy radicals on formed double bonds will compete with the hydrogen atom abstraction[30] (viz reaction 3). On Fig. 3-2 the gel curves have a small initial maxima. As it was already mentioned in the previous sections 3.2.1. and 3.2.4. the gels formed initially were considered to be the gels containing peroxy-linkages which could be formed by the addition of ROO$^\bullet$ radicals on double bonds and could be described by the reaction 5:



$$\sim CH = CH - \underset{\substack{| \\ OO\cdot}}{CH} - CH_2 - \underset{\substack{| \\ Cl}}{CH}\sim + \sim CH = CH - CH = CH\sim \longrightarrow$$

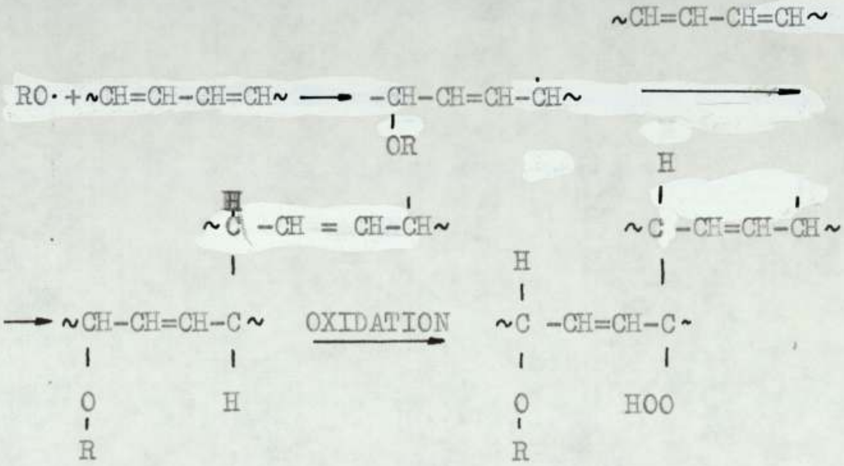
$$\longrightarrow \sim CH = CH - \underset{\substack{| \\ O - O \\ | \\ \sim CH - CH = CH - \underset{\cdot}{C}H\sim}}{CH} - CH_2 - \underset{\substack{| \\ Cl}}{CH}\sim \qquad (5)$$

In further discussion two processing temperatures are considered separately. At 170°C (Fig. 3-4) after the rapid initial increase of unsaturation the reaction proceeds with constant rate. Considering the radical - chain scheme the constant rate dehydrochlorination has been considered[4] to arise from two radical-chain schemes viz a) rapid initiation and little or no termination or b) steady-state conditions with termination and slow initiation. Crosslinking is a well established feature of thermal degradation[19,31,32] and the termination of the kinetic chain by crosslinking has been considered[18,33]. For example in the radical process Winkler[33] considered formation of crosslinks by the combination of two polymeric radicals. Another mechanism suggested was the addition of polymeric radicals to the conjugated unsaturation in an analogous manner to butadiene polymerization. In the presence of oxygen, the resulting alkylperoxy and alkoxy radicals will add to double bonds with formation of peroxy (viz reaction 5) and ether linkages. Also the free chlorine atom, which has been shown[37] to be present during PVC degradation, can for example abstract a hydrogen atom from another molecule. Whereas the combination of two polymeric radicals represents the true termination step, the H-atom abstraction by free chlorine atom or the addition of the polymeric, alkylperoxy or alkoxy radicals to the conjugation represents the kinetic chain transfer step.

The distribution of molecular weights (MWD) in Fig. 3-12 for 170°C and also for 210°C (Fig. 3-13) up to 5min is shown to have a high molecular weight tail. This molecular enlargement suggests the occurrence of a crosslinking reaction. The broadening at the high molecular weight end of the distribution was also shown in unstabilized PVC processed in Brabender plastograph[7] and in the polymer degraded under static conditions[34,35].

For 210°C temperature after the initial period the rate of dehydrochlorination reaction is considerably higher than for 170°C and is autoaccelerating (Fig. 3-4). The torque and the gel content increased rapidly after 5min because of rapid crosslinking reaction. Because of the rapid increase in the peroxide content (Fig. 3-7) the extent of hydrogen atom abstraction by the reaction 3 is much higher and the concentration of macroradical $R^{\bullet}$ capable of further dehydrochlorination is increased.

The increase in the peroxide content is also consistent with the extent of the crosslinking reaction. As it was mentioned earlier, several crosslinking mechanisms were suggested[33] and because of the presence of oxidation the crosslinking could be a result of addition of alkoxy radicals to the conjugated double bond with formation of ether and/or carbon-carbon crosslinks. This crosslinking can be described by the following reaction:



$$RO\cdot + \sim CH{=}CH{-}CH{=}CH\sim \longrightarrow \underset{\displaystyle OR}{\underset{|}{-CH}}{-}CH{=}CH{-}\dot{C}H\sim \xrightarrow{\sim CH=CH-CH=CH\sim}$$

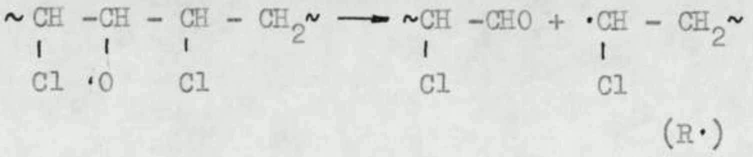
$$\longrightarrow \sim\underset{\underset{\displaystyle R}{\underset{|}{O}}}{\underset{|}{CH}}{-}CH{=}CH{-}\overset{\overset{\displaystyle \sim \overset{H}{C}{-}CH{=}CH{-}\overset{|}{CH}\sim}{|}}{\underset{\underset{\displaystyle H}{|}}{C}}\sim \xrightarrow{\text{OXIDATION}} \sim\underset{\underset{\displaystyle R}{\underset{|}{O}}}{\underset{|}{\overset{\overset{H}{|}}{C}}}{-}CH{=}CH{-}\overset{\overset{\displaystyle \sim \overset{\overset{H}{|}}{C}{-}CH{=}CH{-}\overset{|}{CH}\sim}{|}}{\underset{\underset{\displaystyle HOO}{|}}{C}}\sim \qquad (6)$$

This crosslinked structure contains an easily oxidizable tertiary position (tertiary allylic hydrogen atom) and that is why there is again an increase in the peroxide content. (e.g. at 170°C the peroxide was again detected after 15min when the crosslinking again increased).

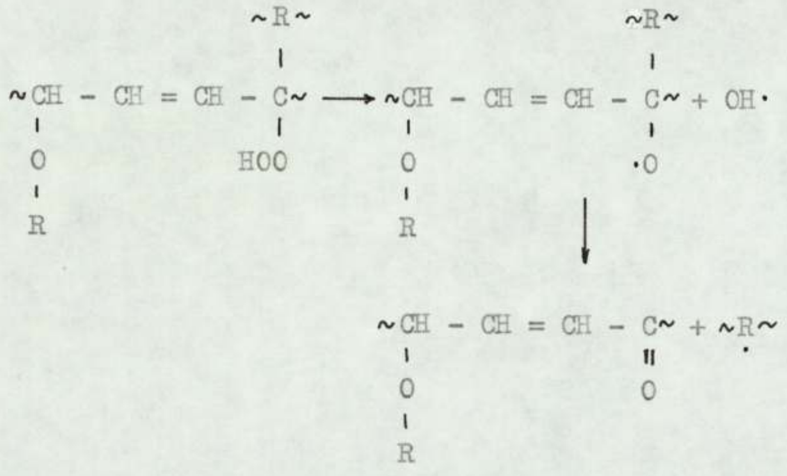
The molecular weight distribution of the soluble phase (Fig. 3-13) has shifted after 5min to lower molecular weight region as a result of a chain scission reaction. In Fig.3-9 the absorbance of the observed UV absorption peaks rapidly increased. The concentration of the crosslinked phase also increased (Fig. 3-2) and therefore the increased UV-absorbance results from the progressively smaller proportion of the total sample being examined (from 93% at 5min to 11.1% at 20min). This result itself also shows the existence of the chain scission reaction.

Furthermore, the decrease in the rate of torque increase after 10min (Fig.3-2) suggests that the lower molecular weight species (as a result of the chain scission) have a plasticizing effect.

Because of the increase in the carbonyl index (Fig.3-7) and also formation of a conjugated carbonyl band at $1675 cm^{-1}$ - $85 cm^{-1}$ (Fig.3-5), the chain scission has oxidative character. The rearrangement of the alkoxy radical would lead to scission[18,30,33,34] with formation of a lower molecular weight species:



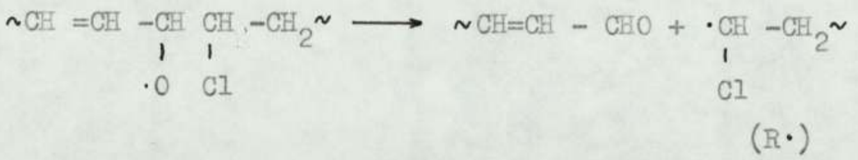
$$\sim\underset{Cl}{CH}-\underset{\cdot O}{CH}-\underset{Cl}{CH}-CH_2\sim \longrightarrow \sim\underset{Cl}{CH}-CHO+\underset{Cl}{\cdot CH}-CH_2\sim \quad (R\cdot) \qquad (7)$$



$$\sim\underset{\underset{R}{O}}{CH}-CH=CH-\overset{\sim R\sim}{\underset{HOO}{C}}\sim \longrightarrow \sim\underset{\underset{R}{O}}{CH}-CH=CH-\overset{\sim R\sim}{\underset{\cdot O}{C}}\sim + OH\cdot$$

$$\downarrow$$

$$\sim\underset{\underset{R}{O}}{CH}-CH=CH-\underset{\underset{O}{\|}}{C}\sim + \sim\underset{\cdot}{R}\sim \qquad (7a)$$



$$\sim CH=CH-\underset{\cdot O}{CH}\ \underset{Cl}{CH}-CH_2\sim \longrightarrow \sim CH=CH-CHO+\underset{Cl}{\cdot CH}-CH_2\sim \quad (R\cdot) \qquad (7b)$$

The chain scission reactions result in an increase in the concentration of macromolecular radicals $R^{\bullet}$. These radicals can continue the dehydrochlorination and therefore oxidative polymer chain scission is associated with kinetic chain branching. The oxidation of the polymers' crosslinked structure with the formation of peroxide (viz reaction 3) involves hydrogen atom abstraction from a PVC chain and leaves another macroradical capable of further dehydrochlorination. Also decomposition of hydroperoxide at the same time (reaction 7a) will provide alkoxy and hydroxyl radicals. They are involved in the competitive crosslinking (reaction 6) but may also abstract hydrogen atoms and create ~~a~~ new propagating radicals.

The intermediate free radical species formed by the oxidative chain scission ($R^\bullet, OH^\bullet, {}^\bullet\underset{Cl}{\underset{|}{CH}}-CH_2-$) together with the thermal energy will increase HCl elimination and that is why the unsaturation curve for 210°C has accelerated character.

Reaction time dependence of I_2 with processed PVC.

PVC processed without additives.

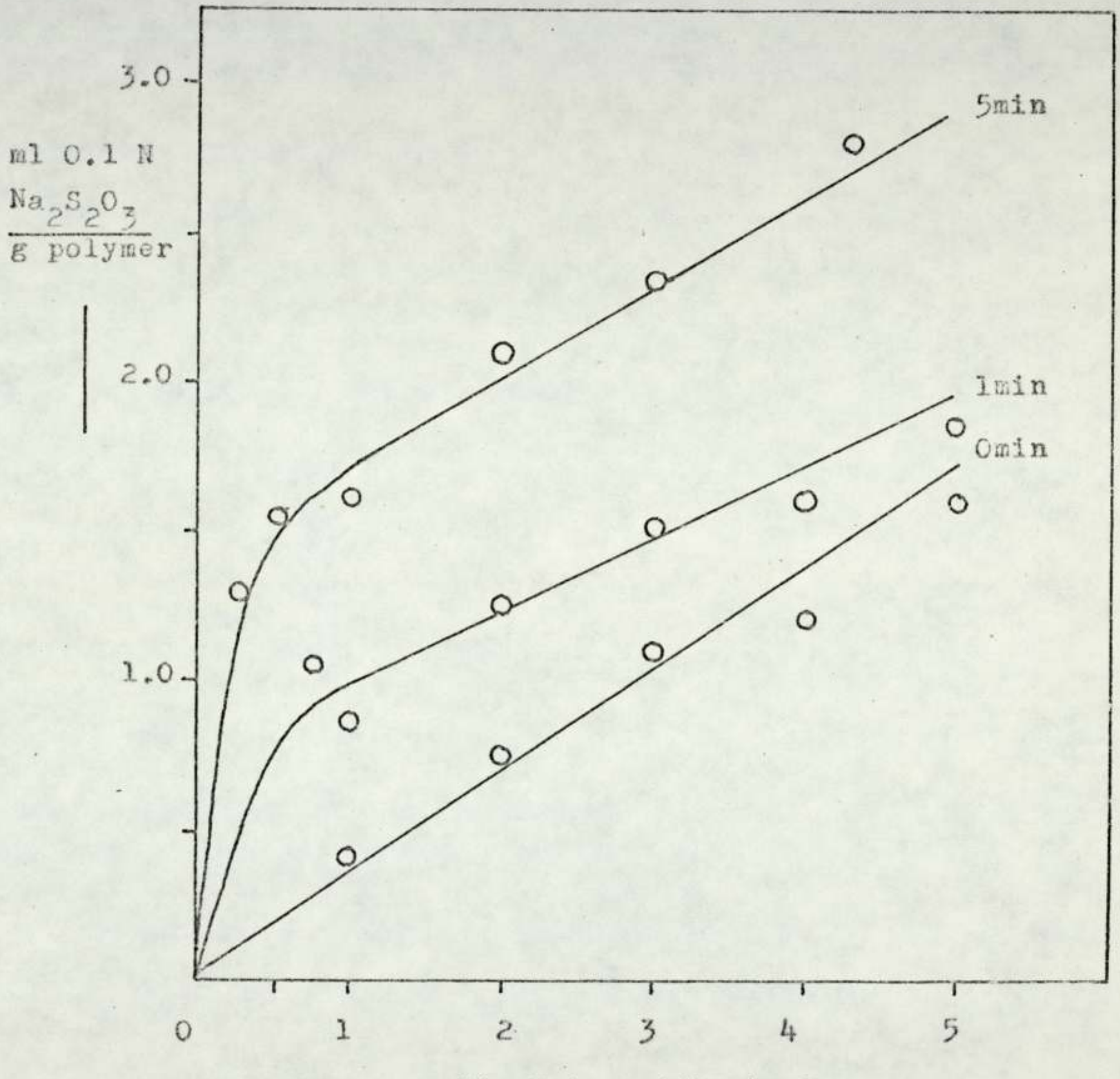


Fig.3-1 t(hrs) of reaction

TORQUE AND GEL CONTENT VS PROCESSING TIME. PVC PROCESSED AT 170°C AND 210°C WITHOUT ADDITIVES.

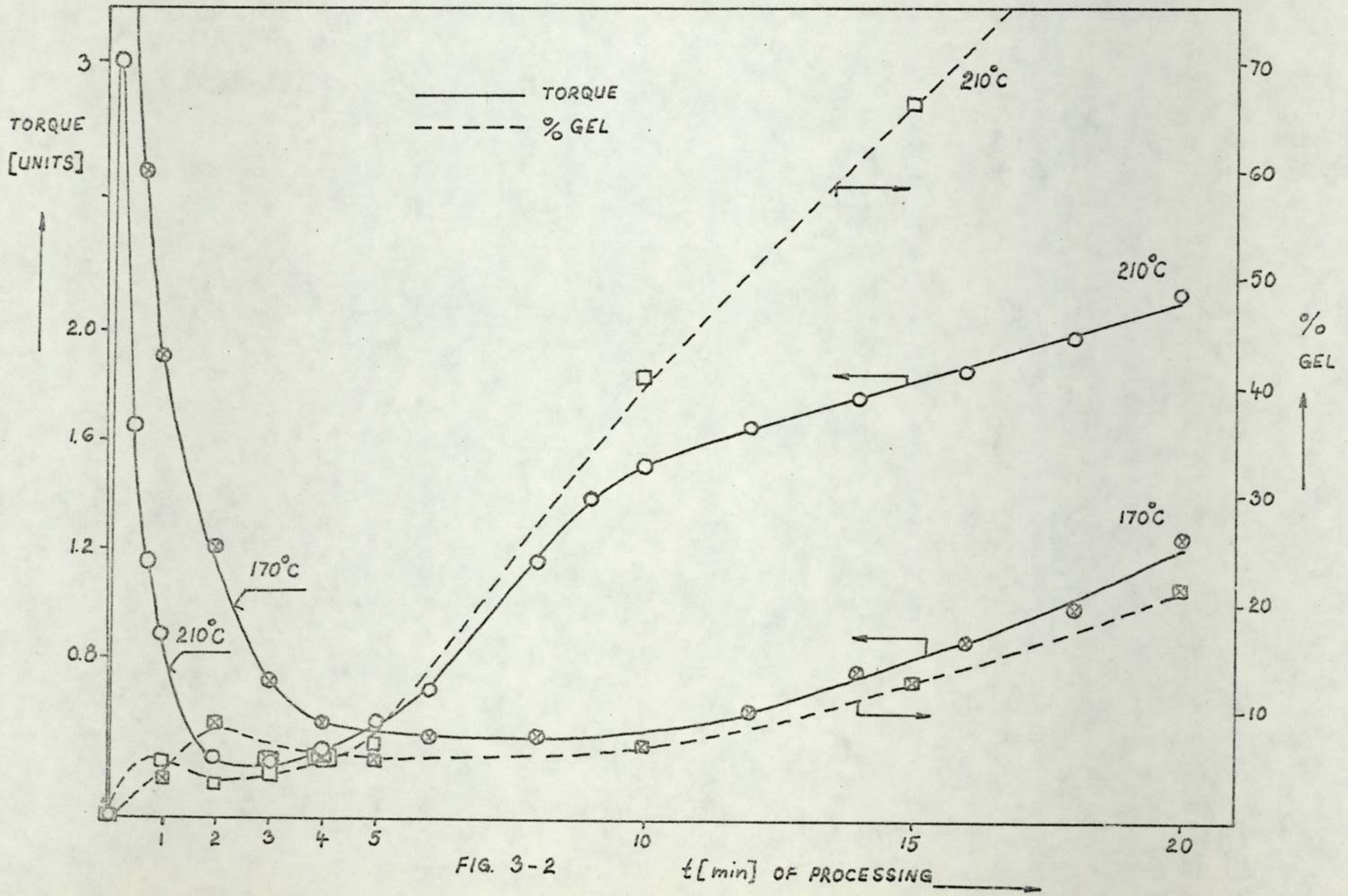


FIG. 3-2

Colour change during processing of PVC in torque rheometer without additives.

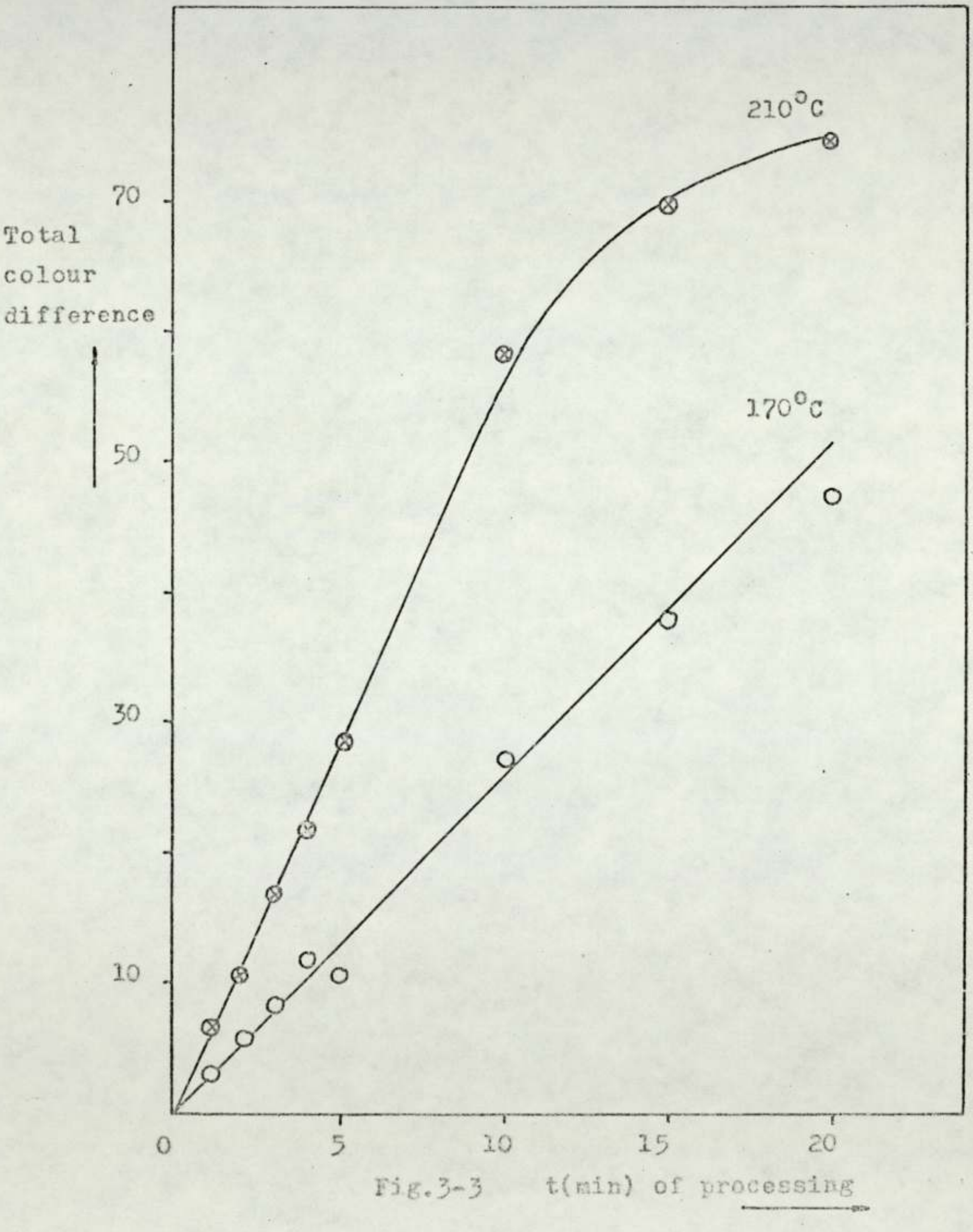


Fig.3-3

Unsaturation vs processing time. PVC processed in torque rheometer without additives

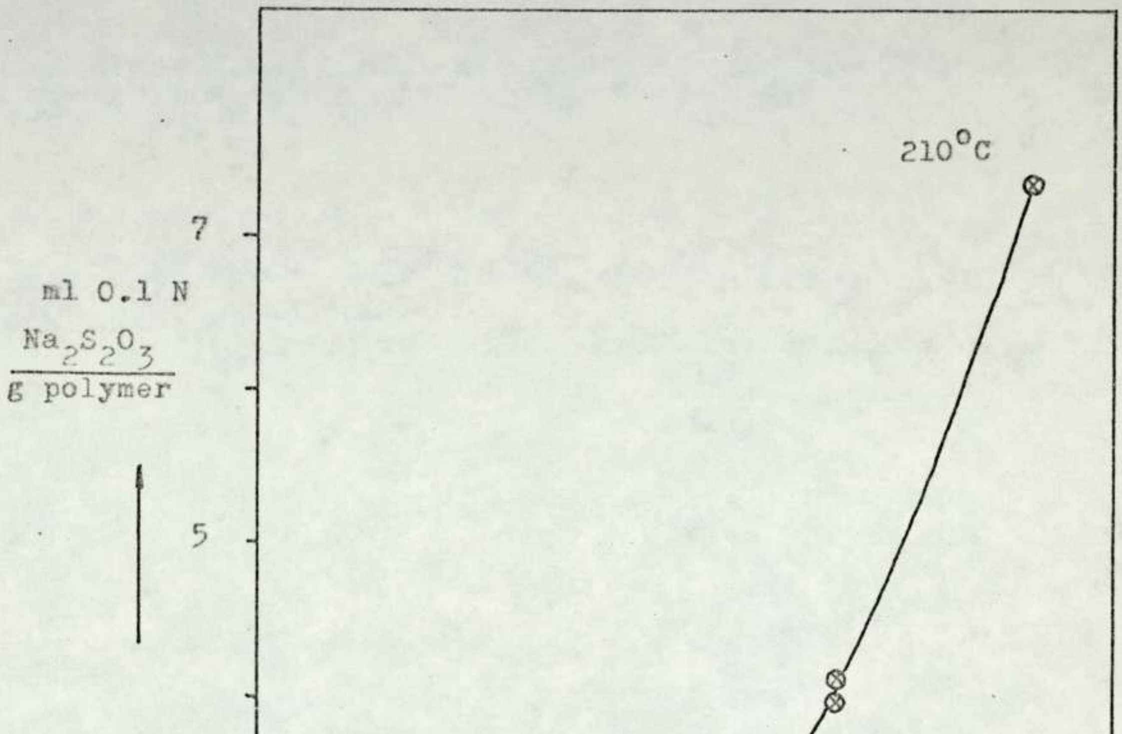


Fig.3-4 t(min) of processing

Compensated IR-spectrum of PVC processed in torque rheometer for 20min at 210°C without additives (7% solution in CH_2Cl_2).

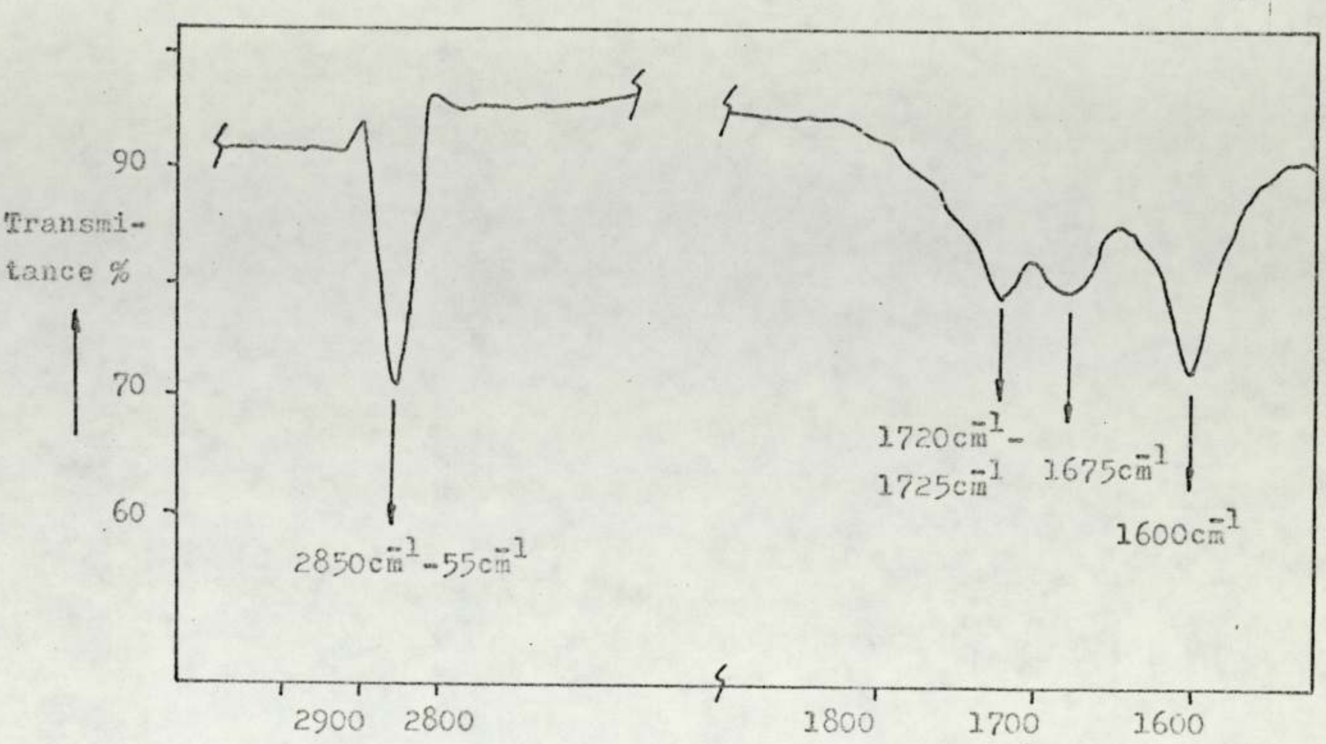


Fig.3-5 Wavenumber (cm^{-1})

$I_{2850-55cm^{-1}}$ index of processed PVC, no additives, sol phase

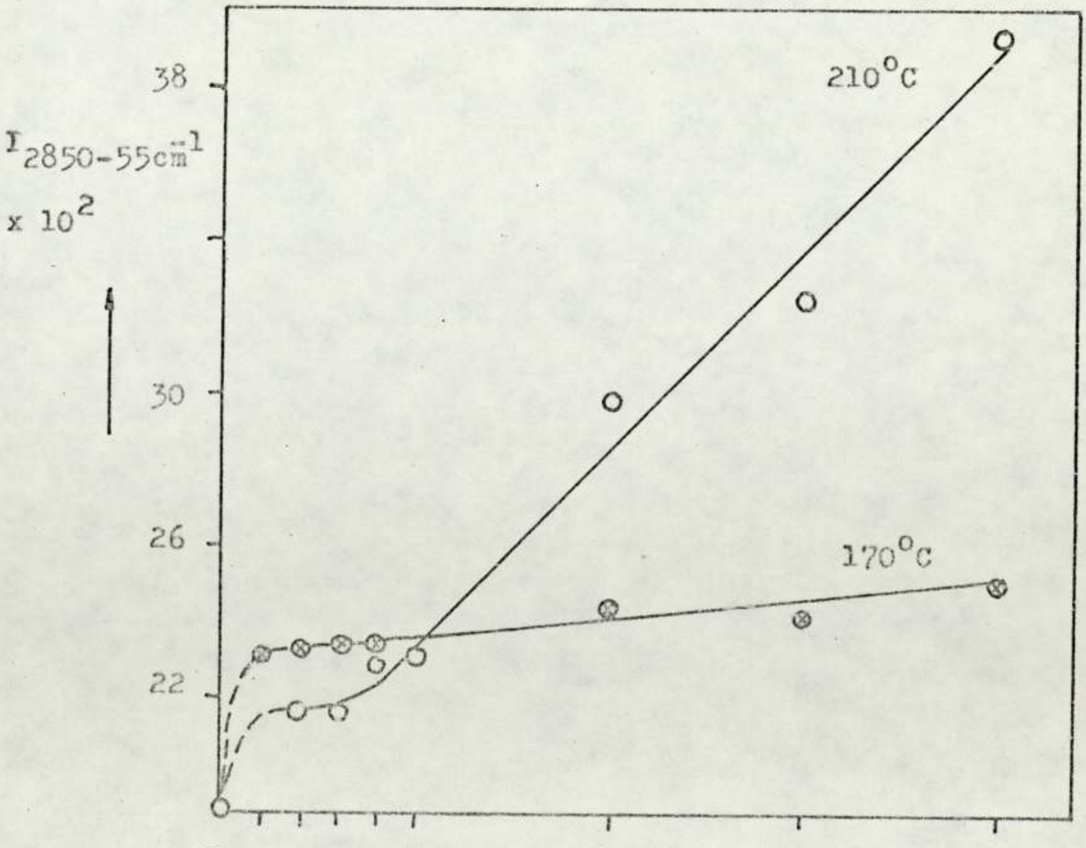


Fig.3-6 t(min) of processing

Peroxide content and carbonyl index vs processing time.

PVC processed in torque rheometer without additives.

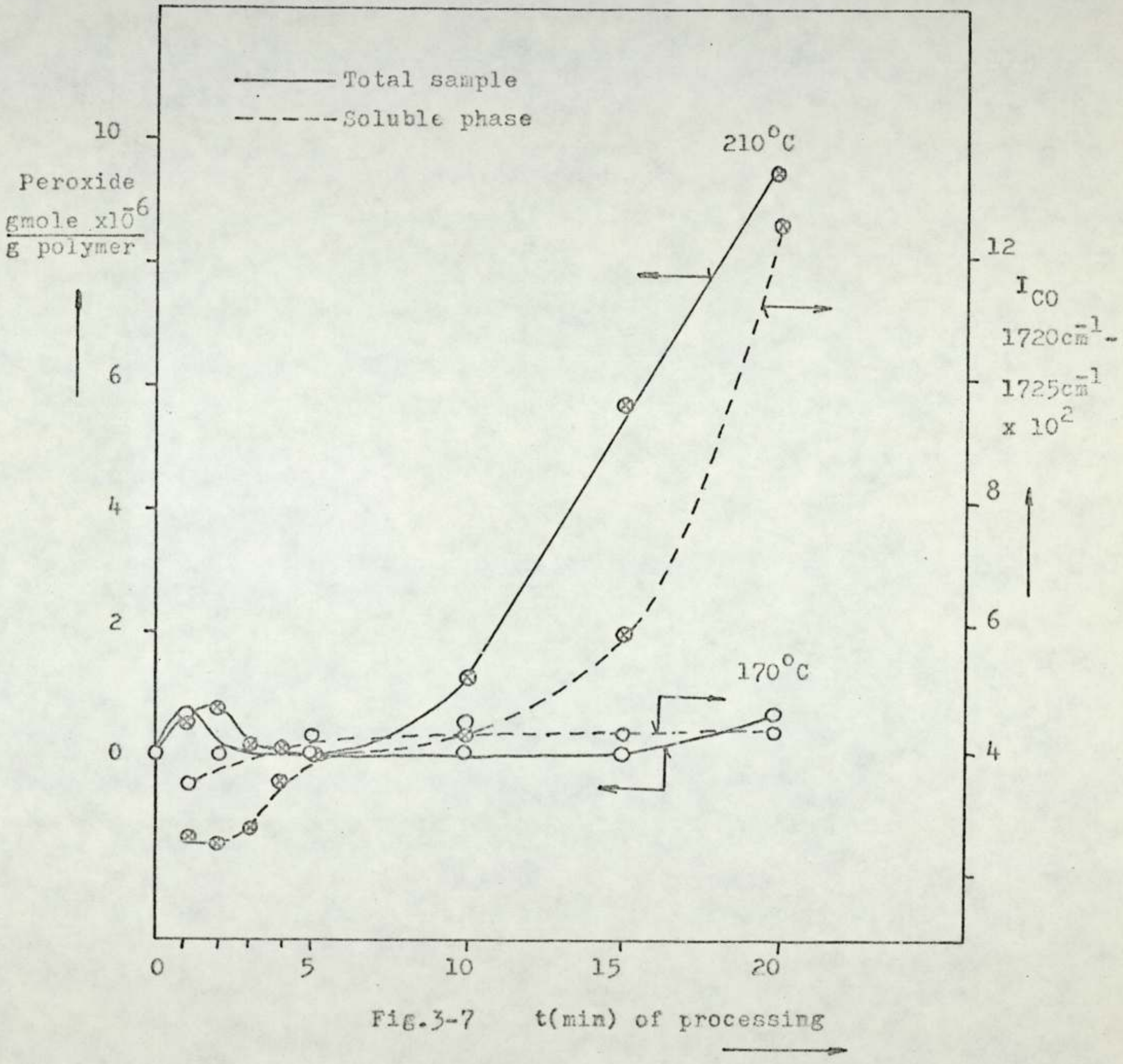


Fig.3-7 t(min) of processing

IR-spectrum of unprocessed PVC. Insoluble part (0.45 %) in methylene dichloride.

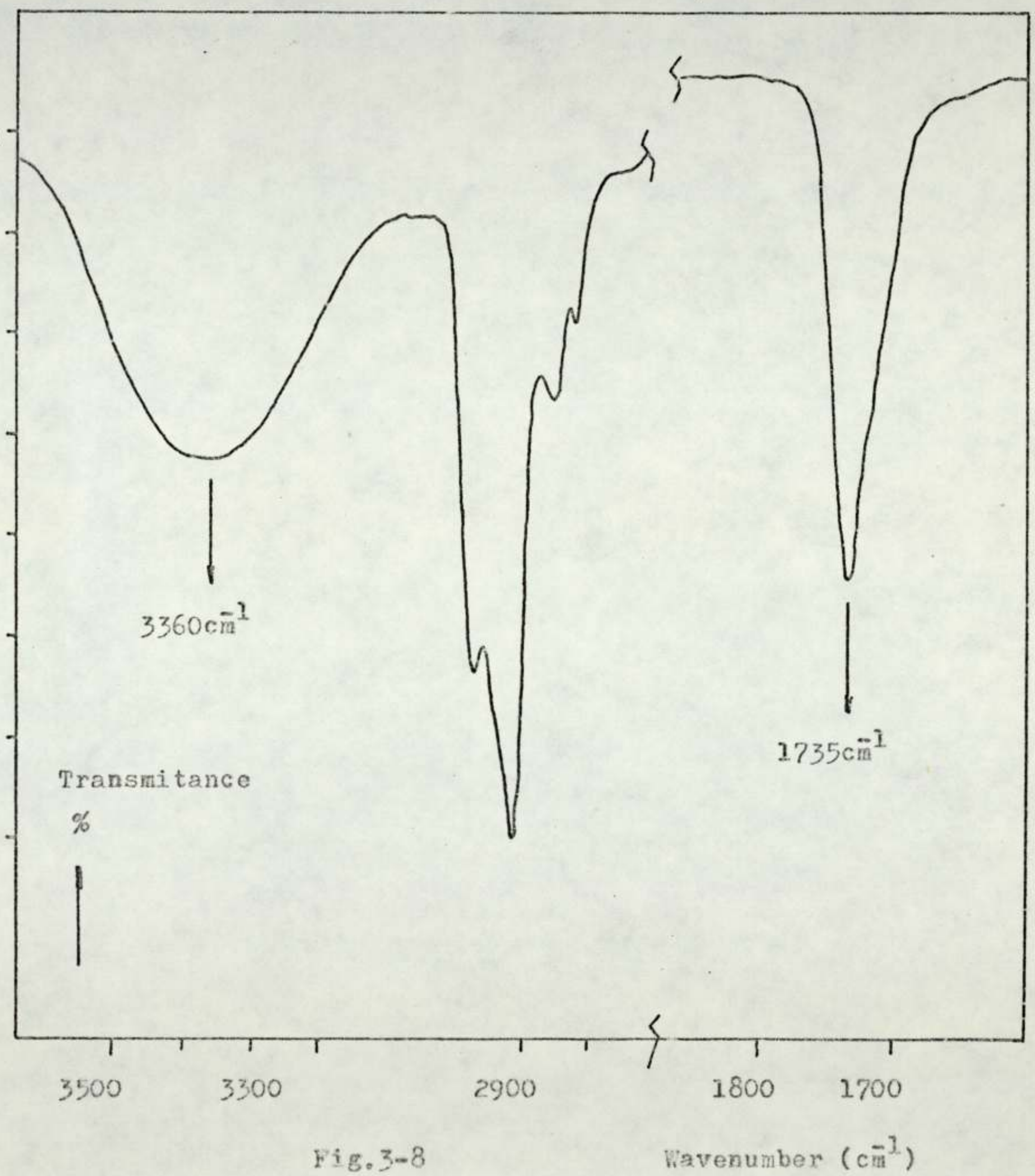
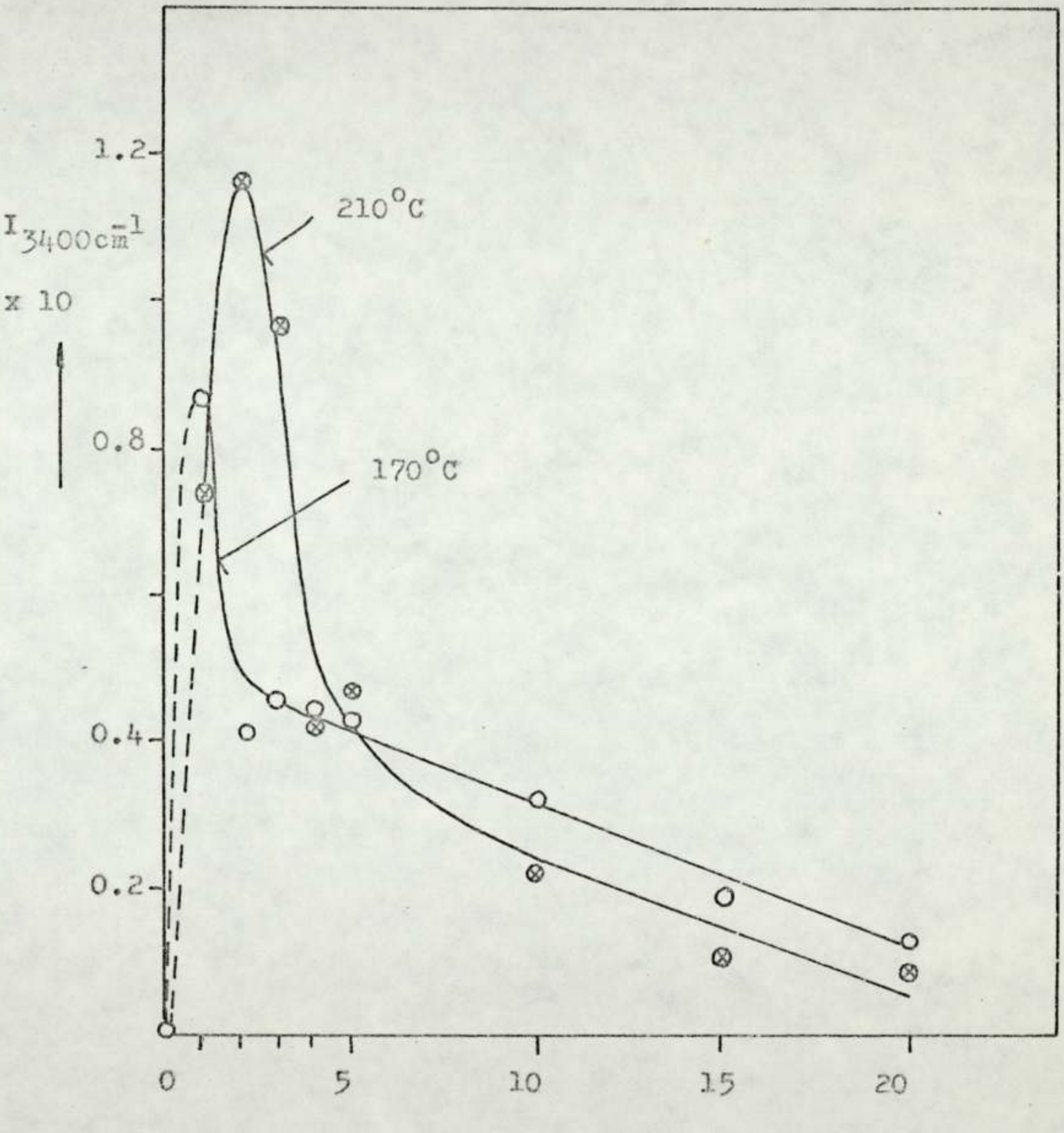


Fig. 3-8

$I_{3400cm^{-1}}$ index vs processing time, PVC gel phase.

PVC processed without additives.



t(min) of processing

Fig.3-8a

UV-absorbance vs processing time. PVC processed at 210°C without additives. (0.2 % solution in methylene dichloride, 1 mm cell used).

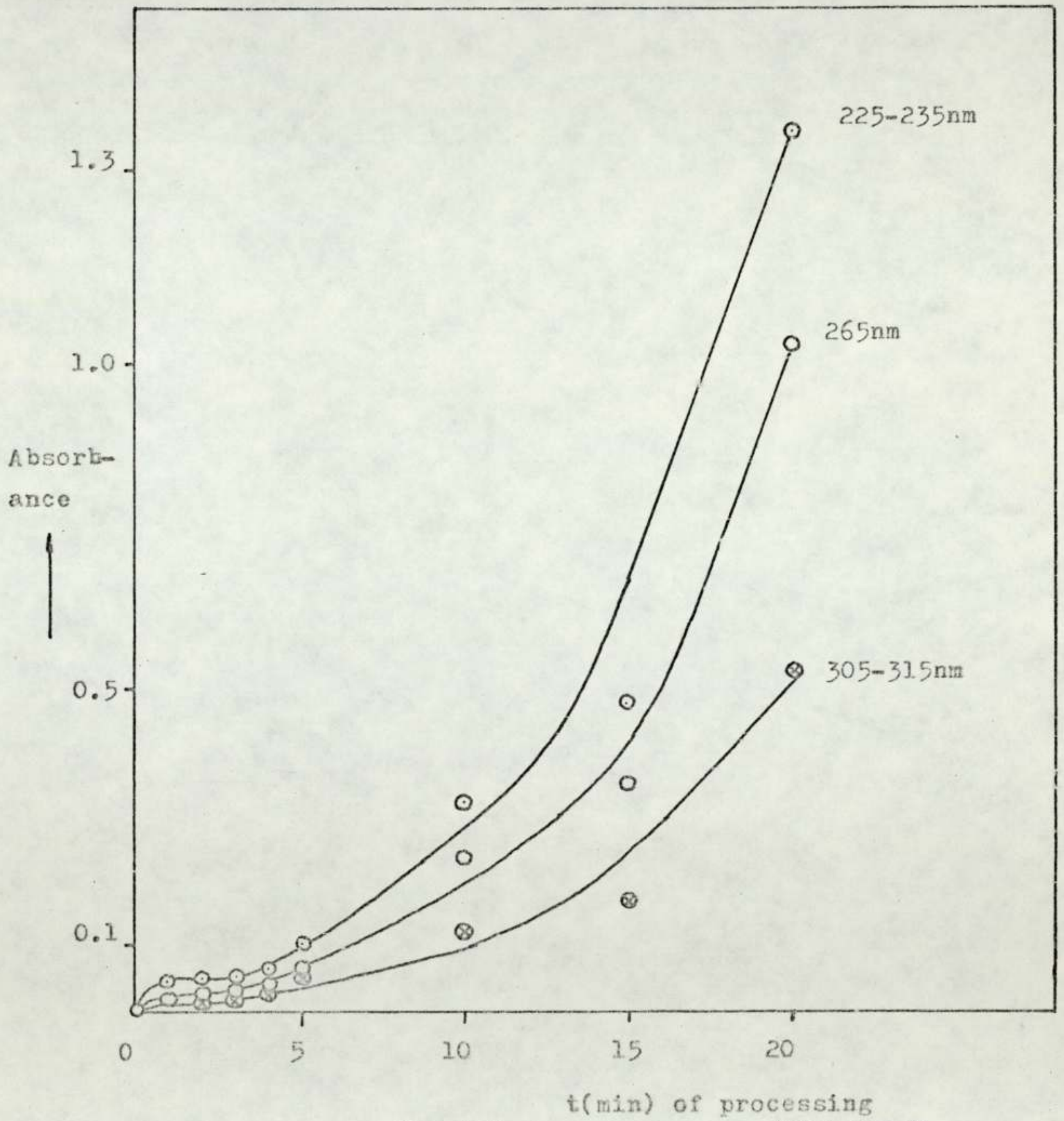


Fig.3-9

UV-absorbance vs processing time. PVC processed at 170°C without additives. (0.2 % solution in methylene dichloride, 1mm and 10mm cells used).

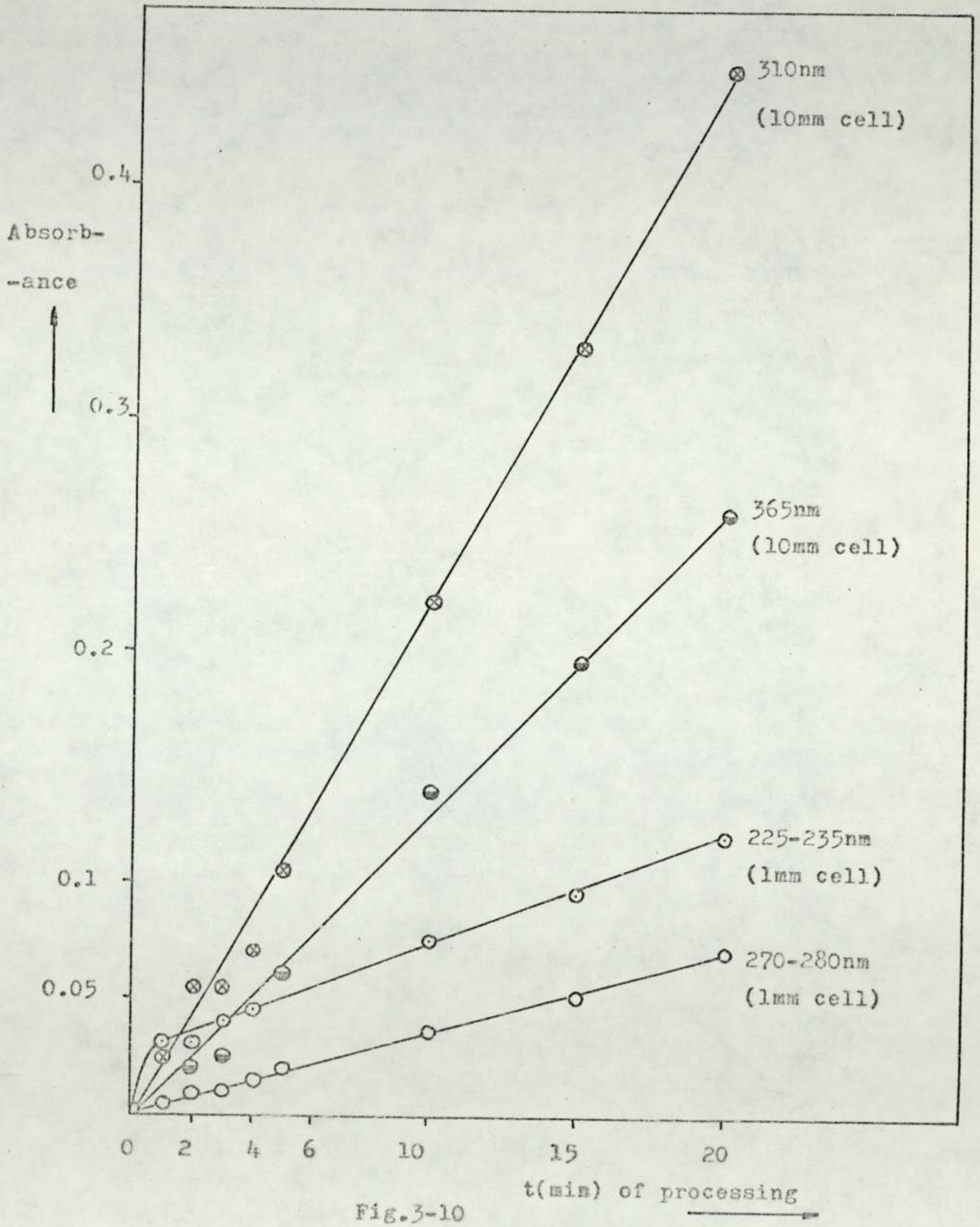


Fig. 3-10

UV-absorbance vs processing time. PVC processed at $170^{\circ}C$ and $210^{\circ}C$ without additives. (0.07 % solution in methylene dichloride, 10mm cell used).

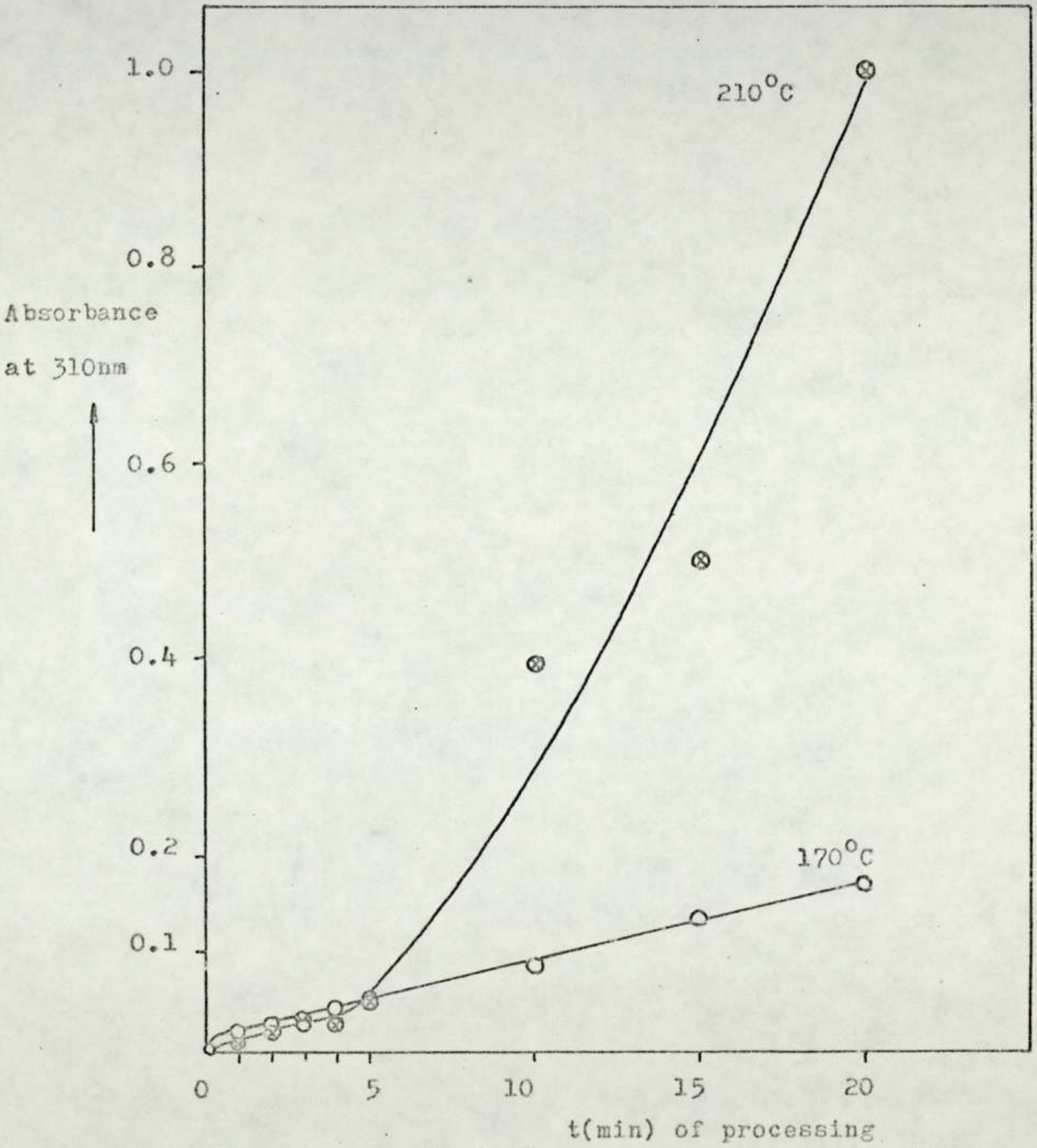


Fig.3-11

Molecular weight distribution of PVC processed in torque rheometer at 170°C without additives.(Soluble phase in methylene dichloride).

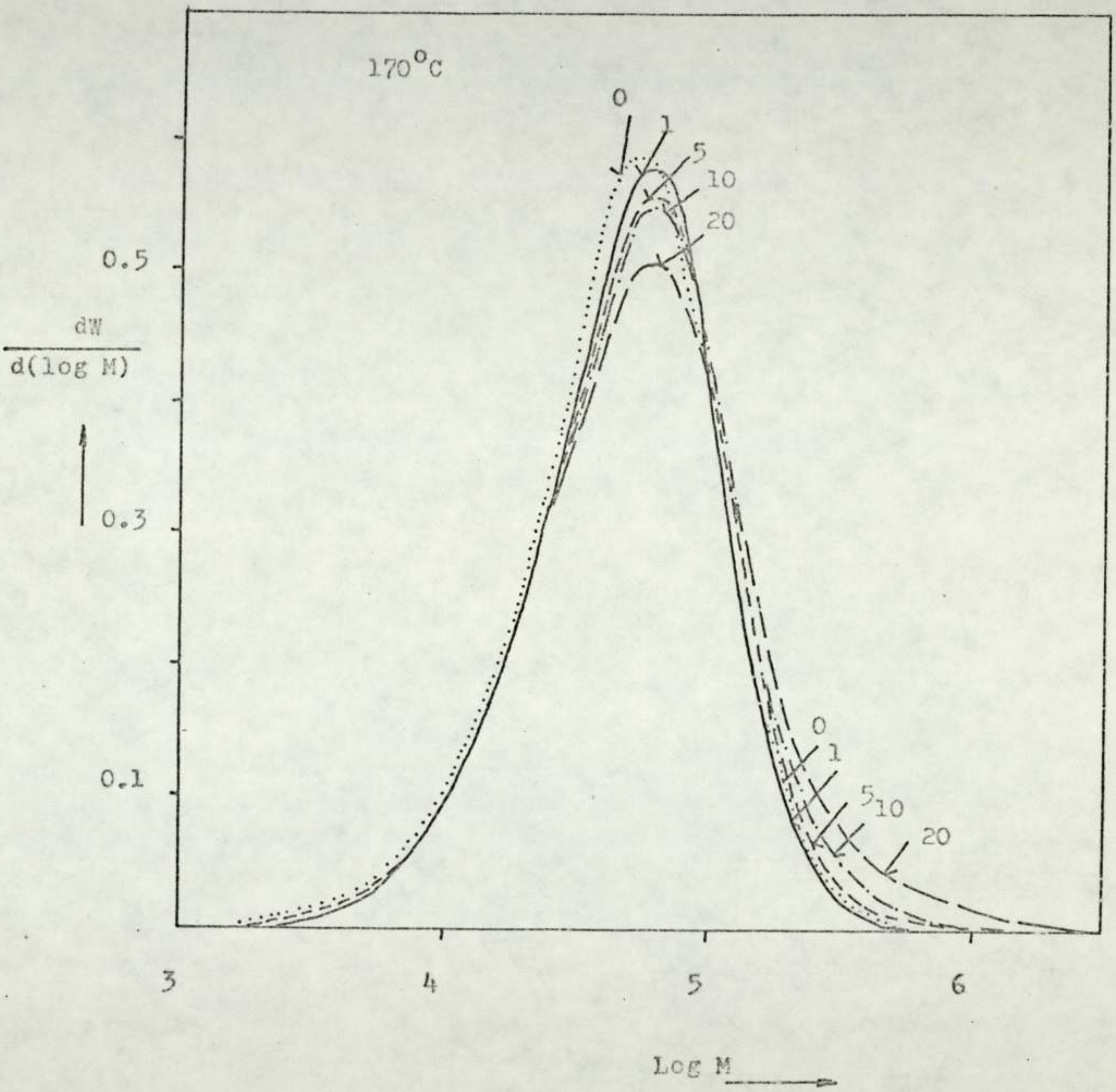


Fig.3-12

Molecular weight distribution of PVC processed in torque rheometer at 210°C without additives.(Soluble phase in methylene dichloride).

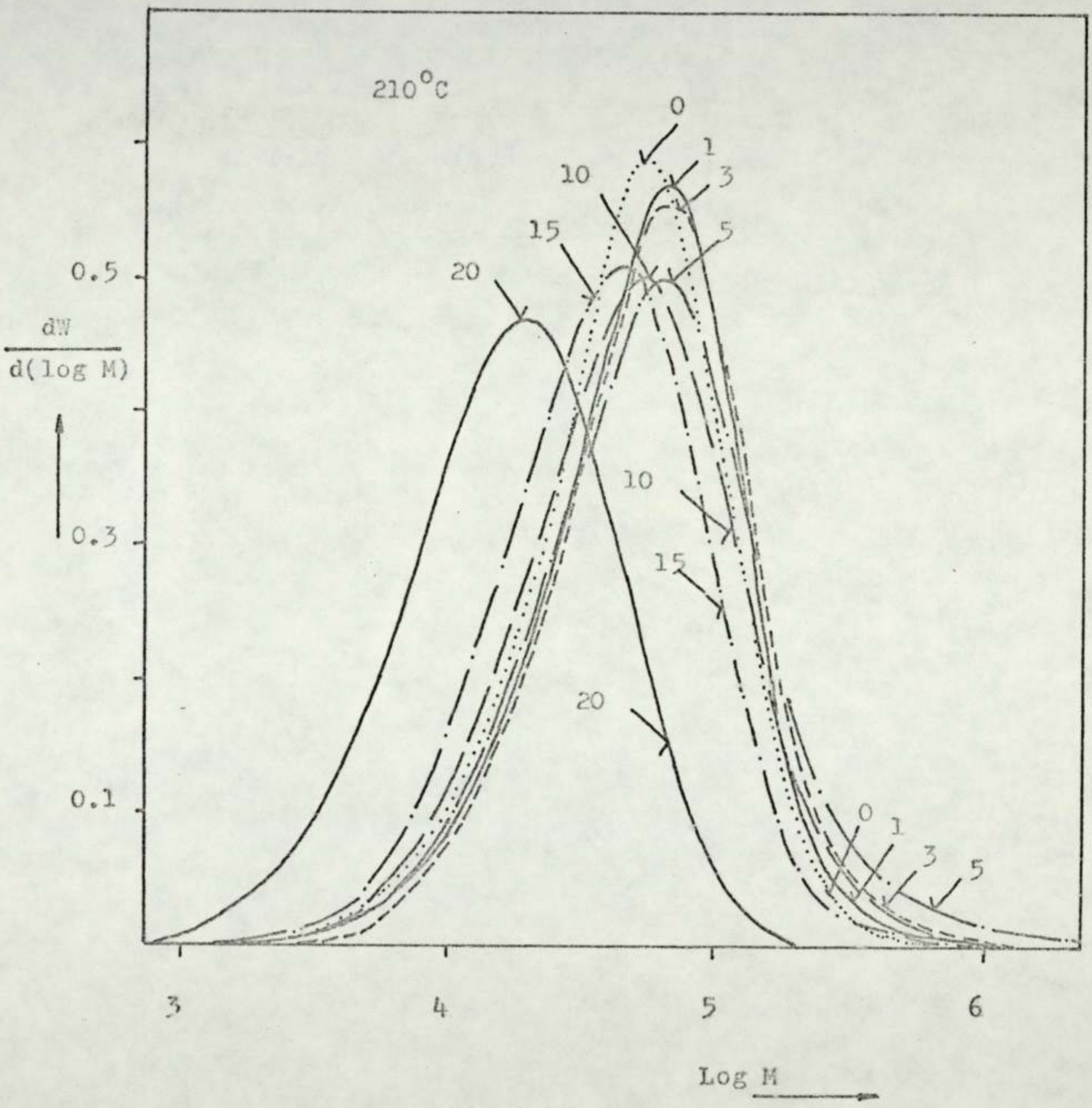


Fig.3-13

CHAPTER 4. Processing of PVC with dibutyltin maleate (Irgastab T290), lubricants Ca-stearate and Wax E.

4-1. PVC with Irgastab T290 only

4-1.1. Results

4-1.1.1. Processing in torque rheometer and the gel content measurement.

The change of torque with time together with the gel content in the polymer are shown in Fig. 4-1 for two temperatures. After the initial increase of the torque which is frequently described as the fusion or flux point[38,39,40] and which takes place within the first minute of processing, the torque reaches an equilibrium value and remains constant for 8min at 210°C and 20min for 170°C. During this time there is no significant increase in the gel content. This suggests the existence of an induction period during which the polymer is stabilized. The level of the torque during this period for 210°C is higher than for 170°C. As we saw earlier in the discussion on unstabilized polymer where the torque at 170°C was higher up to 5min, this behaviour at 210°C may be the result of the presence of stabilizer. After 10min at 210°C there was a rapid increase of the torque and the gel content. Also at 170°C after 25min the torque and the gel increased. The changes of the torque[39] and the gel content are important parameters used for the characterization of the efficiency of PVC stabilizers and have also been used for the study of thermal degradation[18]. However, other methods can be used for more detailed investigation of the processes involved.

4-1.1.2. Colour change

In practice discolouration is normally the first and most important effect of degradation[18] and the change of colour has been used[41] for the study of the degradation in the presence of the thermal stabilizers.

In Fig. 4-2 there is a plot of the total colour difference (see experimental chapter 2) vs processing time of PVC processed with Irgastab T290 at 170°C and 210°C. As can be seen in Fig. 4-2 there is no significant discolouration of the polymer for 8min at 210°C and 25min at 170°C. This suggests the existence of an induction period and this is in good agreement with the induction period of the gel formation and the torque increase (see Fig. 4-1). After this period the total colour difference increased and the rate was faster for 210°C.

4-1.1.3. IR-spectroscopy results

An examination of the IR-spectra revealed several absorption bands in the region 1500 cm^{-1} - 1900 cm^{-1}. The IR-spectrum of the unprocessed polymer in this region contained only a small band near 1735 cm^{-1} and therefore it proved to be useful for following the changes during processing.

During processing the growth of absorption peaks at 1725 cm^{-1}-1750 cm^{-1}, 1778 cm^{-1} and 1848 cm^{-1} was observed. The double peak at 1605 cm^{-1} and 1575 cm^{-1}- 85 cm^{-1}, present at the beginning decreased, 1605 cm^{-1} peak first followed by 1585 cm^{-1} peak. An example of these spectral changes is illustrated in Fig. 4-3a,b for 210°C. The initial peak at 1720 cm^{-1} - 25cm^{-1} shifted during processing to 1750 cm^{-1} and this is also shown in Fig. 4-4. This peak had a shoulder between 1710 cm^{-1} - 20 cm^{-1} which became more evident when the shift towards 1750 cm^{-1} occurred. Also a peak at 342 cm^{-1} appeared especially at long processing times.

The IR-spectra of the stabilizer alone has strong absorptions at 1605 cm^{-1} and 1575 cm^{-1} whereas this part of the spectra of pure polymer has no such peaks and therefore the double peak at 1605 cm^{-1} - 1575 cm^{-1} observed during processing (Fig.4-3a) comes from the stabilizer.

The carboxylate anion of the carboxylic acids gives rise to the strong asymmetrical stretching band in the 1550 cm^{-1} - 1650 cm^{-1} [42] and therefore the peak at 1605 cm^{-1} - 1575 cm^{-1} can be assigned to the carboxylate stretching of dibutyltin maleate. The carboxylate peak is plotted in Fig. 4-5 as an index I_{COO} 1575 cm^{-1} vs processing time for soluble phase and total sample. For 210°C there is a rapid decrease until 10min at which time the carboxylate absorption disappeared. For 170°C this decrease is slower and after 20min the carboxylate absorption was not detected.

It should be mentioned here that the IR-spectra of the stabilizer contained an absorption peak at 3640 cm^{-1}. The position of this peak suggests the presence of an unbonded hydroxyl group[42] and it is possible that Irgastab T290 contained a small concentration of an phenolic antioxidant (probably hindered phenol).

The carbonyl absorption viz Fig. 4-4 is plotted as a carbonyl index I_{CO}1725 cm^{-1} - 50 cm^{-1} in Fig. 4-6. For 210°C the index increased and reached a maximum after 10min. For 170°C the increase was slower with maximum value at 25min. Saturated aliphatic esters have CO absorption at 1735 cm^{-1} - 50 cm^{-1} and for α, β unsaturated esters this absorption is shifted to the 1730 cm^{-1} - 1715 cm^{-1} region[42]. Frye and Horst[43] have shown the formation of ester at 1735 cm^{-1}- 40 cm^{-1} when PVC was heated with metal carboxylates. Other workers made similar observation[44,45]. The esteric carbonyl index I_{CO}1730 $cm^{-1}$of the gel phase is shown in Fig. 4-7. This peak has shifted from 1730 cm^{-1}-35 cm^{-1} to 1750 cm^{-1} only after 10min for 210°C and 20min for 170°C and shows maxima between 5-8min for 210°C and 20min for 170°C. Similar maxima can be seen in Fig. 4-7a of the index I_{OH} 3450 cm^{-1}. OH stretching of unbonded alcoholic hydroxyl group has absorption at frequences 3650 cm^{-1}-3584 cm^{-1} whereas H-bonded absorptions appear at lower frequences 3550 cm^{-1} - 3200 cm^{-1}[42].

In Fig. 4-8 is plotted carbonyl index of the absorption at 1778 cm^{-1}. A similar plot was obtained for the smaller 1848 cm^{-1} absorption band. Saturated non-cyclic anyhydrides display two stretching bands in carbonyl region near 1818 cm^{-1} and near 1750 cm^{-1}[42] as a result of asymmetrical and symmetrical CO stretching modes. Cyclic anhydrides with five-membered rings show absorption at higher frequences and for example succinic anhydride absorbs at 1865 cm^{-1} and at 1782 cm^{-1}[42]. Maleic anhydride alone displays two absorption bands at the same frequency. The observed peaks at 1848 cm^{-1} and at 1778 cm^{-1} (Fig. 4-3a,b) can be attributed to maleic anhydride. To prove the formation of maleic anhydride during processing a sample processed for 8min at 210°C was boiled in distilled water for 45min and 105min and IR-spectra were measured. The result can be seen on Fig. 4-9. Both characteristic anhydride carbonyls were considerably reduced and a new carbonyl peak at 1715 cm^{-1}-20 cm^{-1} and carboxylate bands at 1630 cm^{-1} and 1603 cm^{-1} were formed. The latter bands can be assigned to the carboxylate absorption of the corresponding acid. In Fig. 4-10a and Fig. 4-10b are examples of the IR-spectra of processed polymer for 5 and 8min at 210°C and 5 and 25min at 170°C where absorption at 342 cm^{-1} can be seen. This peak was attributed to Sn-Cl absorption[46].

4-1.1.4. UV-spectroscopy and unsaturation measurement.

The UV-spectra of the soluble phase in CH_2Cl_2 were recorded and absorption peaks centred at 225nm-235nm, 255nm, 288nm and a small ill-defined absorption at 337nm were observed for 210°C. At the longer wavelength the absorbance progressively decreased and no absorption peaks were observed up to 750nm. For 170°C the growth of the absorption peaks at 220nm-230nm and 280nm was observed. Above 300nm the absorbance again progressively decreased up to 750nm as for 210°C. The absorbance of the observed peaks are plotted vs processing time in Fig. 4-11a for 170°C and in Fig. 4-11b for 210°C, respectively. At 170°C the absorbance initially increased and remained constant up to 20min. After 20min there was further increase. At 210°C after the initial increase the absorbance did not increase until after 10min. This result suggests the presence of an induction period of the unsaturation formation of 20min at 170°C and 8-10min at 210°C. This is in good agreement with the induction period as it was measured by the torque and the gel content increase (Fig. 4-1), the colour formation (Fig.4-2) and the IR-spectroscopy results (Figs. 4-5,6,8).

The unsaturation of the total sample was determined by the iodine method and was described earlier in the section 3.1.2. The result for both temperatures is shown in Fig.4-12. Here again after the initial increase the unsaturation increased only after 8min at 210°C and 20min at 170°C. This result is in good agreement with the induction period discussed above.

4-1.1.5. Peroxide determination

The peroxide content of PVC processed with Irgastab T290 was determined by the iodine - liberation method described in the section 3.1.1. The result for 170°C and 210°C is shown in Fig. 4-13. No peroxide was detected up to 5min at 210°C but with further processing the peroxide content increased and reached maximum at 20min. At 170°C the peroxide was detected only for the sample processed for 30min. It appears that there is no peroxide formed during the induction period.

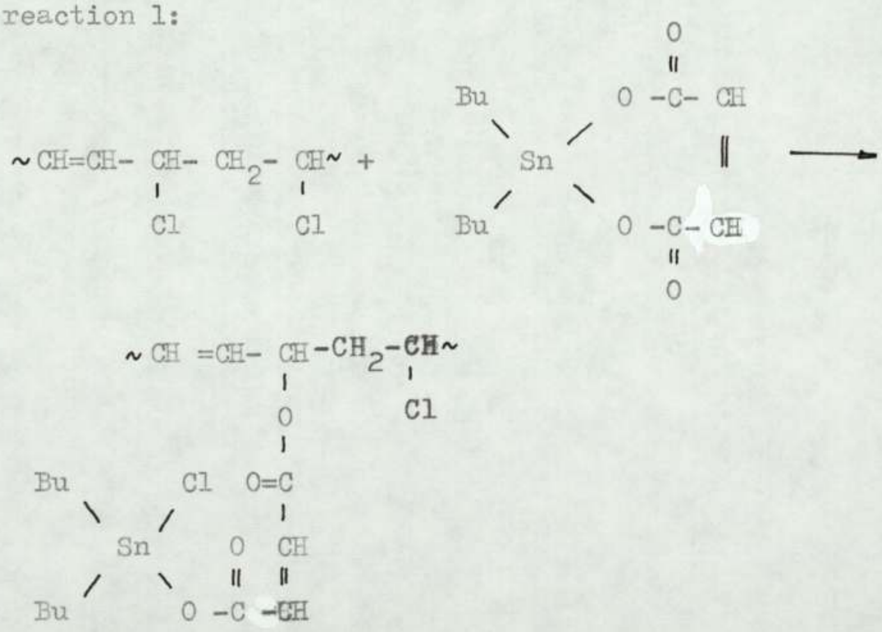
4-1.1.6. Molecular weight measurement

For the molecular weight and molecular weight distribution measurement the gel permeation chromatography was used as described in the experimental chapter 2. The measurement was made on the soluble phase after the removal of the insoluble gel in methylene dichloride from the processed samples. MWD for 170°C is shown in Fig. 4-14a and for 210°C in Fig. 4-14b, respectively. Soluble phase for 170°C represents between 98.8% - 91.9% of the total sample (2-30min) and for 210°C between 97%-31.8% (2-25min). As can be seen in Fig. 4-14a the high molecular weight tail of the MWD is formed up to 30min of processing. This result suggests the occurrence of a crosslinking reaction. For 210°C (Fig.4-14b) the high molecular weight end can also be observed. However, after 10min of processing this part of the MWD is shifted to the lower molecular weight region and this indicates that up to 10min the crosslinking reaction occurred and with further processing both the crosslinking and the chain scission took place.

4-1.2. Discussion

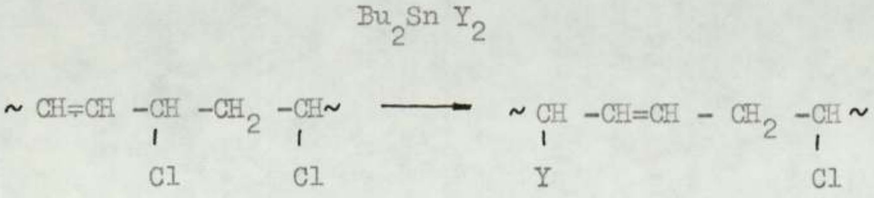
It is clear from Fig.4-1 that dibutyltin maleate prevents increase of the equilibrium torque and crosslinking for 10min at 210°C and 20min at 170°C and only a small amount of the gel (0.5-3%) is present during these periods. Discolouration is also prevented (Fig.4-2). During this stabilization (or induction) period the carboxylate moiety of the stabilizer decreases (Fig.4-5) and ester is formed (see Fig.4-6). Frye and Horst[43] demonstrated exchange of 'labile chlorine atoms' with carboxylate group of metal carboxylate stabilizers and Bengough and Onozuka[47] have shown that the ester exchange reaction with allylic chlorine is faster than with tertiary chlorine both in model compounds and in the polymer. Frye, Horst and Paliobagis[48], using a radioactive tracer method, have shown that the polymer, degraded in the presence of organotin stabilizers of the general formula $Bu_2Sn\ Y_2$ with radioactive ^{14}C atom located in the Y group, retained its radioactivity after six successive dissolutions in THF and precipitations with methanol. They suggested that the Y groups replaced labile chlorine atoms and this replacement is the part of stabilizing action of organotin stabilizers. However, the IR-spectra did not indicate the formation of ester carbonyl and thiswas explained as being due to the low concentration of ester which did not permit spectroscopic detection. The formation of ester during the induction period in the present work is shown in Fig.4-6. This coupled with the decrease of the carboxylate (Fig.4-5) strongly supports theory of Frye and co-workers[48]. It has also been supported by the demonstration[49] that dibutyltin dicarboxylates (laurate, acetate) react with model compounds e.g. tert.-butylchloride and allylic chlorine (3-chlorobutene-1). Reaction with 3-chlorobutene-1 was slower than with tert.-butylchloride and dibutyltin monochloride carboxylate was isolated. It was also found that the ease of exchange with the tertiary chlorine model did not match the stabilizing ability in the polymer whereas with allylic models it corresponded closely to it. From this observation it was concluded[49,50] that the reaction with allylic chlorine is more important during stabilization.

The formation of ester during processing can be described by reaction 1:



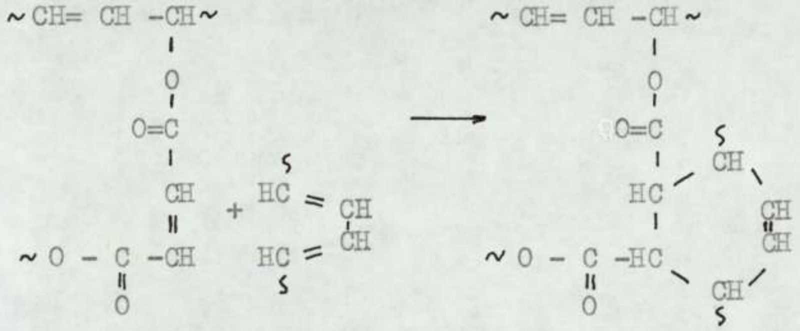
(1)

Allylic rearrangement may also take place as was shown by Ayrey, Poller and Siddiqui[49] with 3-chlorobutene-1 and 1-chlorobut-2-ene models



$$\sim CH{=}CH-\underset{Cl}{CH}-CH_2-\underset{Cl}{CH}\sim \xrightarrow{Bu_2Sn\,Y_2} \sim\underset{Y}{CH}-CH{=}CH-CH_2-\underset{Cl}{CH}\sim$$

so that even if subsequent elimination of Y occurred it would not lead to allylic activation of the next Cl-atom on the chain.
The esteric carbonyl band followed in Fig. 4-4 and 4-6 has shifted at the beginning of processing from 1725 cm^{-1} to 1750 cm^{-1}. It is known[42] that the C=O frequency of unsaturated esters is lower (1715 cm^{-1}-1730 cm^{-1}) than that of saturated (1735 cm^{-1}-1750 cm^{-1}) and therefore the observed shift would be explained if the unsaturation was disrupted. Mufti and Poller[51] have shown that dibutyltin maleate undergoes a Diels-Alder reaction with cyclopentadiene. It may be that the maleate moiety of the stabilizer reacts with the conjugated unsaturation by reaction 2:

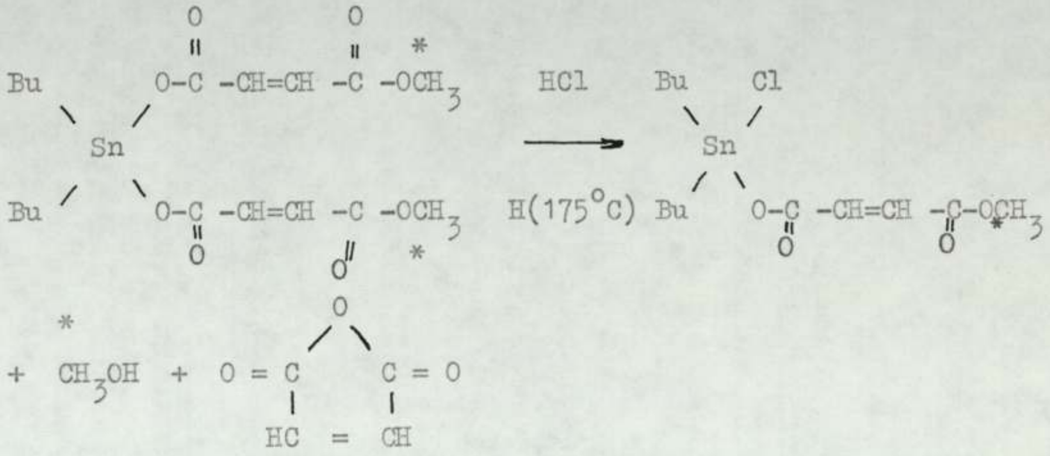


(2)

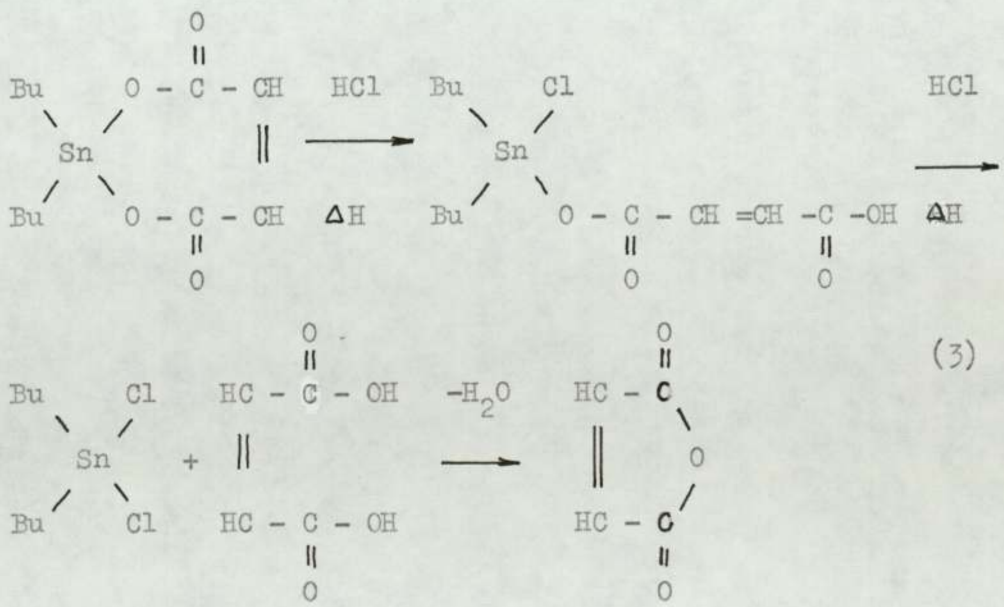
It is generally believed[53,19] that the species responsible for the colour in degraded PVC has the form of conjugated polyenes formed by the loss of hydrogen chloride from successive units in the polymer chain. A minimum of five to seven double bonds in conjugation are required for the material to be coloured[53]. It is also known[56] that PVC previously discoloured by heating in nitrogen is temporarily bleached on subsequent heating in air but eventually leads to more rapid discolouration. The bleaching effect is considered to be a result of a shorter polyene sequences formed by the oxidation.

The reaction 2 will prevent the formation of a longer conjugated polyenes and therefore will contribute to the inhibition of colour formation as it was shown in Fig. 4-2.

Frye, Horst and Paliobagis in their original work[48] observed relatively low retention of radioactivity in the polymer degraded with dibutyltin-bis (monomethyl-^{14}C maleate). They argued that this was possible if maleate had undergone thermal cleavage in the presence of HCl to form alcohol and anhydride:

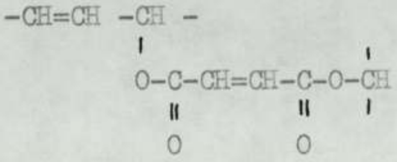


However, they did not show formation of anhydride. From Fig. 4-8 and 4-9 it may be concluded that anhydride is formed within the induction period. Also the formation of the Sn-Cl species is demonstrated in Fig.4-10a,b. The following reaction can explain these results and indicates probably the main function of the stabilizer as an HCl acceptor:



(3)

Fig. 4-1 shows the formation of a small amount of gel during the induction period. This gel phase contains esteric carbonyl at 1730 cm^{-1} (Fig.4-7) which increases and has a maximum between 5-8min for 210°C and 20min for 170°C. It may be that maleate moiety participates in the formation of this gel:



$$-\mathrm{CH{=}CH-\underset{\displaystyle |}{CH}}-\quad \mathrm{O-\underset{\displaystyle O}{\underset{\|}{C}}-CH{=}CH-\underset{\displaystyle O}{\underset{\|}{C}}-O-\overset{|}{\underset{|}{CH}}}$$

However, the formation of an absorption band at 3450 cm^{-1} (Fig. 4-7a) is not so readily explainable. Possible deactivation of hydroperoxide by the stabilizer, as it was suggested by Frye and co-workers[48] would yield alcoholic hydroxyl,

but also would shift the esteric carbonyl to higher frequency which was not observed during the induction period. The OH-stretching of an alkyl hydroperoxides is in the region of 3360 cm^{-1} - 3450 cm^{-1} [57] but the chemical analysis did not show the presence of peroxide during the induction period (see Fig. 4-13). A possible alternative explanation that the broad hydroxyl band centred at 3360 cm^{-1} in the insoluble part of the original polymer (see Fig. 3-8, chapter 3) contributes to the hydroxyl absorption of the gel phase may be plausible.

The presence of an induction period was shown by the torque measurement, in the absence of significant crosslinking and by the IR-spectroscopy results and is further shown by the unsaturation measurement in Fig. 4-11a,b and 4-12. It should be noted that during the induction period the solution phase represents 97-99.5% of the total sample. The organotin stabilizer significantly prevents the formation of unsaturation. The small amount of unsaturation observed might be the result of insufficient dispersion of the stabilizer especially during the fusion period. A similar view was expressed by Gale[52] who found that the fusion rate decreased with increasing concentration of lubricant and therefore polymer particles were not effectively stabilized during the fusion by a solid lead stabilizer.

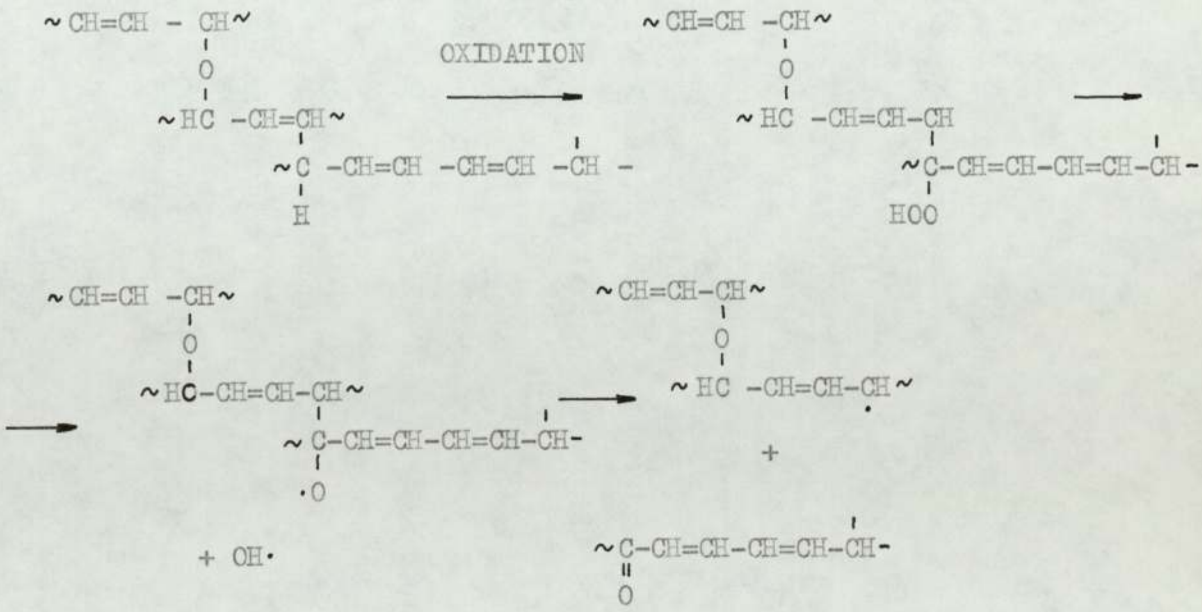
After the induction period the absorbance of the UV-absorption bands of the soluble phase increased. The concentration of the crosslinked phase also increased especially at 210°C (Fig.4-1) and therefore increased UV-absorbance results from progressively smaller proportions of the total sample being examined (from 98% at 10min to 31.8% at 25min for 210°C but there is only negligible degrease from 98.8% to 91.9% for 170°C). MWD on Fig. 4-14b is shifted after 10min to lower mol. weight region indicating a chain scission. This chain scission reaction increases the amount of lower mol. weight species readily soluble in CH_2Cl_2 and that is why UV-absorbance increases in Fig. 4-11b. For 170°C the concentration of crosslinked phase increased only marginally after 20min by 6.9% and therefore there is no significant increase in absorbance (Fig. 4-11a) and only crosslinking or chain extension occurred (Fig. 4-14a). Previous studies have shown that chain scission occurred when PVC was degraded in oxygen and both crosslinking and chain scission were observed when PVC was degraded in air[34].

Alkoxy radicals formed by decomposition of hydroperoxide undergo chain scission reactions which are responsible for the reduction of mol. weight[30].

Fig. 4-13 shows that peroxide concentration increased to a maximum at 20min for 210°C but for 170°C there was a small increase only after 25min.

From these results it may be concluded that at higher temperature oxidative chain scission takes place parallel to the crosslinking reaction. It is known[54] that the breakdown of alkoxy radicals is temperature dependent and that carbon-carbon bond scission becomes more important at higher temperatures. Therefore at lower temperature crosslinking or chain extension predominates (see Fig. 4-14a). Radicals formed by the decomposition of peroxide followed by chain scission and addition reactions of alkoxy radicals increase dehydrochlorination and crosslinking.

Chain scission in the gel phase can be accounted for by the oxidative attack on tertiary hydrogen in the allylic position of the crosslinked phase:



It can also be accounted for by the breakdown of peroxy-cross-link~~ed~~s which may be present in the crosslinked phase. This reaction was shown to occur during the degradation of high impact polystyrene[58].

It should be pointed out that no peroxide was detected during the induction period in stabilized PVC (Fig.4-13). If the degradation proceeds by a radical chain mechanism the stabilizer, if it disrupts radical chain processes, ~~it~~ should react with the radicals formed by the decomposition of hydroperoxide. Winkler[33] has shown that the induced decomposition of tert.-butylhydroperoxide by cobalt octoate was effectively retarded by dibutyltin dilaurate which is good stabilizer for PVC. On the other hand Ayrey, Poller and Siddiqui[55] have found that neither the presence of free radical acceptor (diphenyl disulphide) nor an inhibitor (2, 5-di-t-butylhydroquinone) had any effect on the rate of reactions between organotin-carboxylates with 3-chloro-but-1-ene and t-butylchloride. They concluded that the replacement of reactive allylic chlorine atom did not involve radicals. However, they observed that some of the most effective organotin stabilizers have some activity towards the free radicals in methylmethacrylate polymerizations.

It is probably important to differentiate two modes of stabilization[55]. The first involves reaction of the stabilizer with PVC to produce a more stable polymer (e.g. ester exchange with allylic chlorine as shown on Fig. 4-4,5,6) and the second where the stabilizer interferes with the degradation process and causes inhibition or retardation (HCl acceptor, reaction 3, disruption of conjugation by Diels-Alder reaction, reaction 2).

It is also possible that the stabilizer deactivates the hydroperoxide (the possible presence of the phenolic antioxidant, as it was mentioned in the section 4.1.1.3., suggests the importance of this function of the thermal stabilizer) but it is equally possible that if no allylic groups are formed, no hydroperoxide will be formed either.

4-1.3. Conclusions

Dibutyltin maleate during processing with PVC in the torque rheometer prevents increase of the equilibrium torque for 10min at 210°C and 20-25min at 170°C. During this induction period crosslinking is prevented together with discoloration.

The formation of male~~ate~~ic anhydride and dibutyltinchloride demonstrates the main function of the stabilizer to be an acceptor of hydrogen chloride. The stabilizer also reacts with labile chlorine atom (probably allylic) with formation of a more stable ester. The formation of conjugated unsaturation is minimized by the Diels-Alder reaction of the stabilizer's maleate moiety. The hydroperoxide was not detected during the induction period probably because no allylic positions are formed.

After the induction period peroxide is formed, unsaturation increases because of HCl evolution and the polymer becomes coloured as a result of the presence of conjugated unsaturation.

At 210°C rapid crosslinking occurs. Part of the crosslinked polymer is oxidized with formation of peroxide and subsequent chain scission occurs parallely with crosslinking. At 170°C crosslinking or chain extension predominates.

IR-spectroscopy results strongly support Frye and Horst's esterification theory of stabilization of PVC by organotin stabilizers.

Torque and the gel content vs time of PVC processed with 2.5phr of Irgastab T290 at 170°C and 210°C.

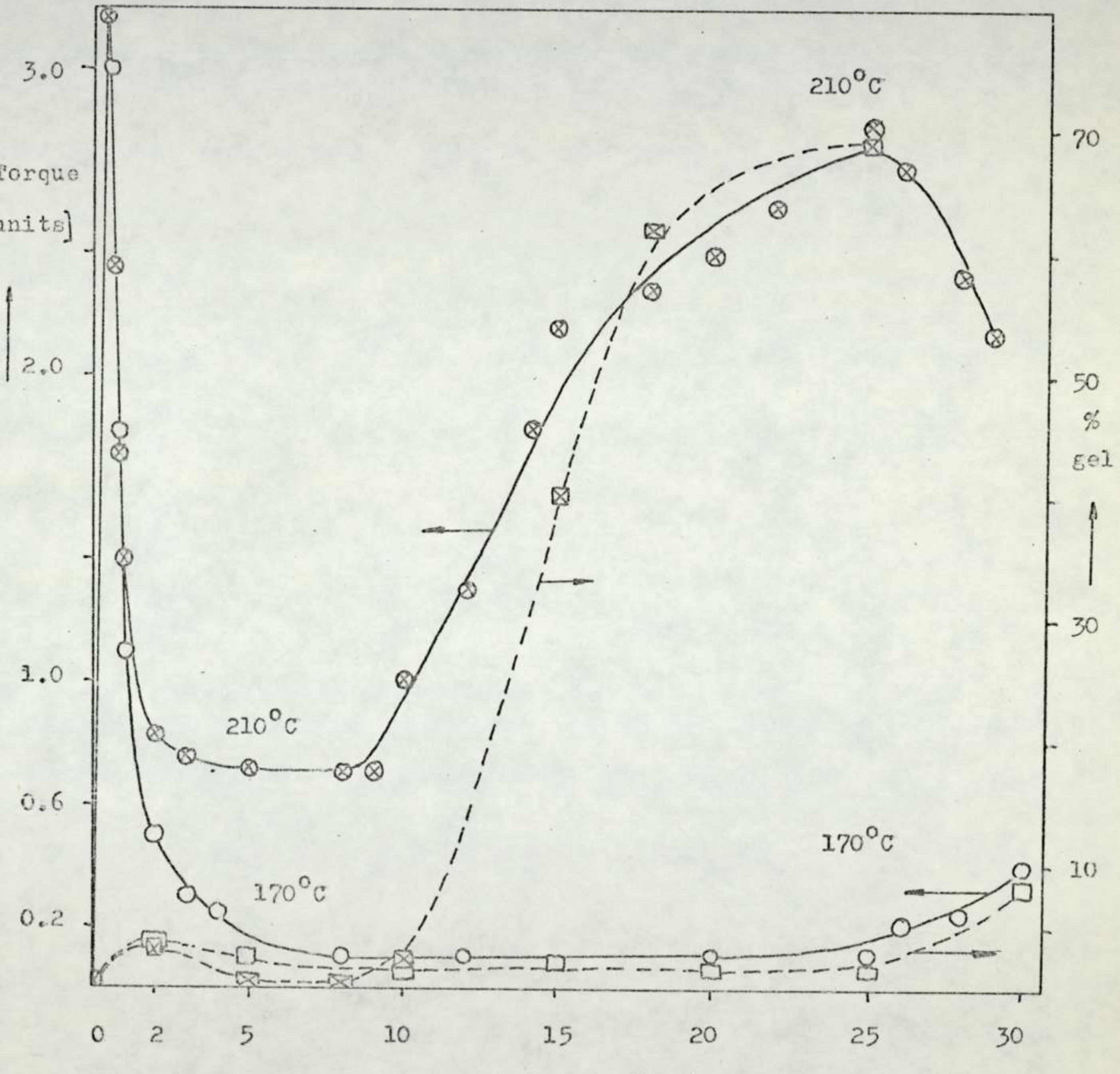


Fig. 4-1

Colour change during processing of PVC with Irgastab T290 at 210°C and 170°C

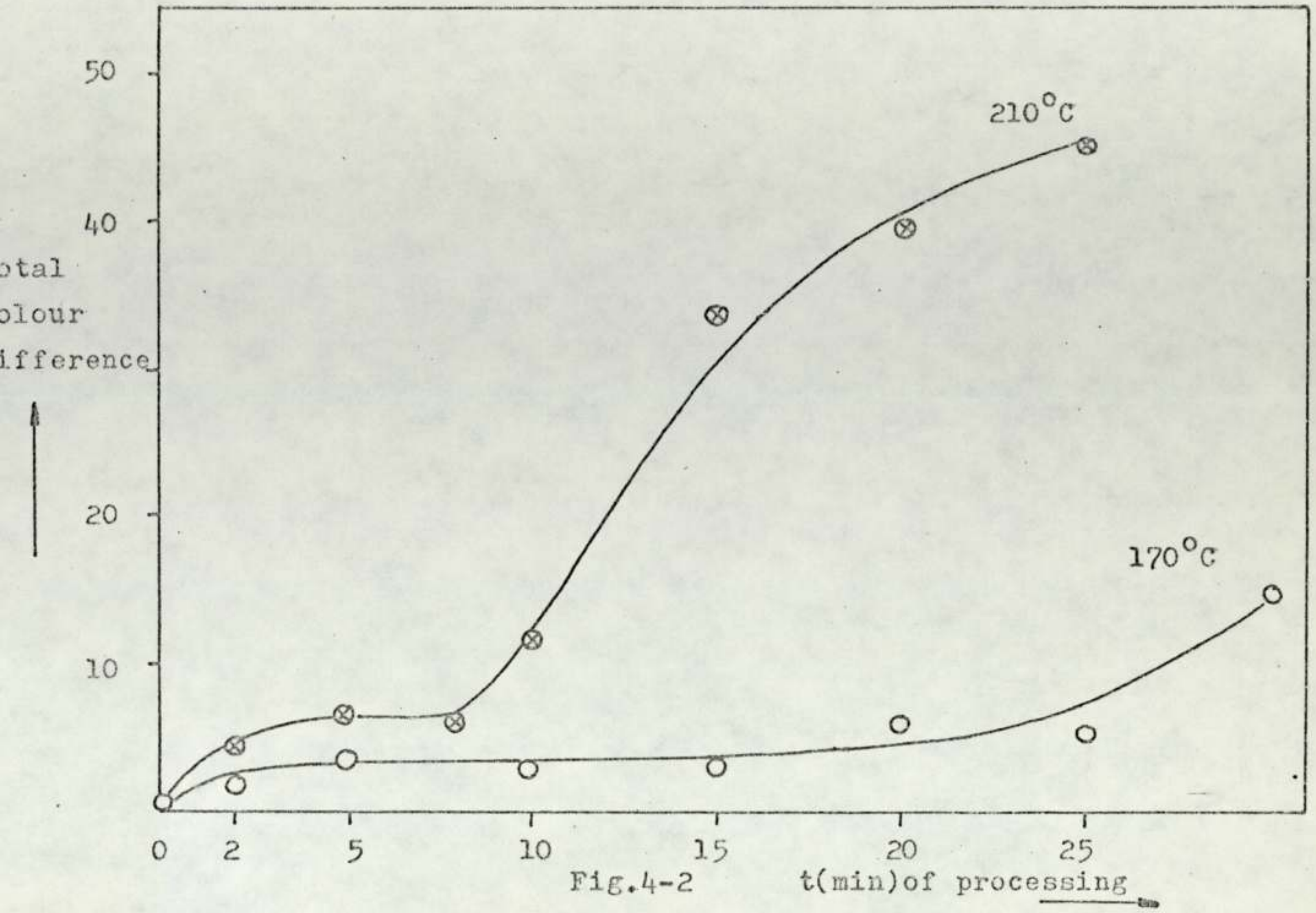


Fig.4-2

PVC processed with Irgastab T290 at 210°C.
The growth of the absorption peak at 1725-45cm^{-1}
with processing time

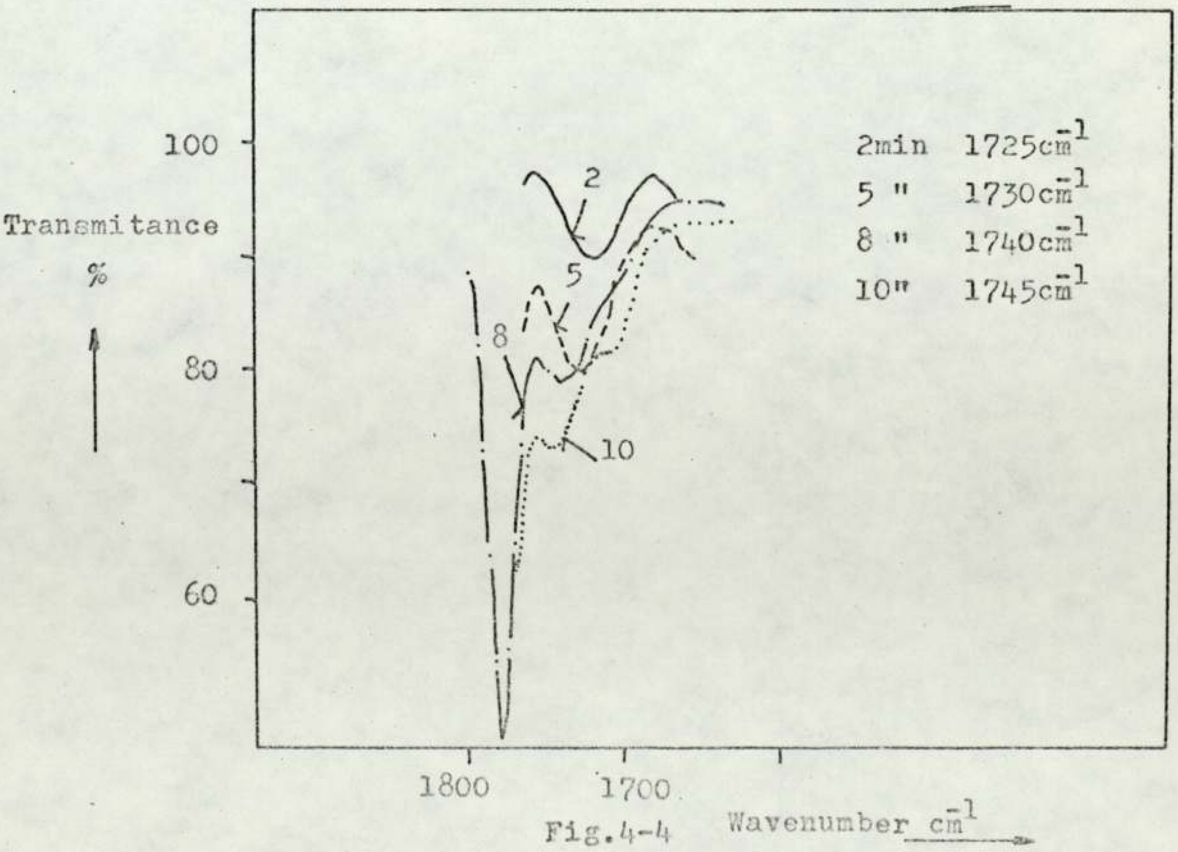


Fig.4-4

IR-spectra of PVC processed with Irgastab T290 for different processing times at 210°C.

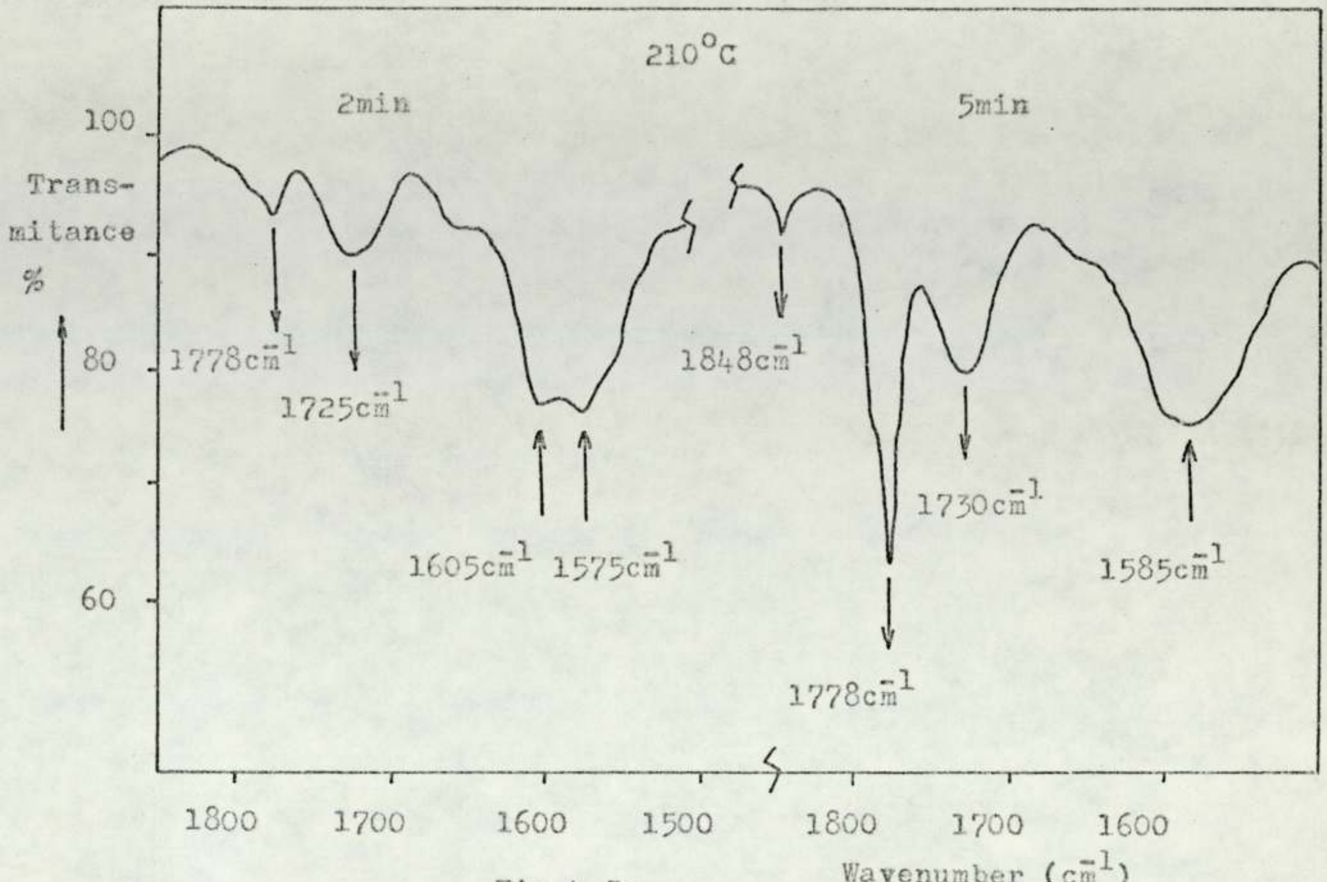


Fig.4-3a

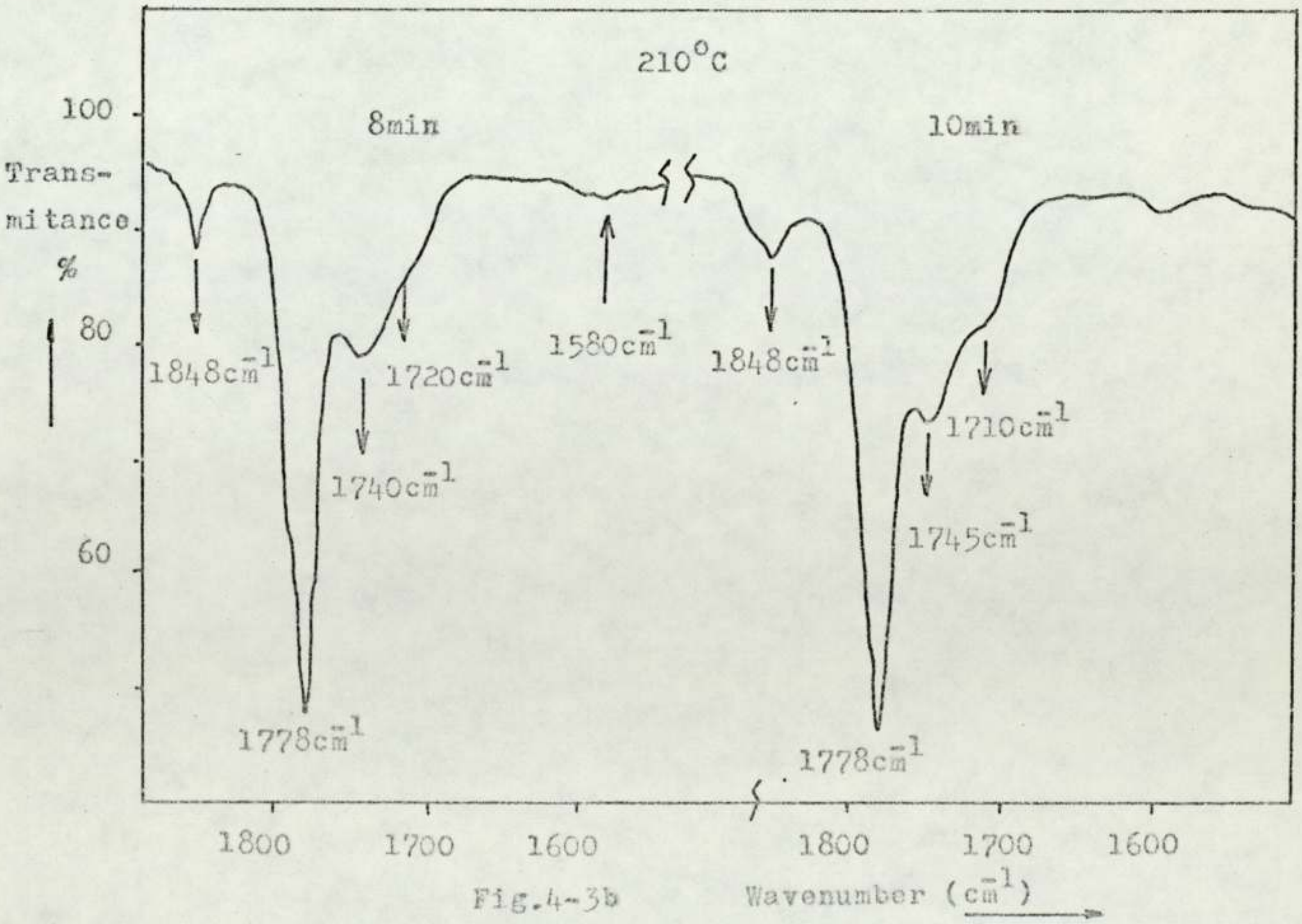


Fig.4-3b

Carboxylate index I_{COO} 1575cm^{-1}-1585cm^{-1} of PVC processed with Irgastab T290 at 170°C and 210°C.

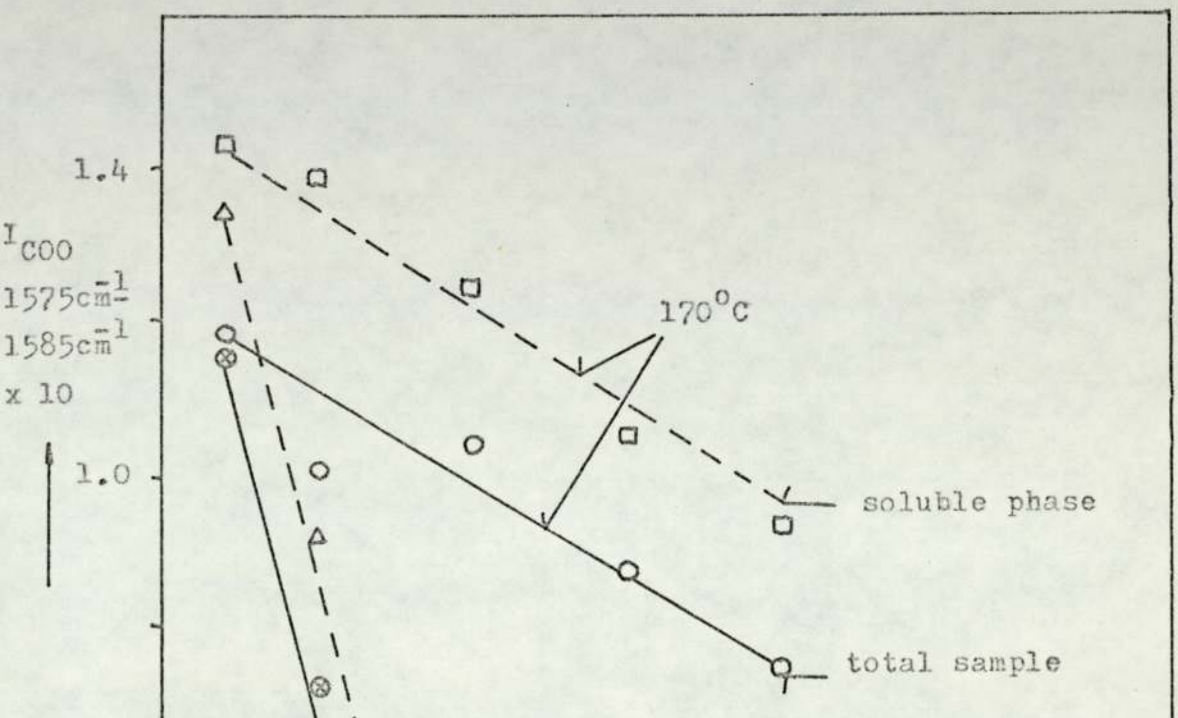


Fig.4-5

Carbonyl index I_{CO} 1725cm^{-1}-1750cm^{-1} of PVC processed with Irgastab T290, total sample and soluble phase.

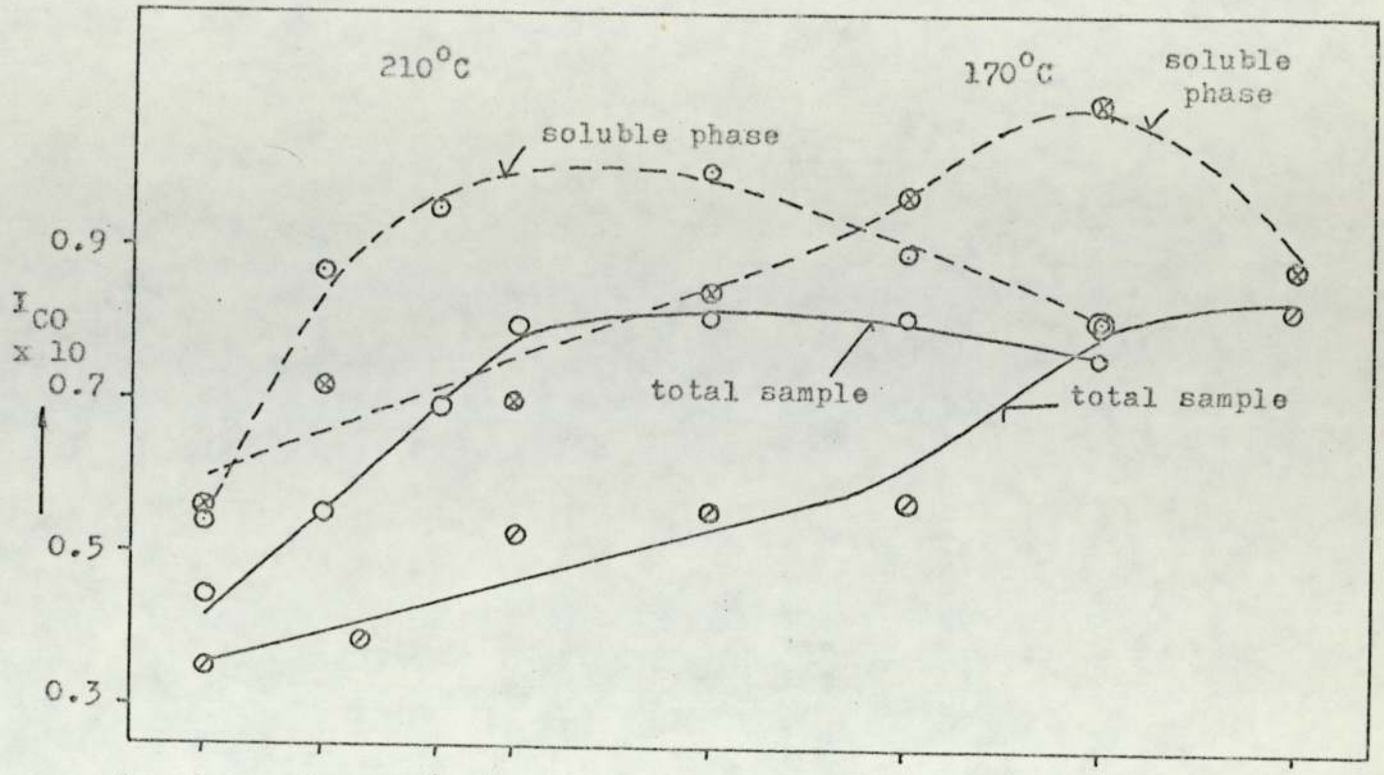


Fig.4-6

Carbonyl index I_{CO} 1730cm^{-1} of PVC processed with Irgastab T290, gel phase.

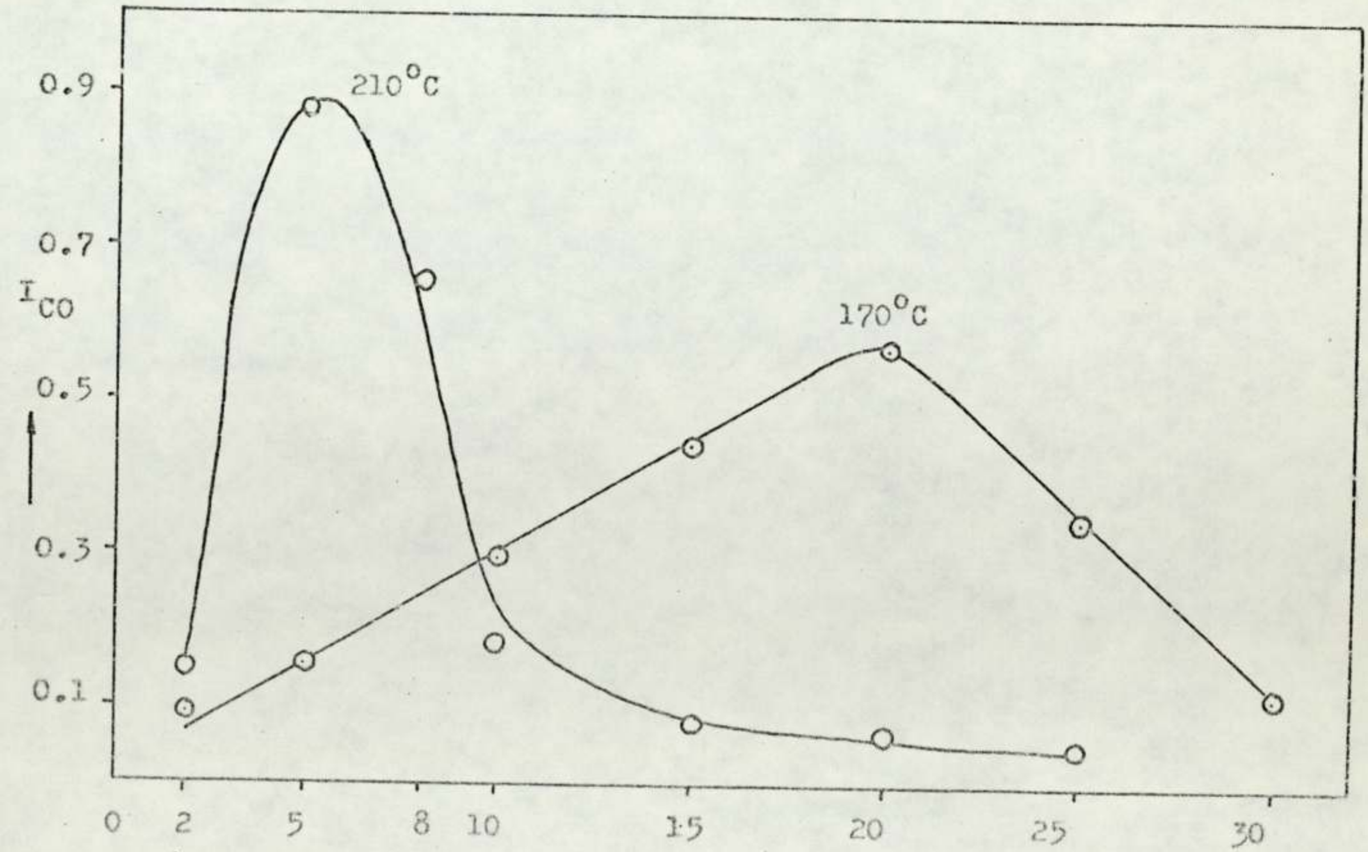


Fig.4-7

Hydroxyl index I_{OH} $3450cm^{-1}$ of PVC processed with Irgastab T290 at 170°C and 210°C, gel phase.

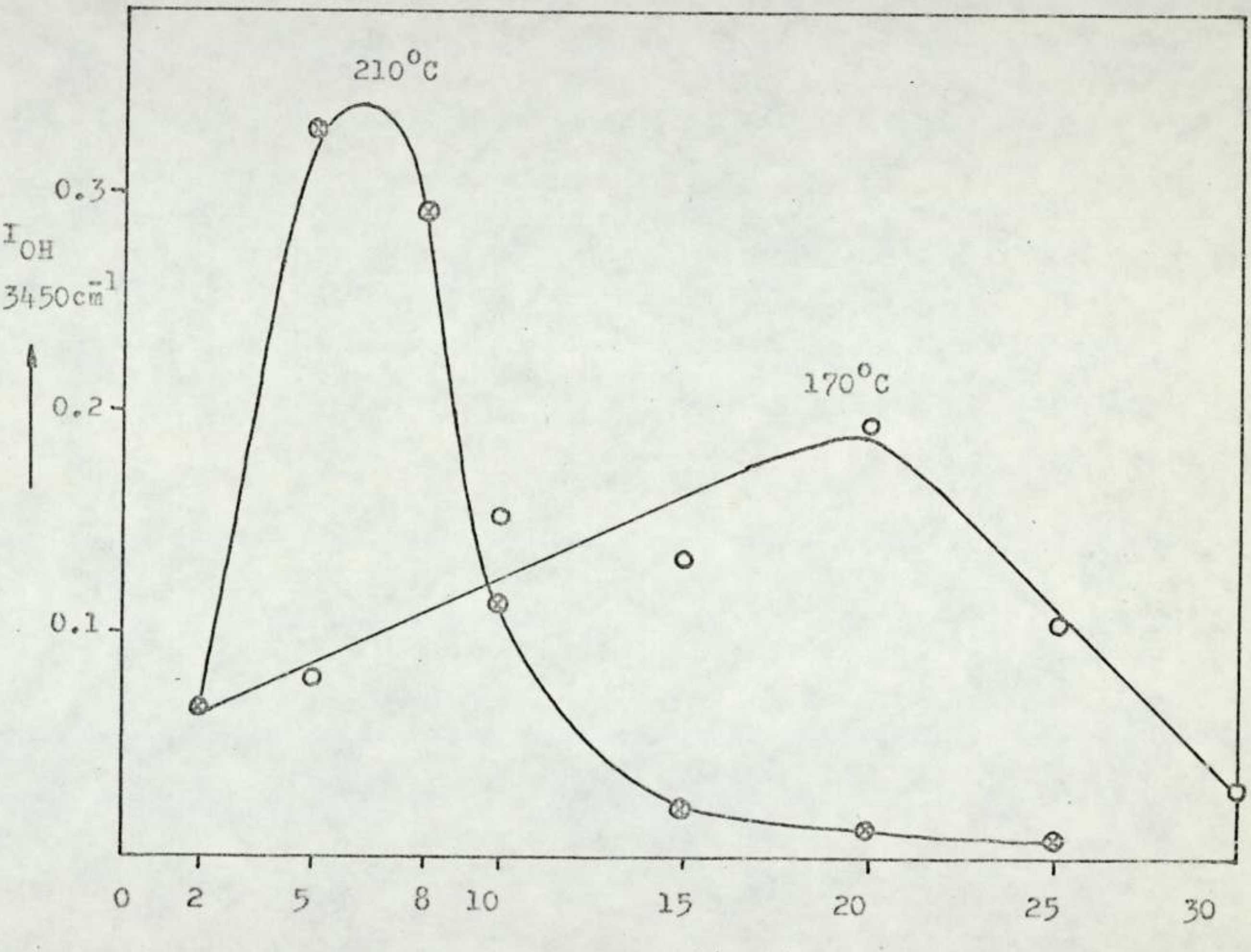


Fig.4-7a

Carbonyl index I_{CO} 1778cm^{-1} of PVC processed with Irgastab T290 at 170°C and 210°C.

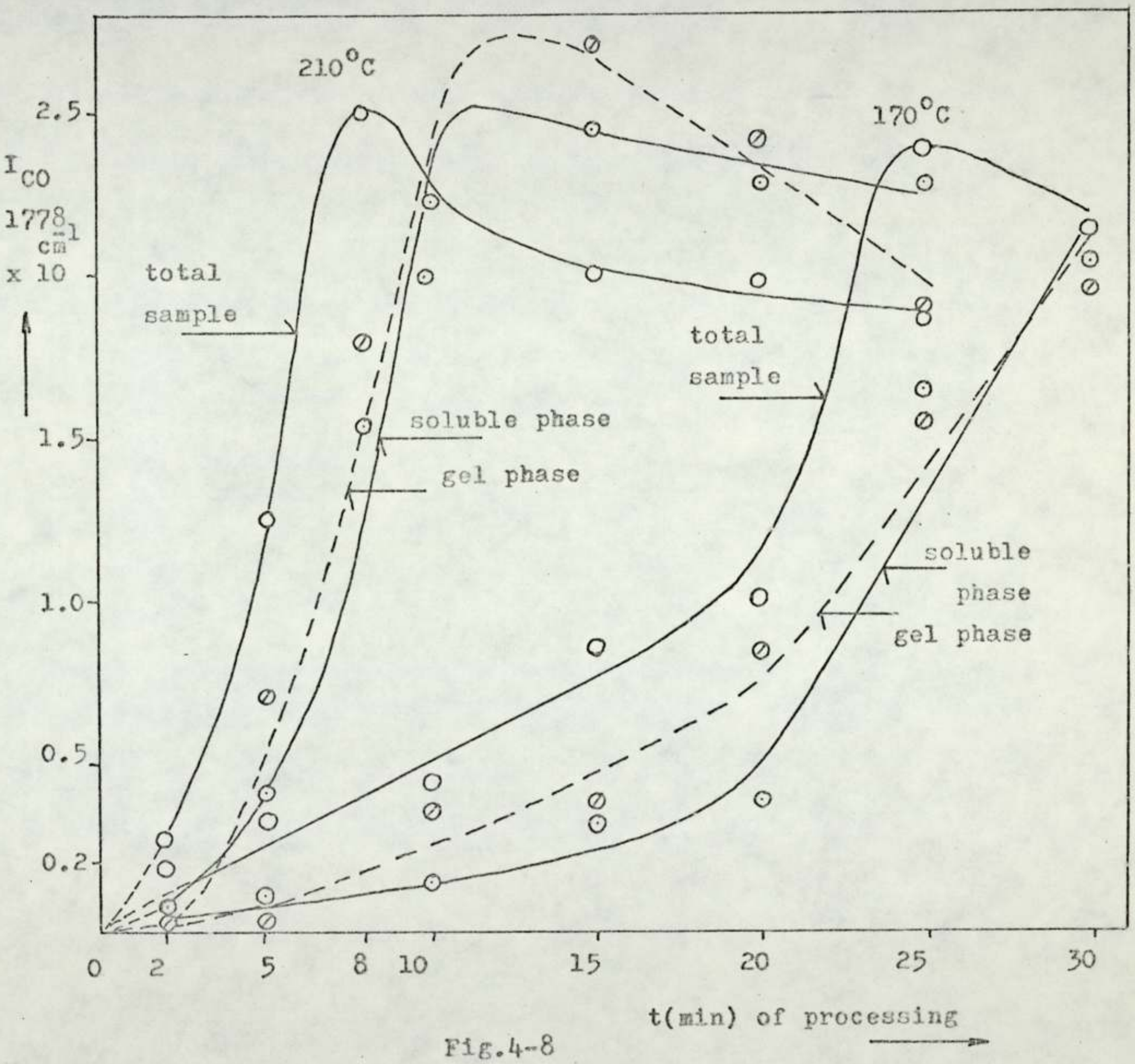


Fig.4-8

IR-spectra of PVC processed with Irgastab T290 for 8min at 210°C measured before and after the treatment with distilled water.

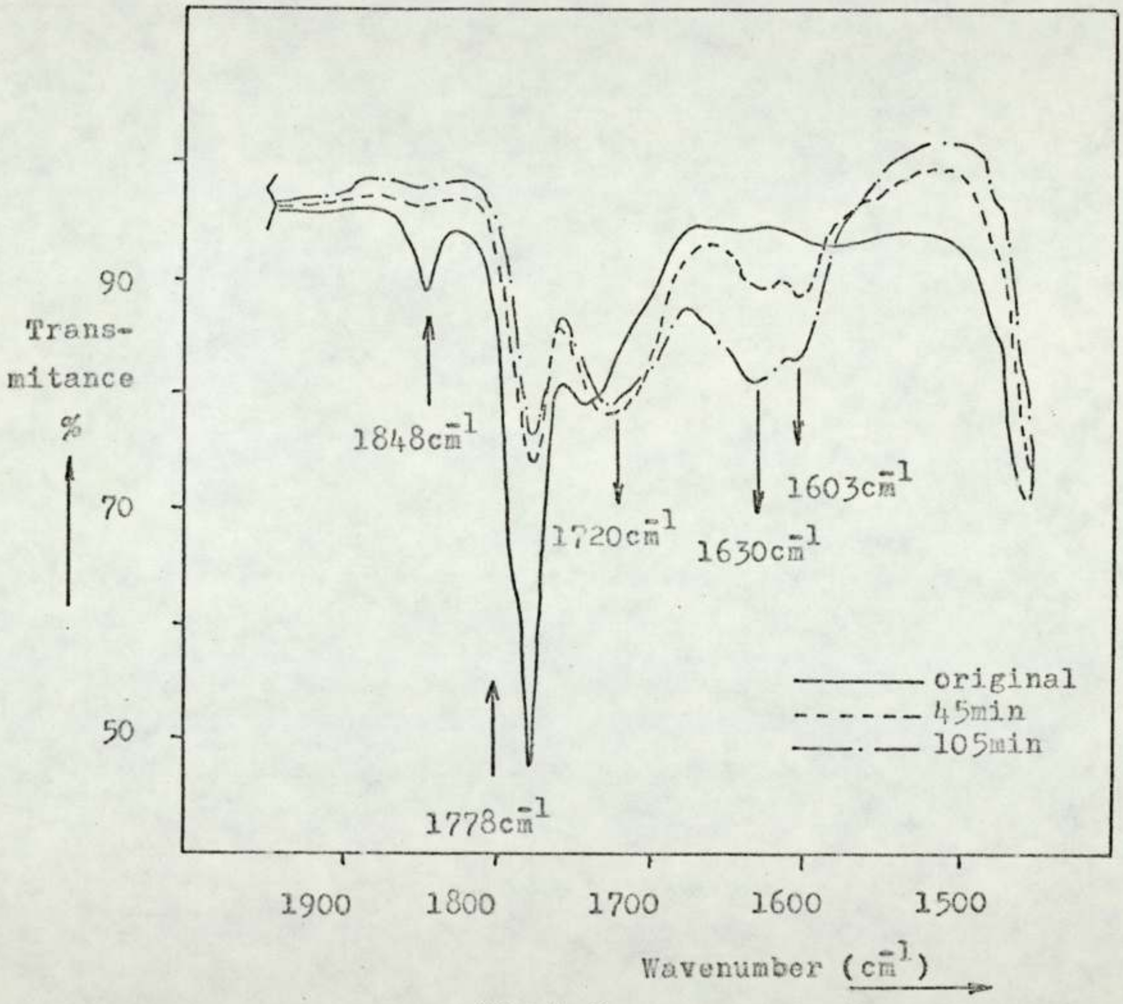


Fig.4-9

IR-spectra of PVC processed with Irgastab T290 at 210°C and 170°C. Formation of Sn-Cl absorption at 342cm^{-1}.

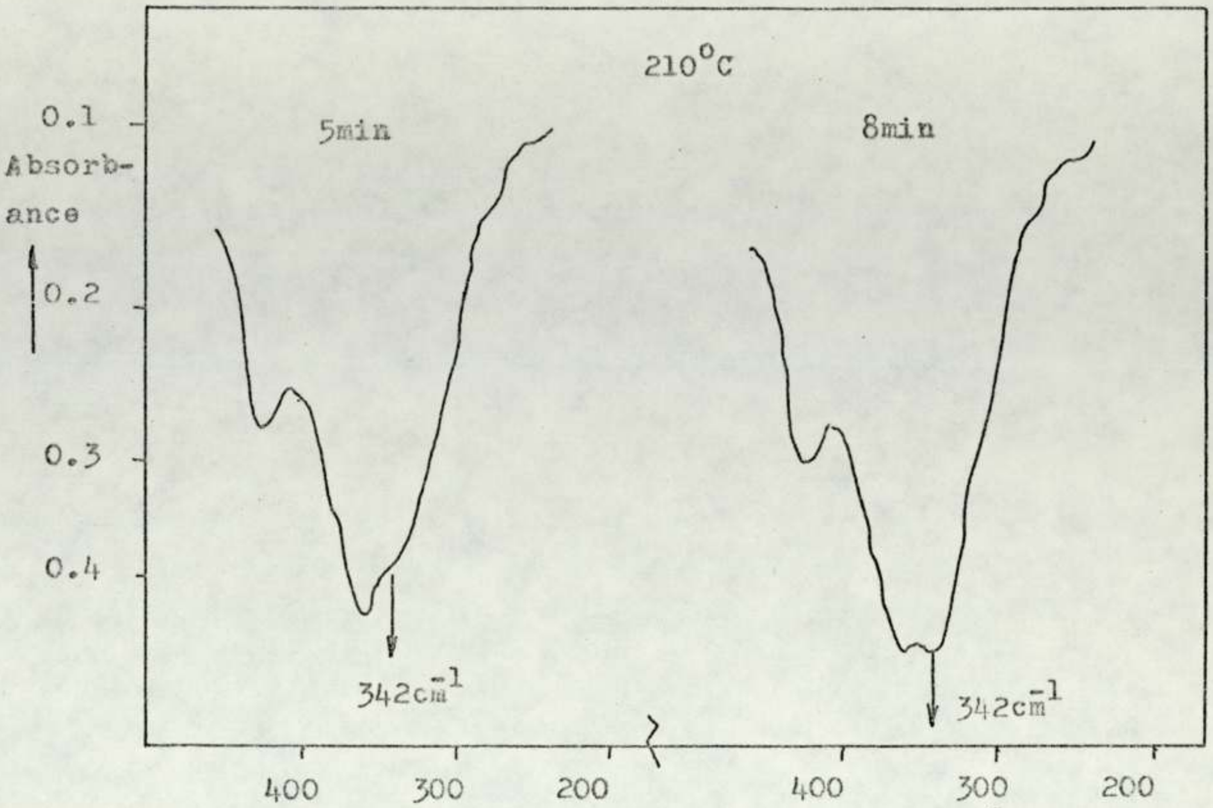


Fig.4-10a

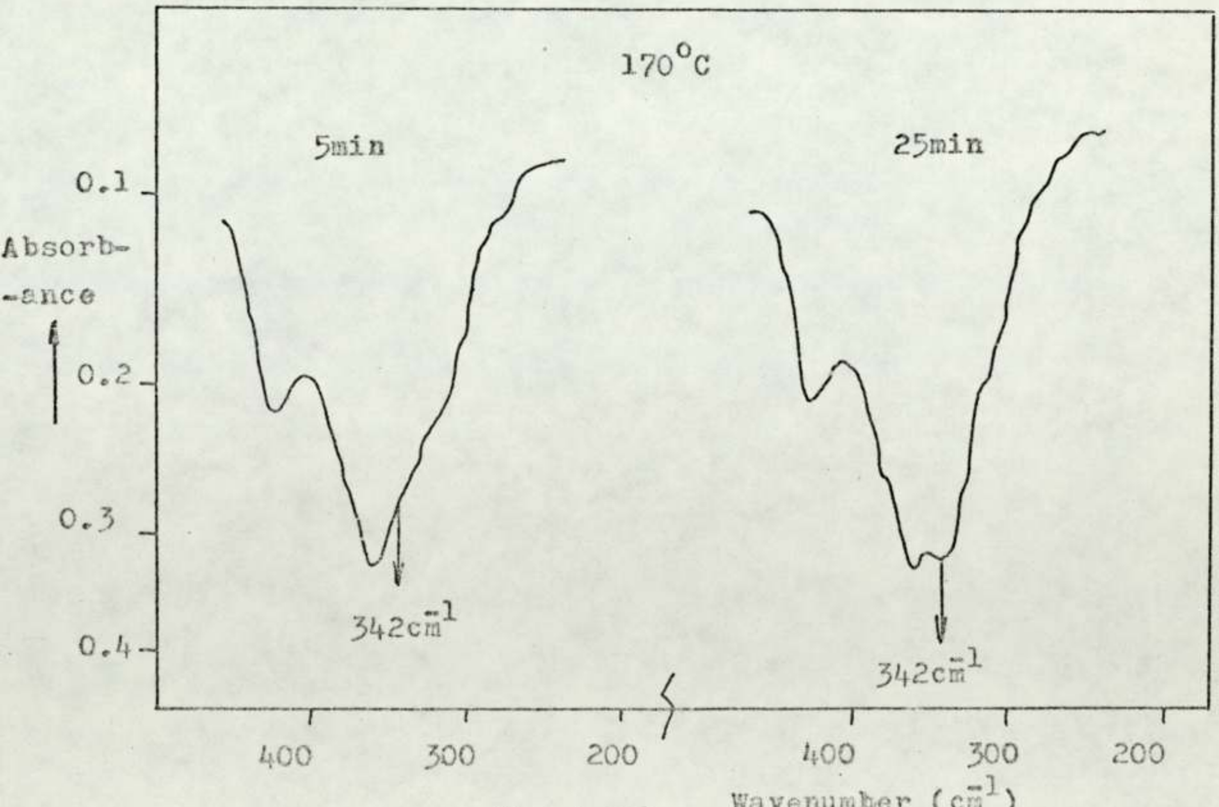


Fig.4-10b

UV-absorbance vs time of PVC processed with Irgastab T290.

Soluble phase, 0.6 % solution in CH_2Cl_2, 1mm cell used.

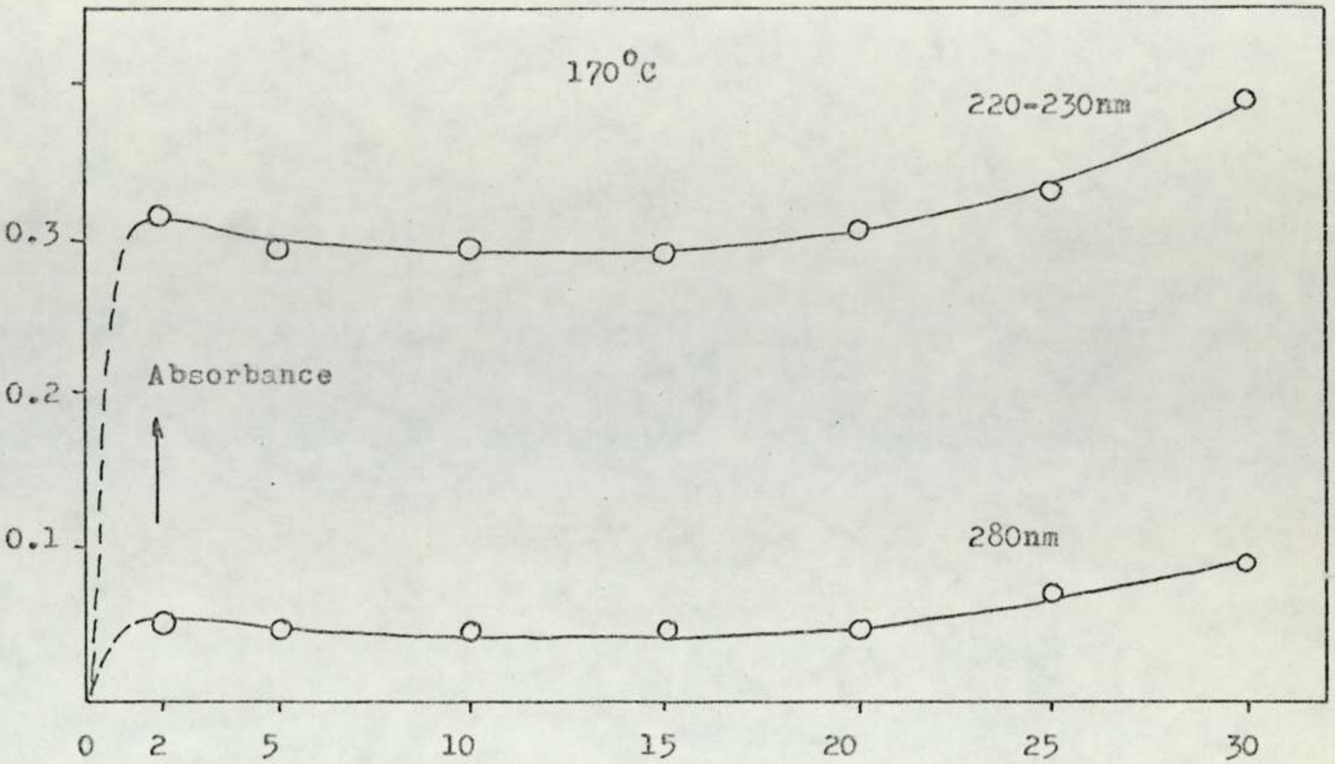


Fig.4-11a

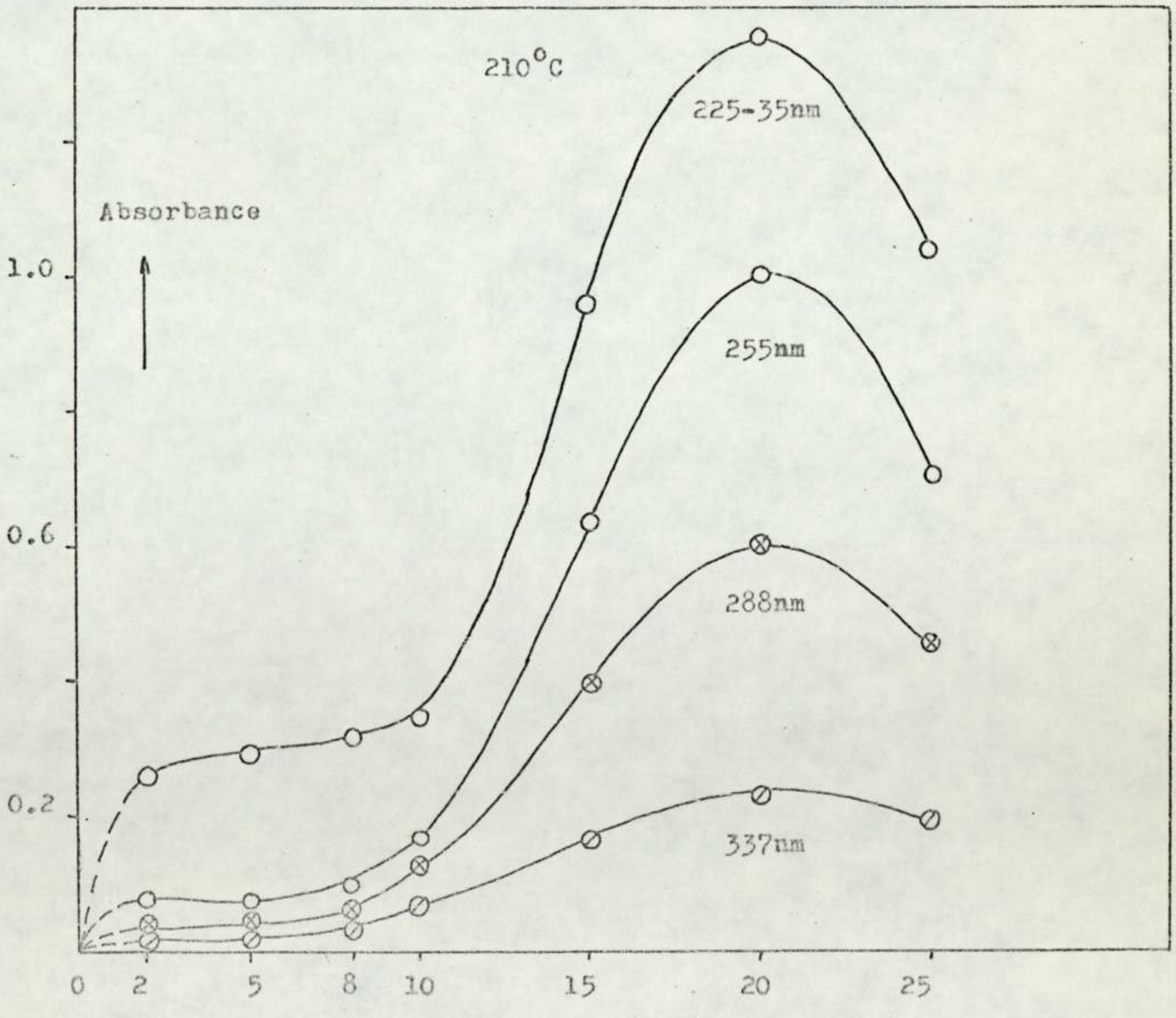


Fig.4-11b

Peroxide content vs time. PVC processed with Irgastab T290 at 170°C and 210°C.

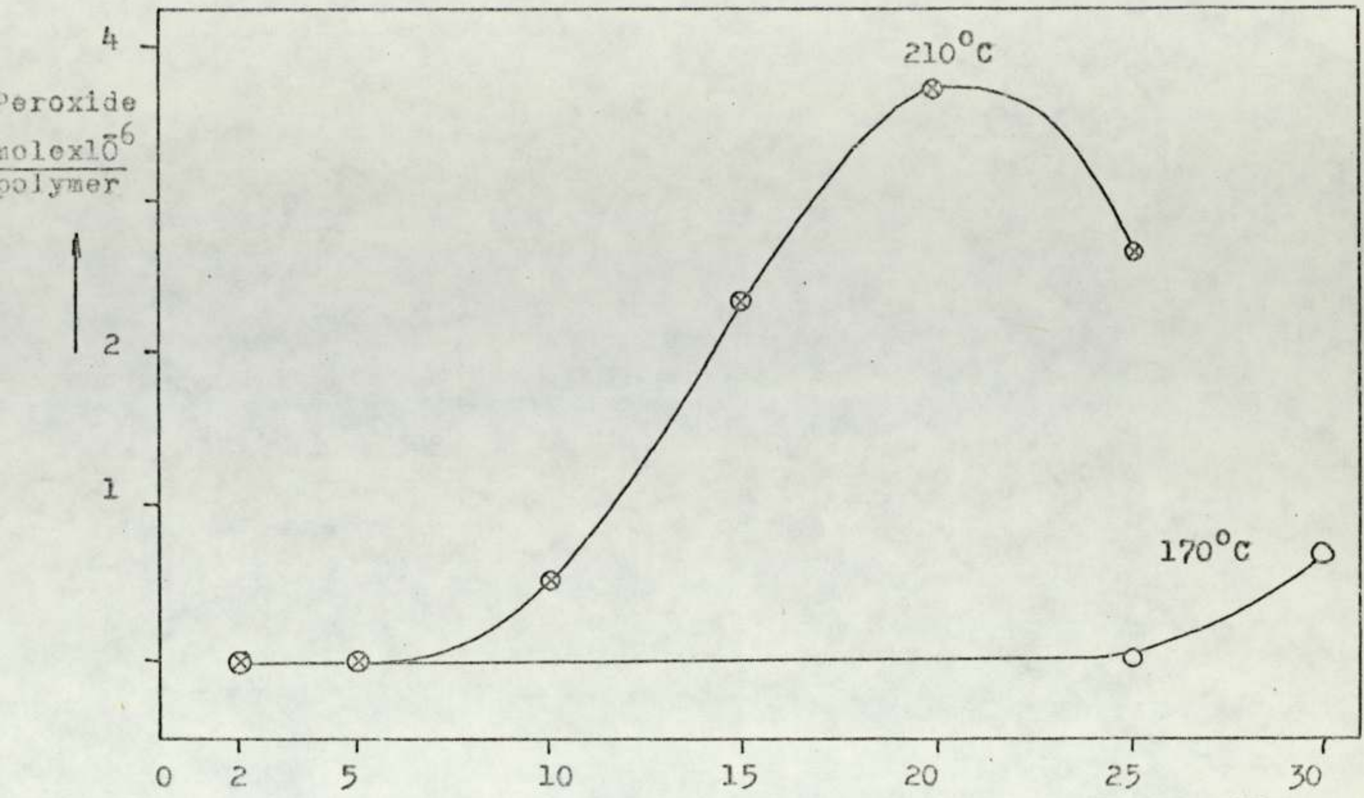


Fig.4-13

Unsaturation vs time. PVC processed with Irgastab T290 at 170°C and 210°C.

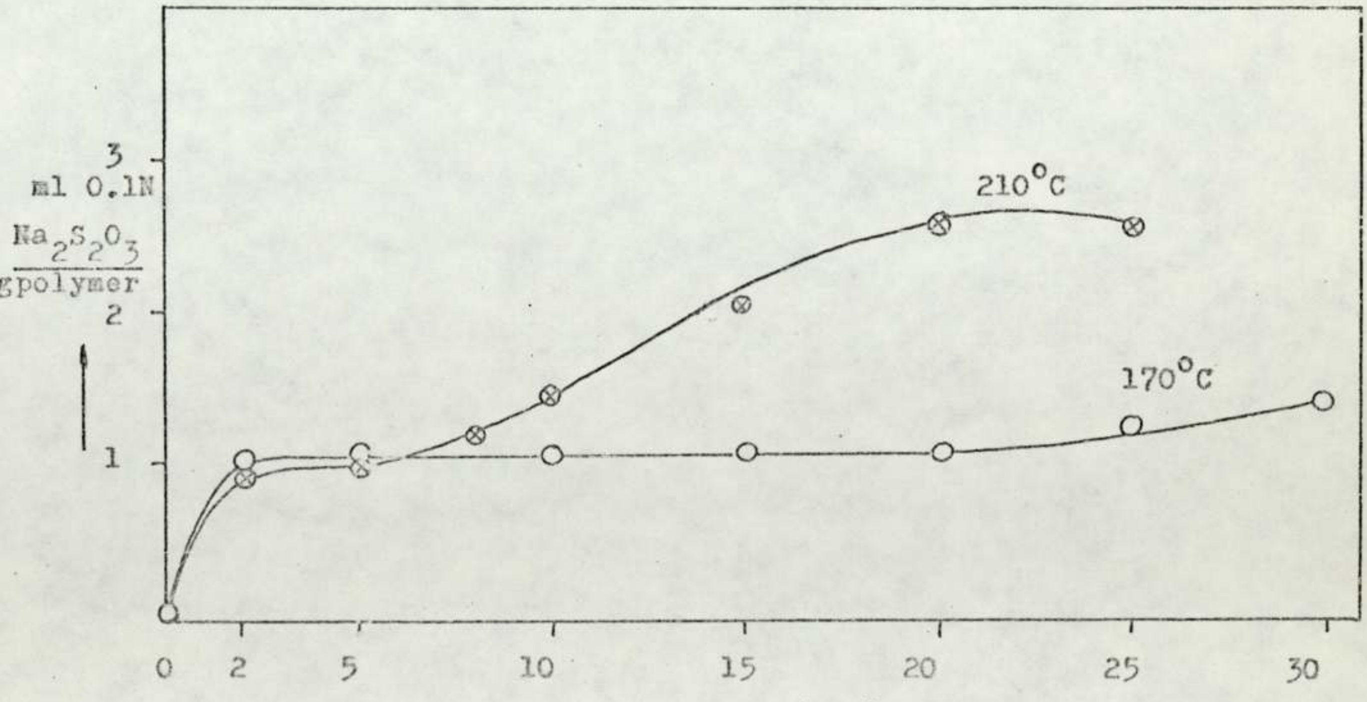


Fig.4-12

Molecular weight distribution of PVC processed with Irgastab T290 at 170°C. Soluble phase in CH_2Cl_2.

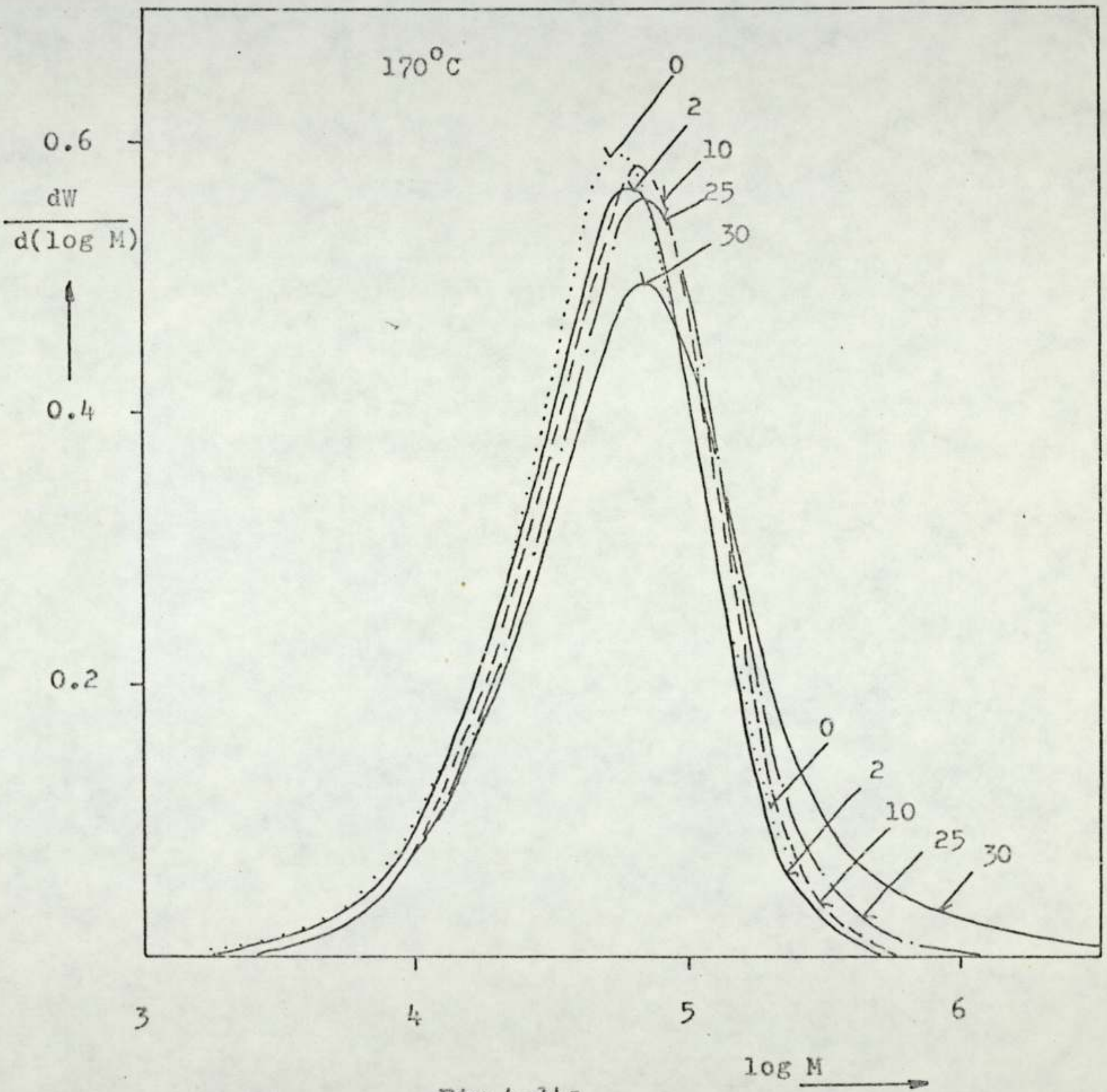


Fig.4-14a

Molecular weight distribution of PVC processed with Irgastab T290 at 210°C. Soluble phase in CH_2Cl_2.

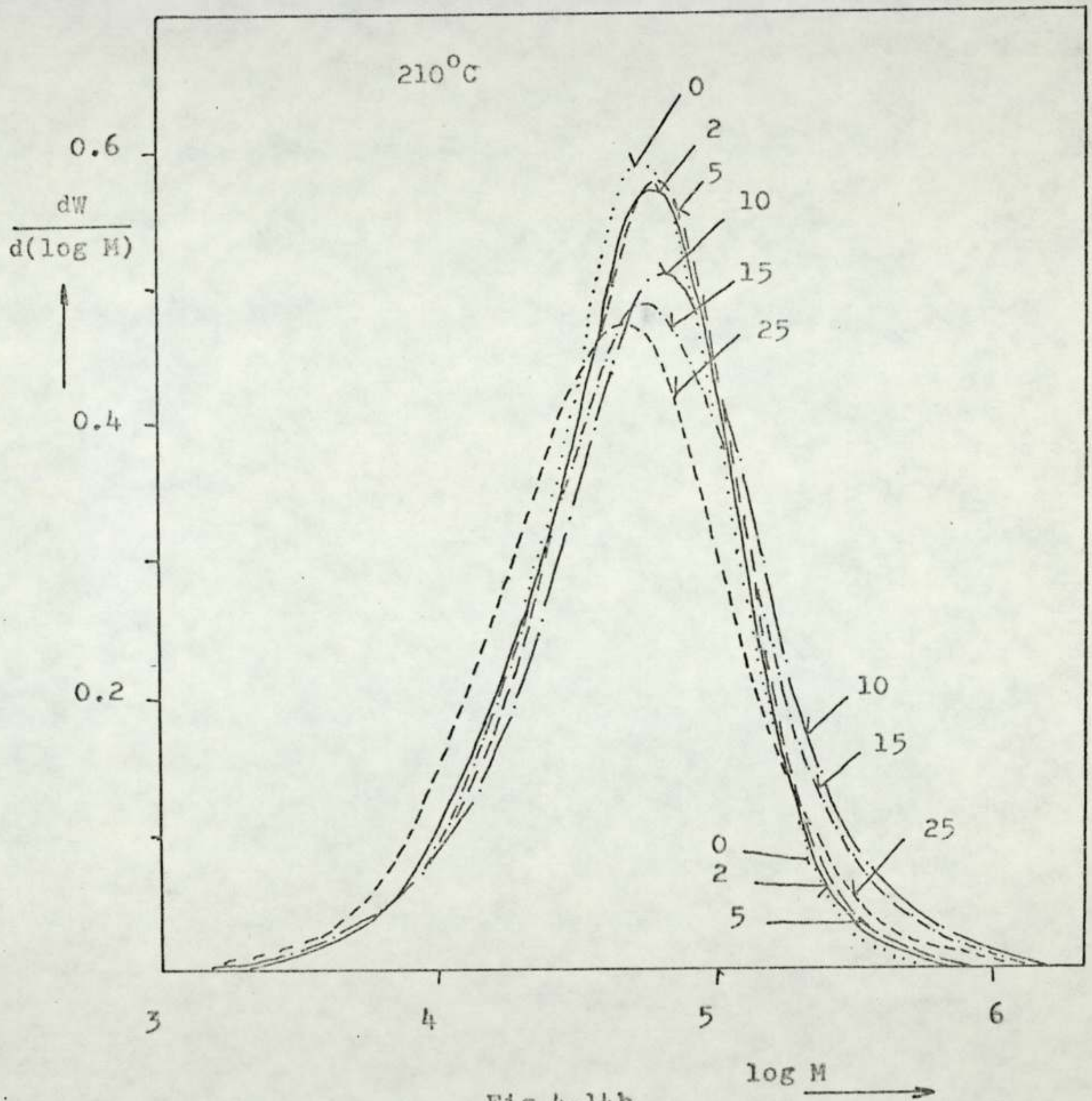


Fig.4-14b

4-2. Processing of PVC with Ca-stearate.

Ca-stearate is extensively used in formulations for rigid PVC extrusions. It is normally considered to have lubricating properties[59], but it has been demonstrated that its influence is not initially that of a lubricant; an increase of Ca-stearate concentration at constant levels of stearic acid increased the apparent melt viscosity and decreased the shear rate and volumetric flow rate.

Because of its use in the formulation in this work, it was of interest to examine its role during processing. The experimental methods used were the measurement of torque, gel content, IR and UV spectroscopy, colour change measurement, molecular weight determination as described earlier (chapter 2) and also unsaturation and peroxide content (chapter 3, section 3.1.1. and 3.1.2.).

4-2.1. Results

4-2.1.1. Torque changes and gel formation.

The torque vs processing time for 210°C and 170°C is illustrated in Fig. 4-15. The gel formed during processing is also plotted on the same graph. After the initial increase of the torque the polymer underwent gelation and the torque decreased. At the lower temperature the torque was higher in the initial period than for the higher temperature, but it continued to decrease and reached a minimum at 10min after which it again started to increase indicating the onset of the crosslinking reaction. A small amount of gel was formed initially (1.7% - 6.5%) and this also increased more rapidly at the end of the induction period. It should be noted that the gel content in the unstabilized polymer (see chapter 3, Fig. 3-2) at 20min was 21.1% and here with Ca-stearate it was 25.7% at 20min. It is apparent that at lower temperature there was an induction period of 5-10min for gel formation and also during this period the torque decreased and reached a minimum.

For 210°C the torque had already reached a minimum at 2min and started to increase rapidly after 3-4min. A small amount of gel formation (4-5%) is also evident up to 5min after which time the gel content rapidly increased and reached 88.9% at 22min. It is interesting to note that for the unstabilized polymer 89% of the gel was formed at 20min as compared with 61.8% for the polymer processed with dibutyltin maleate (viz chapter 3 and chapter 4, part 1).

4-2.1.2. IR-spectroscopy results.

IR-spectra obtained with compression moulded films contained two absorption peaks located at 1535 cm^{-1}-40 cm^{-1} and 1570 cm^{-1}. These peaks were present in the spectra of the polymer processed for a short time and with further processing they disappeared. This is illustrated in Fig. 4-16 for 170°C and in Fig.4-17 for 210°C, respectively. For 170°C these absorption peaks disappeared between 5-10min and for 210°C between 2-5min of processing. The carboxylate ion gives rise to a strong asymmetrical stretching band near 1650 cm^{-1}-1550 cm^{-1} [42]. The 1535 cm^{-1}-1575 cm^{-1} double peak was not present in the polymer with no additives and therefore this absorption is considered to be due to the carboxylate anion of Ca-stearate. The disappearance of the carboxylate absorption during processing is similar to the disappearance of the carboxylate absorption band of dibutyltin maleate which was shown in the previous section (see Fig.4-3a,b).

In the carbonyl region two absorption peaks centred at 1705 cm^{-1} and 1740 cm^{-1} were formed. This can also be seen in Fig. 4-16 and 4-17. The peak at 1705 cm^{-1}, plotted as an index $I_{1705\ cm^{-1}}$ vs processing time is shown in Fig. 4-18. For 170°C the index increased and reached the maximum between 5-10min and for 210°C between 2-3min. The asymmetrical C=0 stretching mode of aliphatic acids gives an absorption in the region of 1720 cm^{-1} - 1706 cm^{-1} [42]. The absorption peak at 1705 cm^{-1} can therefore be assigned to carboxylic acid. The observed absorption peak at 1740 cm^{-1} is plotted as an index $I_{1740\ cm^{-1}}$ in Fig. 4-19. Here again the index increased up to 10min for lower temperature and for higher temperature reached a similar value already at 2min and remained constant with further processing. The C=0 stretching vibration of saturated aliphatic ester is in the region 1750 cm^{-1} - 1735 cm^{-1} [42] and the observed peak at 1740cm^{-1} is therefore attributed to an esteric carbonyl. The absorption at 1735 cm^{-1} has been previously observed after the heat treatment of PVC containing metal carboxylates[43,60] and also in alkali-treated PVC[61].

The IR-spectra of the total samples (pressed films) and also of the gel phase exhibited a broad absorption band centred at 3460 cm^{-1}. This band is plotted as an index in Fig. 4-20 for the total sample and in Fig. 4-21 for the gel phase, respectively. Both plots exhibit maxima and it may be noted that maxima were also observed for the 3450 cm^{-1} absorption in the gel phase which was previously discussed in the section 4-1 (see Fig. 4-7a).

Non-bonded OH-stretching of alcohols and phenols appears at 3650 cm^{-1} - 3584 cm^{-1} and intermolecular H-bonding shifts the frequency to 3550 cm^{-1} -3200 cm^{-1} region[42]. Also if the hydroxyl group is situated adjacent to a proton acceptor group (e.g. heteroatom X or a double bond) intramolecular bonding can occur and a shift of the absorption to longer wavelength 3600 cm^{-1} - 3450 cm^{-1} is observed[42]. Acidic hydroxyl absorbs in the 3300 cm^{-1}-2500 cm^{-1} region and therefore it would appear that observed hydroxyl band is not of an acid. The OH-stretching vibration frequency of cumene hydroperoxide is known[57] to be at 3450 cm^{-1} and of a n-alkyl hydroperoxides is in the region of 3360 cm^{-1}- 3450 cm^{-1} [57]. Chemical analysis did not show the presence of peroxide during the initial period and therefore the observed hydroxyl absorption may be due to a bonded alcoholic hydroxyl group.

The IR-spectrum of the soluble phase contained an absorption at 1720 cm^{-1}- 25 cm^{-1} as a shoulder to the carbonyl peak at 1740 cm^{-1}. The index $I_{1720\ cm^{-1}-25\ cm^{-1}}$ for both temperatures is plotted vs processing time in Fig. 4-22 together with the peroxide content of the total sample. For 210°C the carbonyl index increased rapidly especially after 5min together with peroxide. For 170°C the peroxide was not detected initially (however, the measurement was not taken at 1min at which time the peroxide was found in the unstabilized polymer) and with further processing no significant amount of peroxide was formed. The carbonyl index increased linearly at a slow rate up to 30min of processing.

4-2.1.3. Colour change measurement

The discolouration of the polymer during processing is plotted as a total colour difference in Fig. 4-23. The colour for 210°C increased immediately from the beginning of processing and the rate decreased after 15min. For 170°C the discolouration increased between 2-5min but after 10min it increased more rapidly. It appears that there was a short induction period of 5-10min but no induction period was observed at 210°C. It should be noted that the discolouration within the induction period at 170°C was considerably higher than the discolouration observed during the induction period for PVC processed with Irgastab T290 (see Fig. 4-2 in the previous section).

4-2.1.4. Unsaturation

Chemically measured unsaturation for both temperatures is illustrated in Fig. 4-24. The unsaturation increased initially for both temperatures and for 210°C after 5min it increased more rapidly until 22min of processing. For 170°C the unsaturation continued to increase linearly up to 30min.

The UV-spectra of the soluble phase were also measured after the removal of the insoluble gel in methylene dichloride by the centrifugation. The absorbance of 0.35% solutions in CH_2Cl_2 was measured against the solvent using 10mm and 1mm silica glass cells. The absorbance of absorption bands centred at 225nm-235nm and 260nm for 210°C and at 225nm-235nm, 260nm-280nm for 170°C increased with processing time. Above 300nm no distinct absorption bands were observed and absorbance progressively decreased up to 600nm. The absorbance above 300nm is shown by the chosen absorbance at 340nm for 210°C and 360nm-380nm for 170°C and together with observed absorption bands is plotted vs processing time in Figs. 4-25a,b. For 170°C the absorbance initially increased and with further processing increased linearly up to 30min. For 210°C the absorbance also increased initially but it increased more rapidly after 5min. Similar rapid increase was observed of the unsaturation on Fig. 4-24.

4-2.1.5. Molecular weight measurement

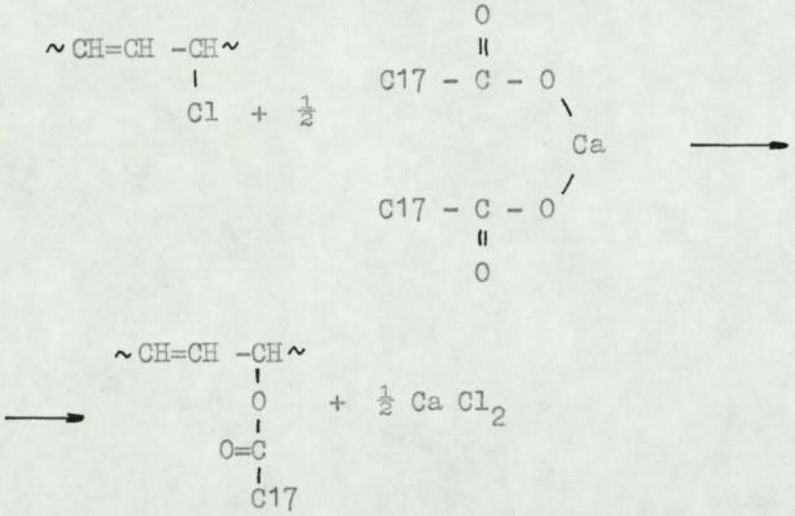
Molecular weight distribution (MWD) of soluble phases are plotted in Fig. 4-26a and 4-26b for 170°C and 210°C, respectively. For the lower temperature the MWD contained a higher molecular weight tail up to 20min. This result shows that molecular enlargement occurred as a result of a crosslinking reaction. The sample processed for 30min contained also lower molecular weight species (Fig. 4-26a). This suggests that after the longer time at this temperature two paralleled reactions took place, crosslinking and chain scission. It should be noted that this sample contained 36.3% (see Fig. 4-15) of the gel. At higher temperature the higher molecular weight tail was formed up to 5min. With further processing the polymer contained also lower molecular weight species because MWD was shifted to the lower molecular weight region (see Fig.4-26b). This suggests the existence of a chain scission reaction. The gel content in Fig. 4-15 increased rapidly and reached 89% at 22min. Consequently the concentration of the soluble phase decreased from 98.85% at 5min to 11.1% at 22min. The UV-absorbance (Fig. 4-25b) rapidly increased and also the peroxide and the carbonyl index (Fig.4-22). These results are in good agreement with the observed chain scission reflected in the shift in MWD.

4-2.2. Discussion

It is generally accepted that there is a need for use of lubricants in the processing of rigid PVC[62]. The most obvious role of the lubricant[63] is to improve the slip between molten PVC and the die surfaces so preventing stagnation and subsequent thermal decomposition of PVC and provide a smooth extrudate surface. It is also known[63,52] that the lubricant influences the rate at which the PVC powder melts (the gelation or fusion time) and the mechanical (or shear) heat developed in the extruder[63]. Lubricants are classified e.g. according to their composition, by the resulting clarity of PVC, by its effect on the glass transition temperature (Tg) or by their effect during processing. Two main groups predominate: external and internal lubricants. The external lubricant collects at the surface of the melt and forms lubricating layer between the polymer and the metal surfaces of the processing equipment. The rate of fusion of PVC is retarded as this lubricant will form a layer around the individual polymer particles. An internal lubricant is more compatible with the PVC so it is able to reduce internal friction and can therefore reduce melt viscosity. Because of this properties it should have little effect on the fusion rate and might, in fact, actually increase it[62].

Ca-stearate is referred to[62,63] as an external lubricant but has been also suggested as an internal lubricant e.g. Tg was lowered from 86.5°C to 83.5°C which suggests a certain degree of compatibility with the polymer. It was also found[59] that the increasing concentration of Ca-stearate at different constant levels of stearic acid lead to an increased apparent viscosity and a decreased shear rate and volumetric flow rate. This is not consistent with the normal characteristics of a lubricant and the 'lubricating' effect was explained by the increased friction as a result of increased viscosity which leads to a heat evolution, higher mass temperature and finally to the lower viscosity of the polymeric melt.

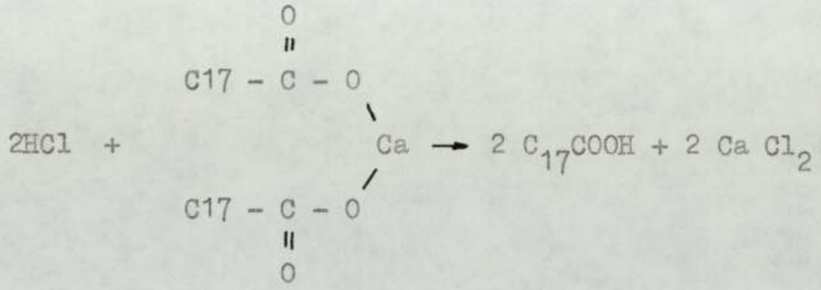
The torque and the gel measurements showed ~~the~~ induction periods of 5-10min for 170°C (Fig. 4-15) and this is also shown by the induction period of colour formation on Fig.4-23. It has been previously demonstrated that the presence of Ca-stearate[32] and Ca-laurate[64] resulted in the induction period of HCl evolution during the degradation of PVC at 180°C and therefore Ca-stearate can be regarded as a lubricant with the stabilizing capability. The disappearance of the carboxylate band (Fig. 4-16,4-17) and the growth of the esteric peak (Fig.4-19) suggests the formation of an ester. The esterification reaction is similar to that observed previously when dibutyltin maleate was used (see section 4-1) and can be described by the following reaction:



$$\sim CH{=}CH-\underset{\displaystyle Cl}{\overset{}{CH}}\sim \; + \; \tfrac{1}{2}\,(C17-\overset{\displaystyle O}{\overset{\|}{C}}-O)_2Ca \longrightarrow \sim CH{=}CH-\underset{\displaystyle O-\overset{}{C}(=O)-C17}{CH}\sim \; + \; \tfrac{1}{2}\,Ca\,Cl_2 \qquad (1)$$

The esterification has been previously shown by Frye and Horst[43,60] to occur between PVC and the carboxylates of barium, cadmium and zinc and it was proposed that the stabilizing action of metal carboxylates arises in part from esterifying displacement of labile chlorine atom.

The observed formation of the acidic carbonyl at 1705 cm^{-1} (Figs. 4-16,17,18) also indicates the formation of stearic acid by the reaction of Ca-stearate with HCl evolved during degradation:



$$, \quad 2HCl + \begin{matrix} C17-\overset{\overset{O}{\|}}{C}-O \\ \diagdown \\ Ca \\ \diagup \\ C17-\underset{\underset{O}{\|}}{C}-O \end{matrix} \rightarrow 2\,C_{17}COOH + 2\,Ca\,Cl_2 \qquad (2)$$

Stearic acid is known to be used as an external lubricant[63] and therefore it is possible that the function of Ca-stearate as a lubricant is the result of the presence of stearic acid formed during processing as illustrated by the reaction 2. The decrease of the torque at 170°C within the small induction period of 5-10min (see Fig.4-15) may suggest the lubricating action of stearic acid.

On Figs. 4-20,21 there are plots of hydroxyl indices of the absorption observed in the spectrum of the total samples (Fig. 4-20) and in the spectrum of the gel phase (Fig.4-21). The observed broad peak was centred at 3460 cm^{-1}. The nature of this peak is not yet clear but because of the formation of acidic carbonyl (see Fig. 4-16) it may be that the hydroxyl plotted as an index in Fig. 4-20 may correspond to stearic acid formed during processing. The presence of the hydroxyl absorption in the gel phase (Fig. 4-21) may originate from the gel present in the unprocessed polymer as it was suggested in the section 4-1.2.

The unsaturation (see Fig. 4-24) is initially lower at 170°C than at 210°C. It may be that the stabilizing action of Ca-stearate at the lower temperature, as described by the reactions 1 and 2, resulted in the lower level of unsaturation than at 210°C. At this temperature the carboxylate double peak at 1570 cm^{-1}-1540 cm^{-1} (see Fig.4-17) was not detected already at

5min and no induction period of colour formation and the torque increase was observed. Thus it appears that at this temperature the stabilizing action of 0.8phr of Ca-stearate was negligible.

For 210°C the torque increased after 2-3min and the gel content increased rapidly from the beginning of processing. The unsaturation increased significantly after 5min (see Fig.4-24) and the similar rapid increase of the UV-absorbance of the soluble phase was observed (see Fig.4-25b). It is clear that the increased absorbance comes from the smaller portion of the total sample examined because the insoluble part also increased (Fig. 4-15). These results are similar to the results obtained for the unstabilized polymer as was discussed in the chapter 3. The molecular weight distribution is shifted after 5min to the lower molecular weight region (Fig. 4-26b) and therefore chain scission reaction occurred. Because of the increase of the carbonyl absorption together with the peroxide content (Fig. 4-22) this chain scission is of oxidative character and reference can be made to the reactions 7,7a,b already discussed in the chapter 3. At 170°C chain scission also occurred when the processing was carried out for longer time (30min) and at which time the gel content had already reached 36.3%. The oxidation of the polymer and the formation of hydroperoxide especially at 210°C involves the abstraction of hydrogen atom which leaves the free macroradical $R^{\bullet}$. Also the oxidative chain scission as a result of the decompostion of hydroperoxide and also breakdown of peroxylinkages (which can also be present in the crosslinked polymer) together with the rearrangement of the resulting alkoxy radical will provide the free intermediate radicals which are involved in the crosslinking reaction and also represent the kinetic chain branching with subsequent increase of the dehydrochlorination reaction.

The IR-spectroscopy results in this section suggest that the esterification occurred during processing of PVC with Ca-stearate and the function of Ca-stearate as a stabilizer is to replace labile chlorine atom (probably allylic) with the ester and also to react with evolved HCl with formation of stearic acid. The possible function of Ca-stearate as a lubricant is the presence of stearic acid formed by the above mentioned reaction during processing.

Torque and gel content of PVC processed with Ca-stearate at 170°C and 210°C.

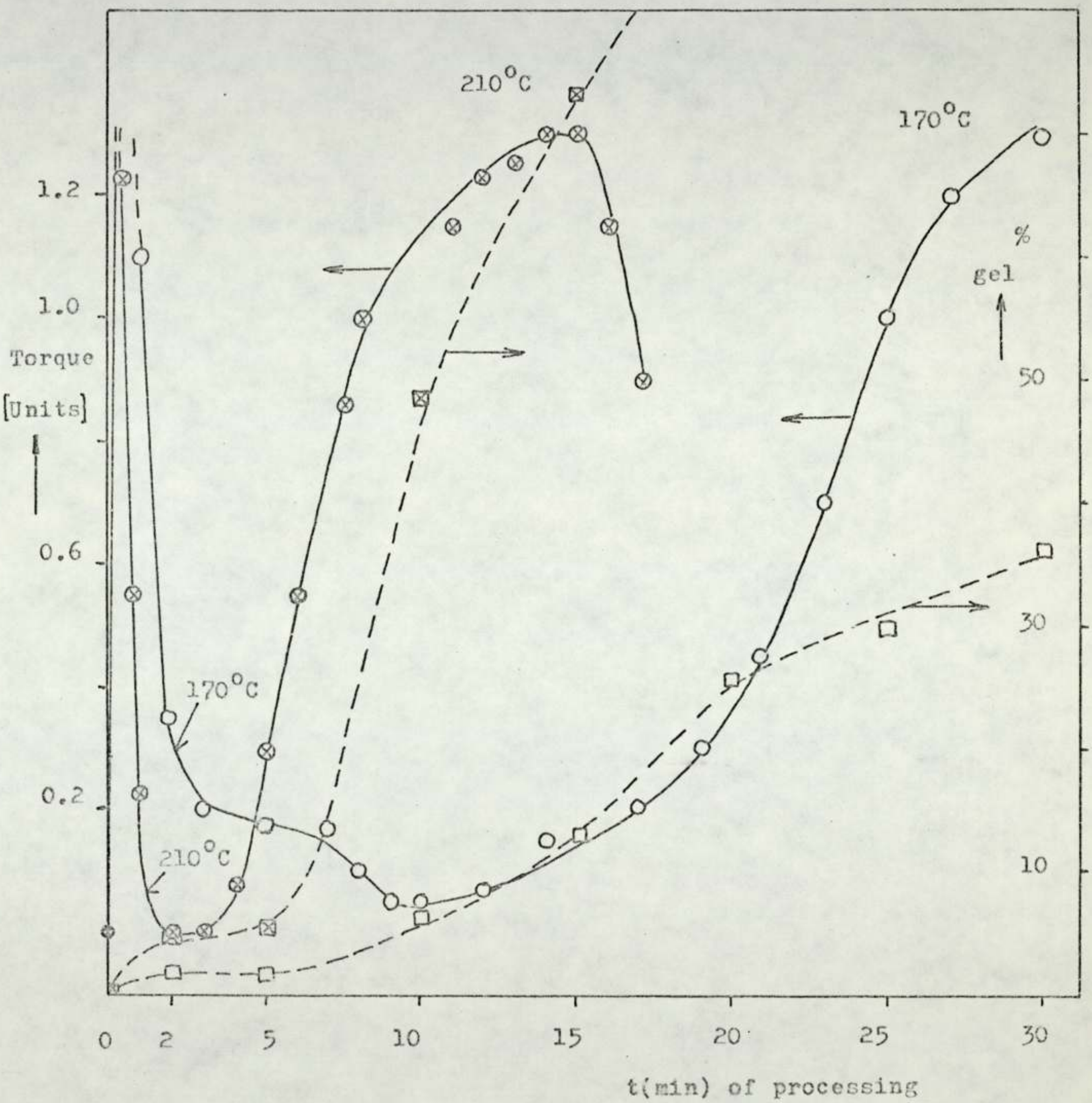


Fig.4-15

IR-spectra of PVC processed with Ca-stearate at 170°C and 210°C. Total sample.

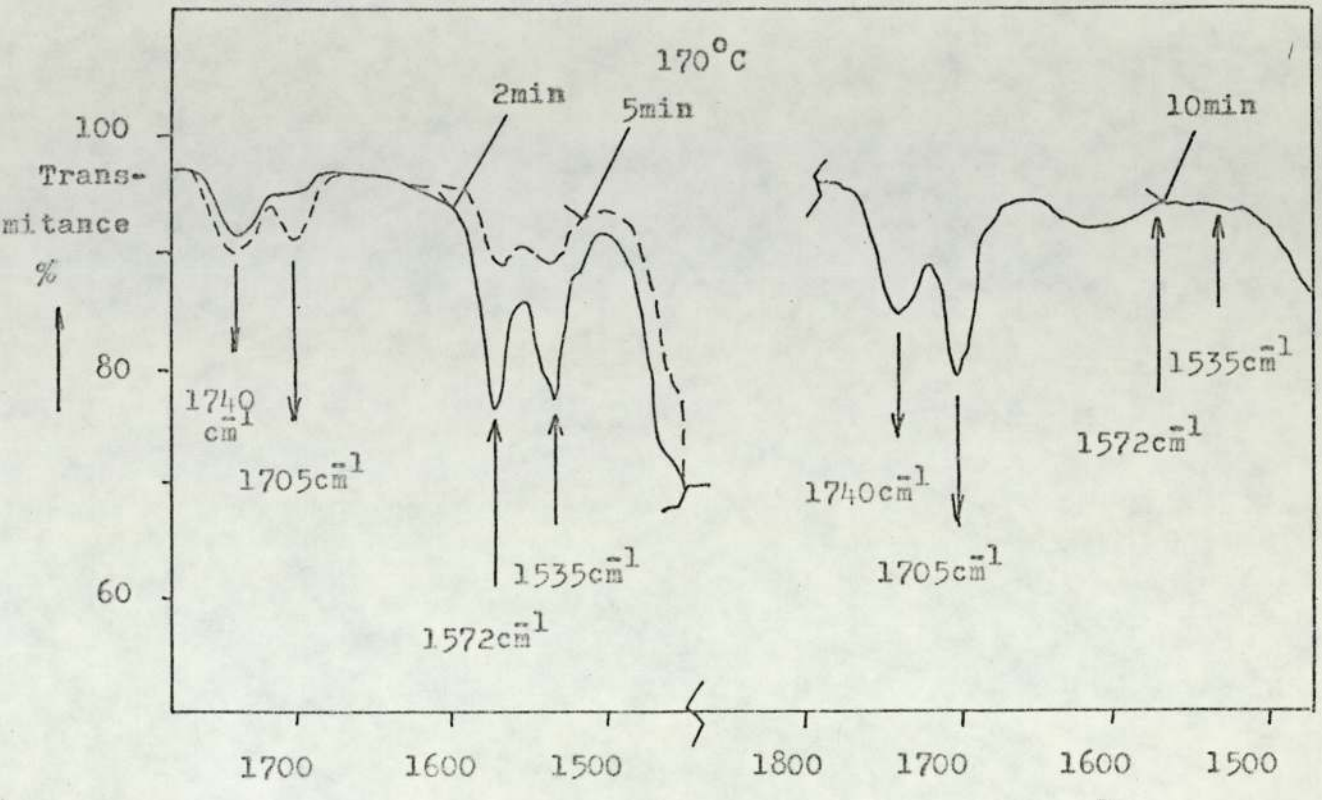


Fig.4-16

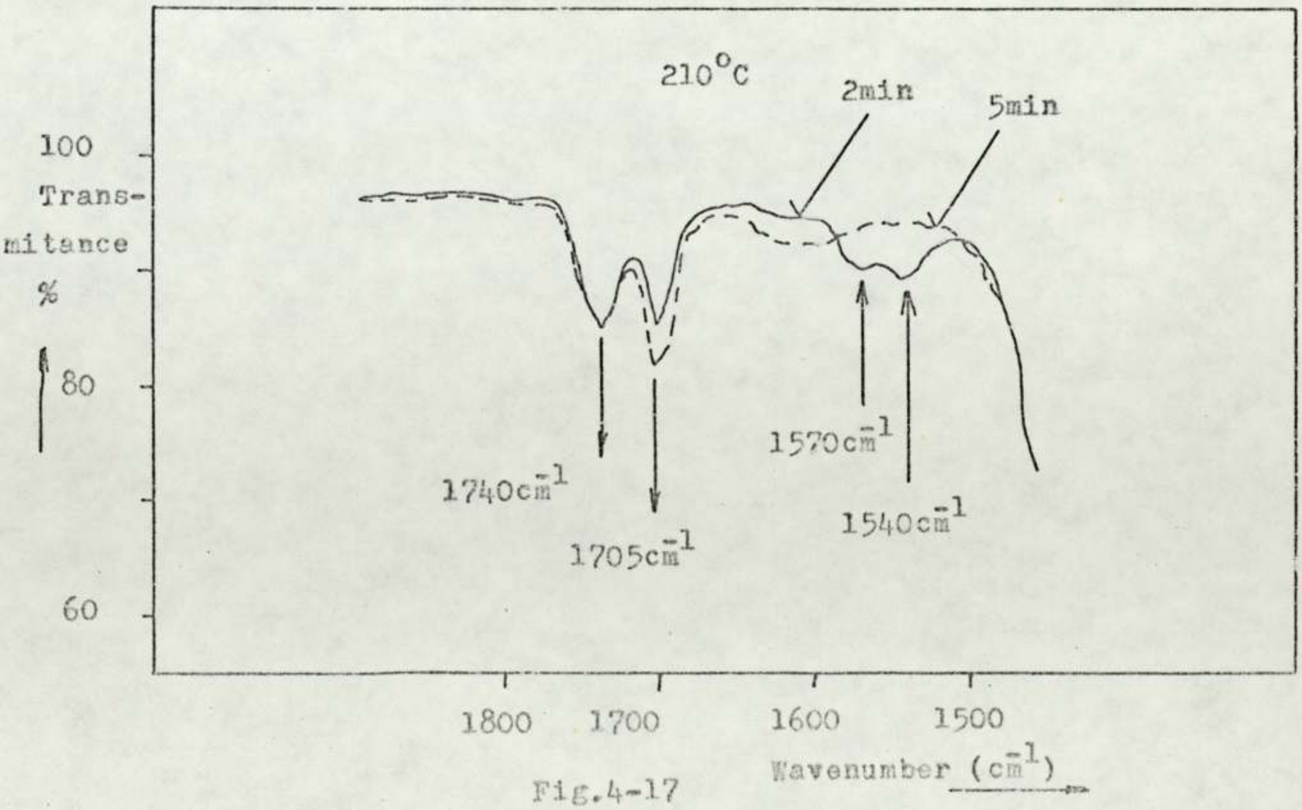


Fig.4-17

Carbonyl index $I_{1705cm^{-1}}$ of PVC processed with Ca-stearate at 170°C and 210°C. Total sample.

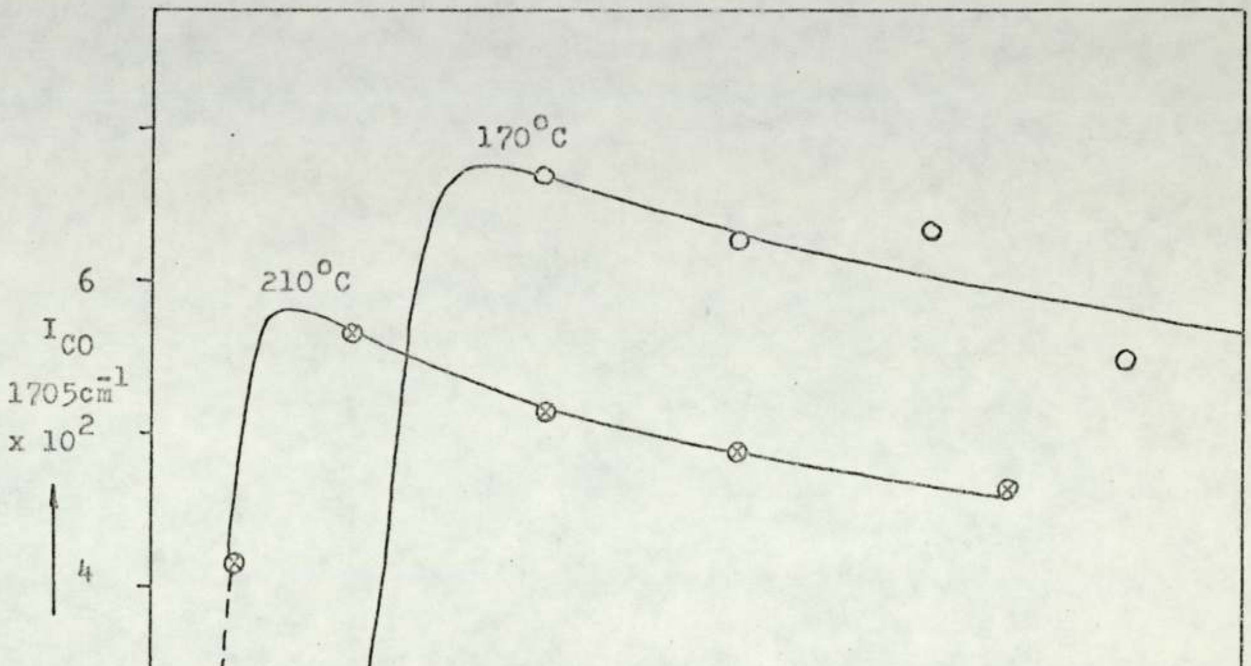


Fig.4-18

Carbonyl index I_{CO} 1740 cm^{-1} of PVC processed with Ca-stearate at 170°C and 210°C. Total sample.

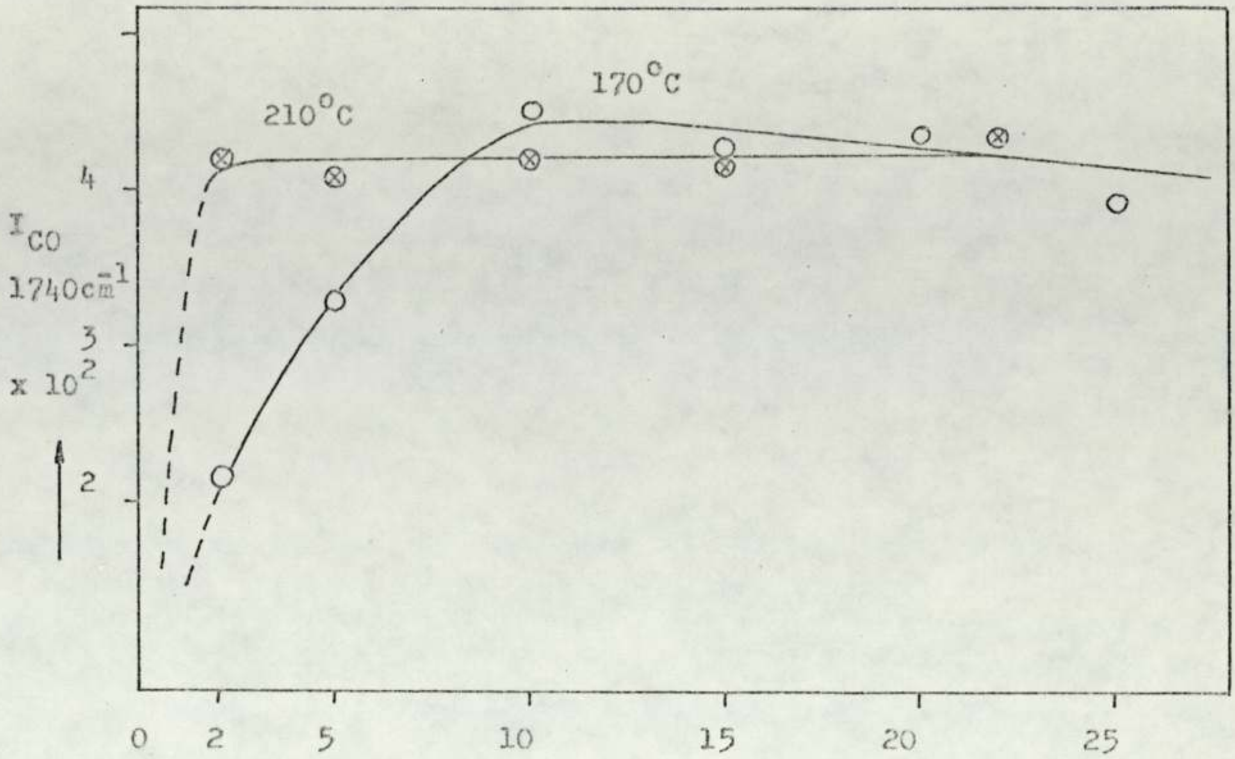


Fig.4-19 t(min) of processing

Hydroxyl index $I_{3420cm^{-1}-3470cm^{-1}}$ of PVC processed with Ca-stearate at 170°C and 210°C. Gel phase.

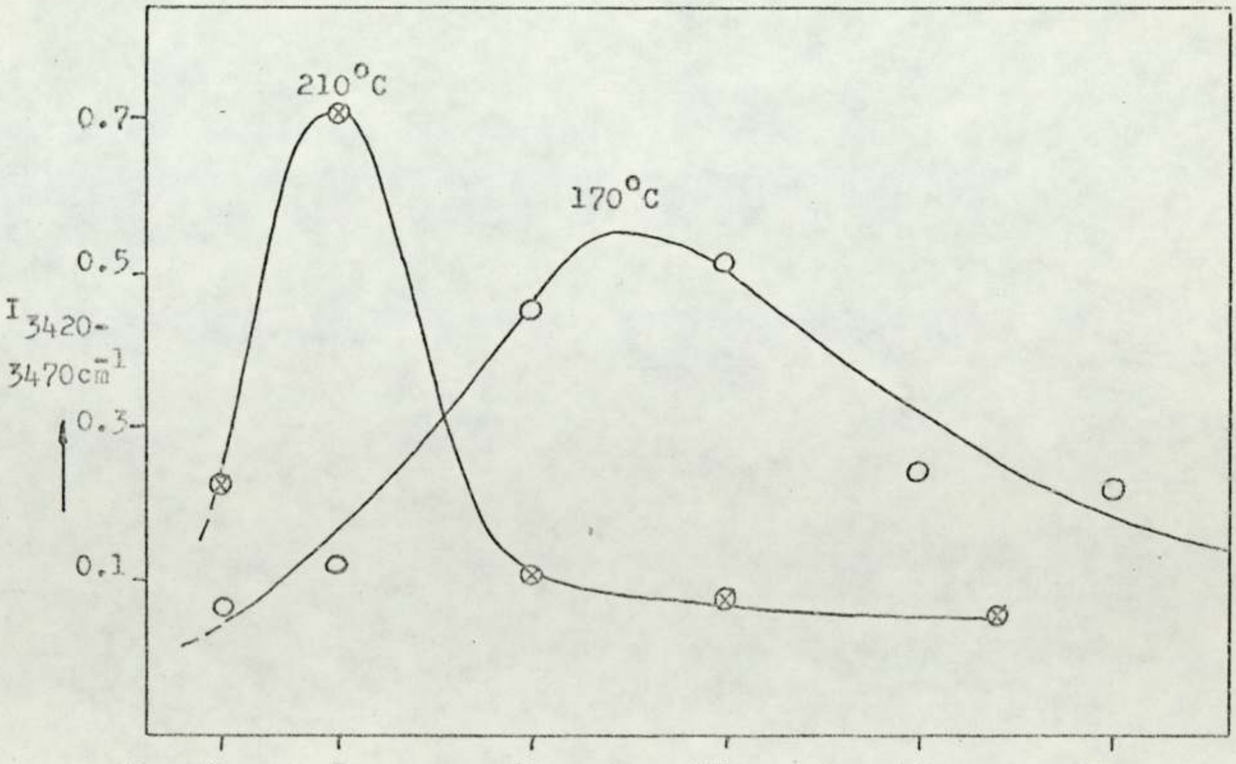


Fig.4-21 t(min) of processing

Hydroxyl index $I_{3460cm^{-1}}$ of PVC processed with Ca-stearate at 170°C and 210°C. Total sample.

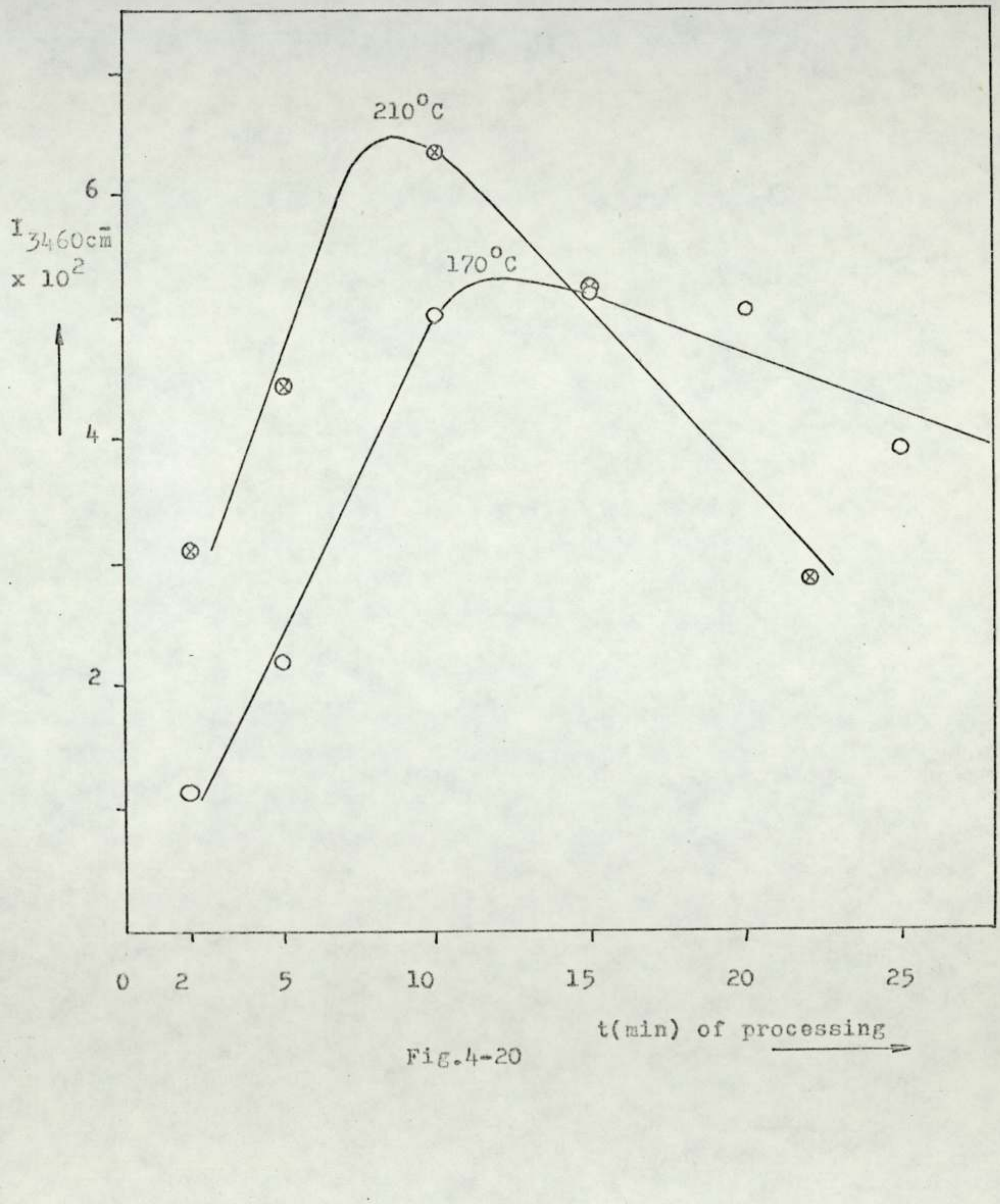


Fig.4-20

Carbonyl index $I_{1720-25cm^{-1}}$ and peroxide content vs processing time, PVC processed with Ca-stearate.

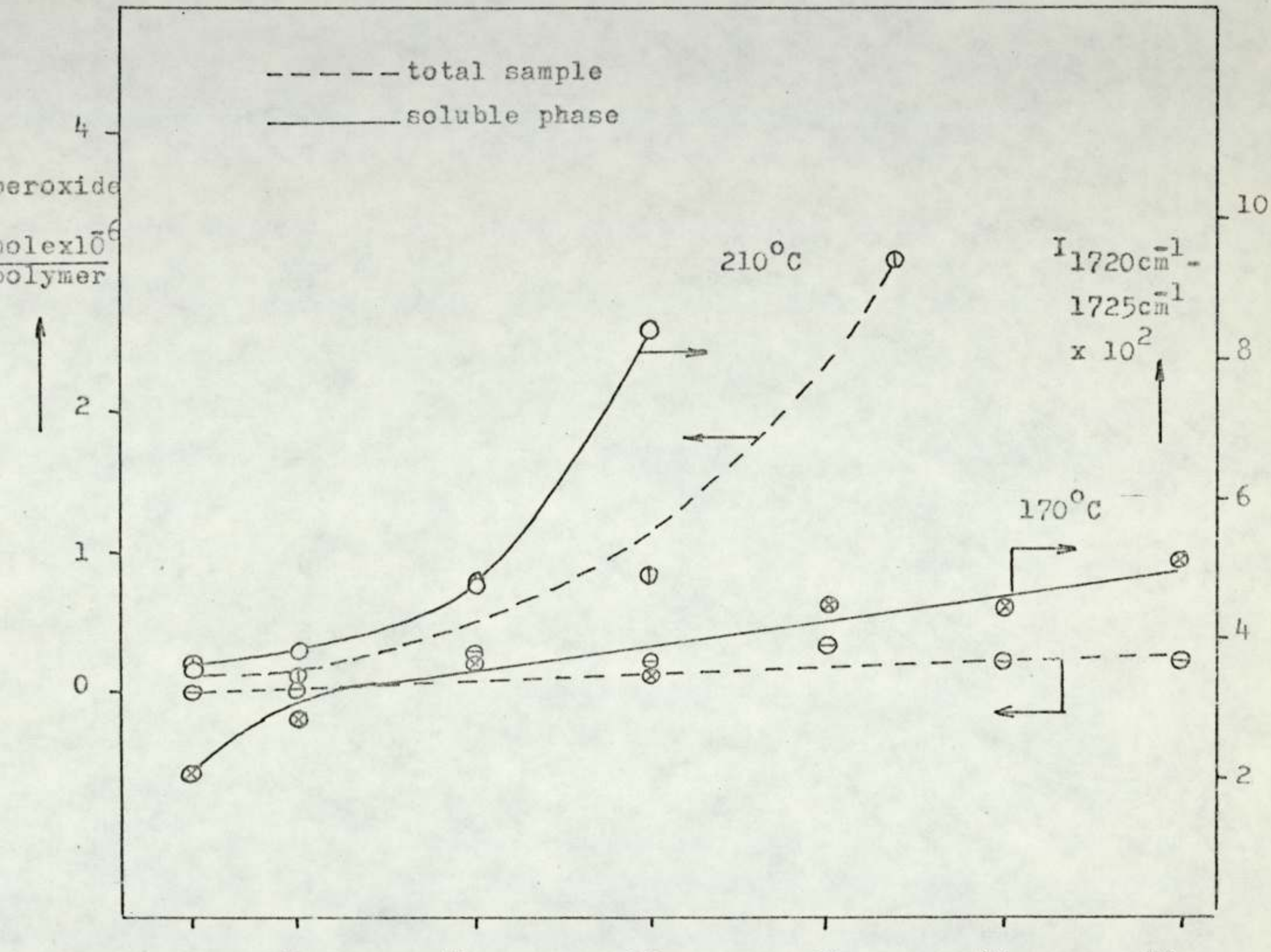


Fig.4-22

Colour change of PVC processed with Ca-stearate at 170°C and 210°C.

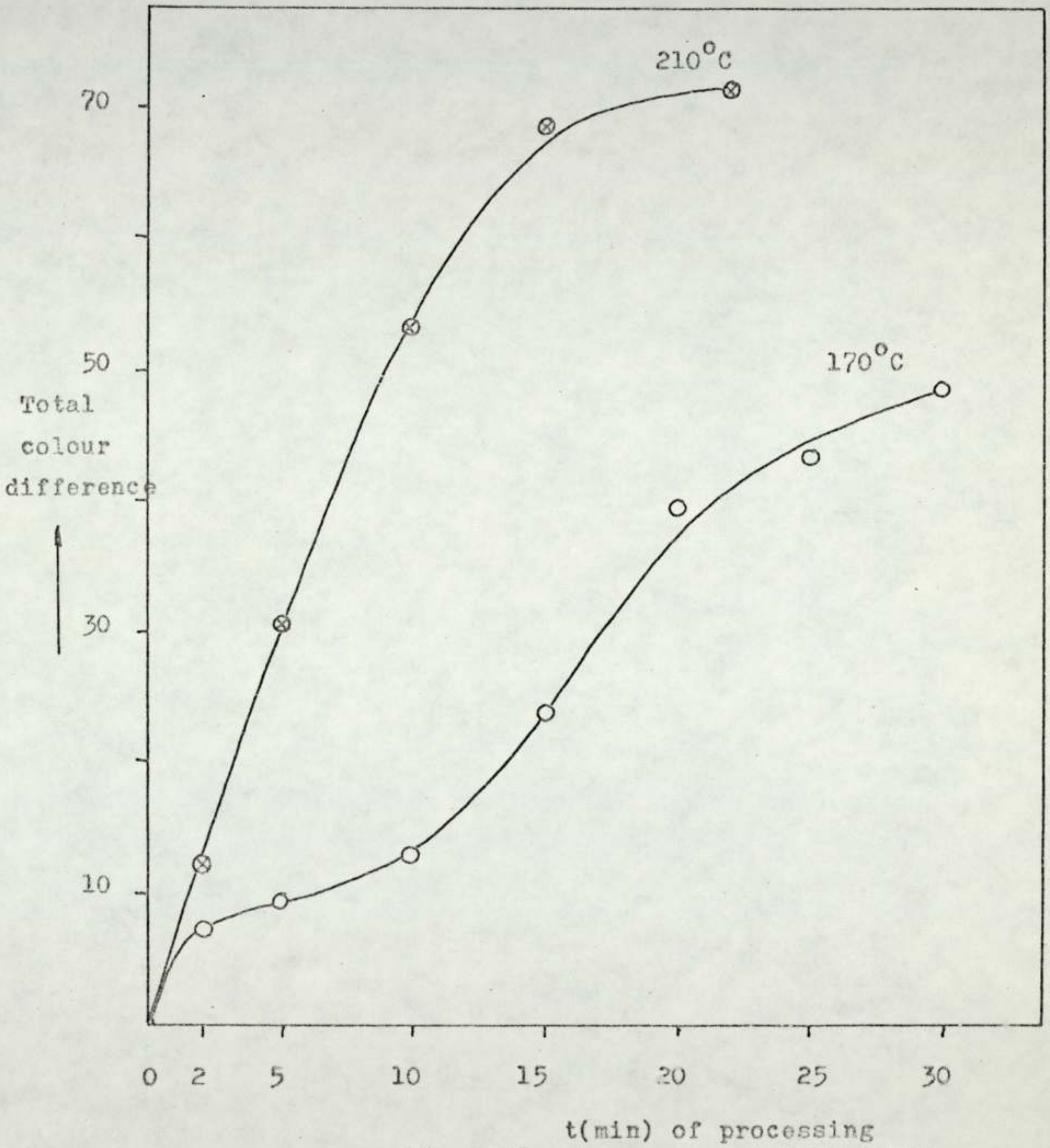


Fig.4-23

Unsaturation vs processing time.PVC processed with Ca--stearate at 170°C and 210°C.

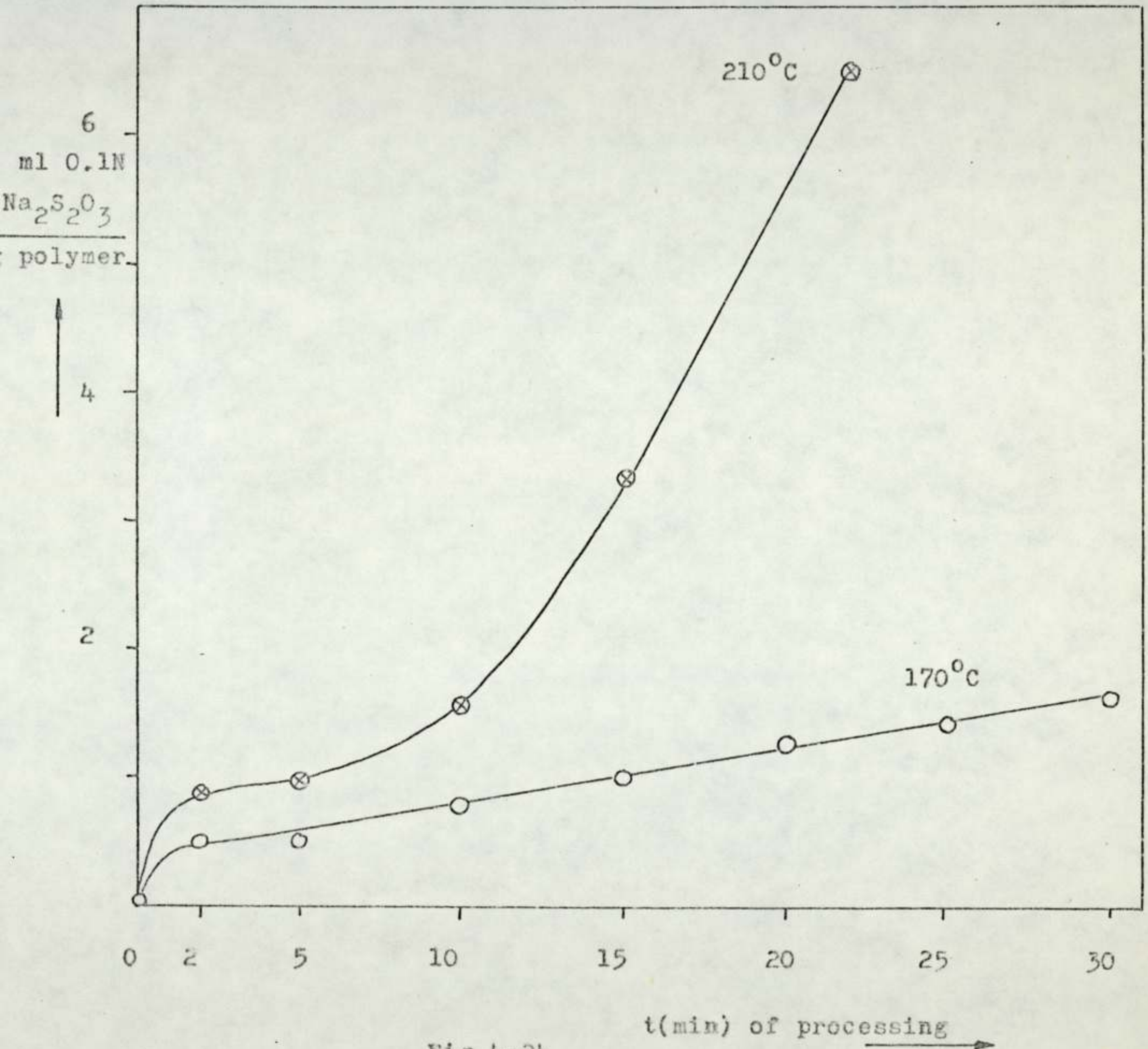


Fig.4-24

UV-absorbance vs time of PVC processed with 0.8phr of Ca-stearate at 170°C and 210°C (Soluble phase in CH_2Cl_2,0.35%)

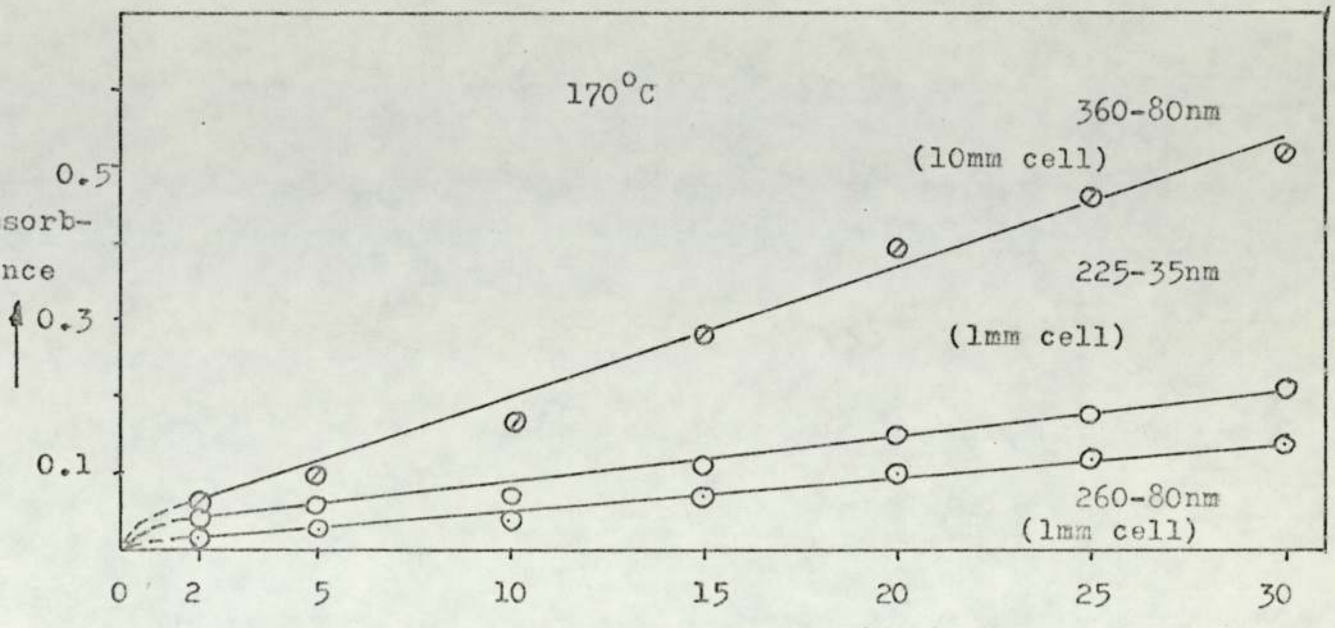


Fig.4-25a

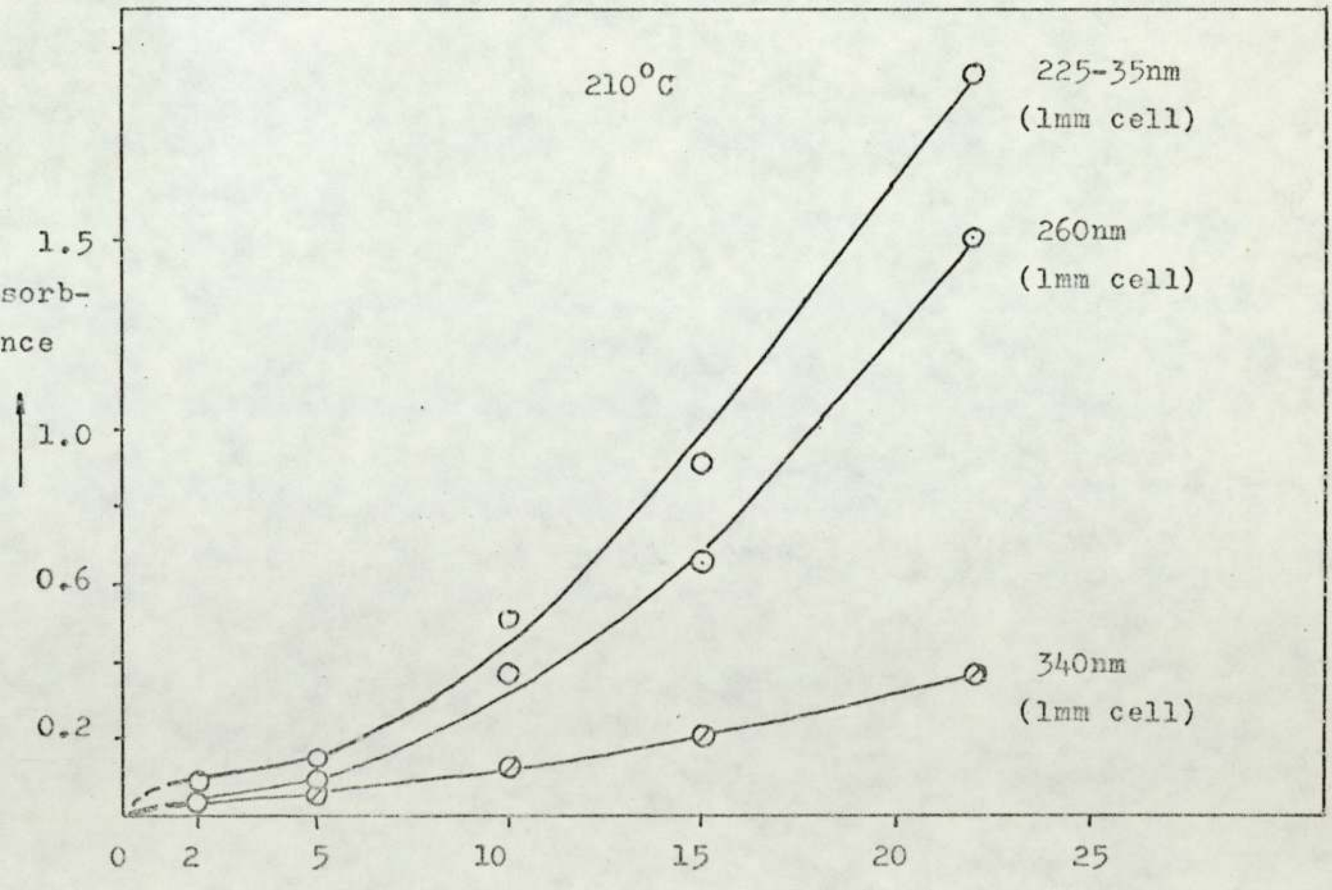


Fig.4-25b

Molecular weight distribution of PVC processed with Ca-stearate. Soluble phase in methylene dichloride.

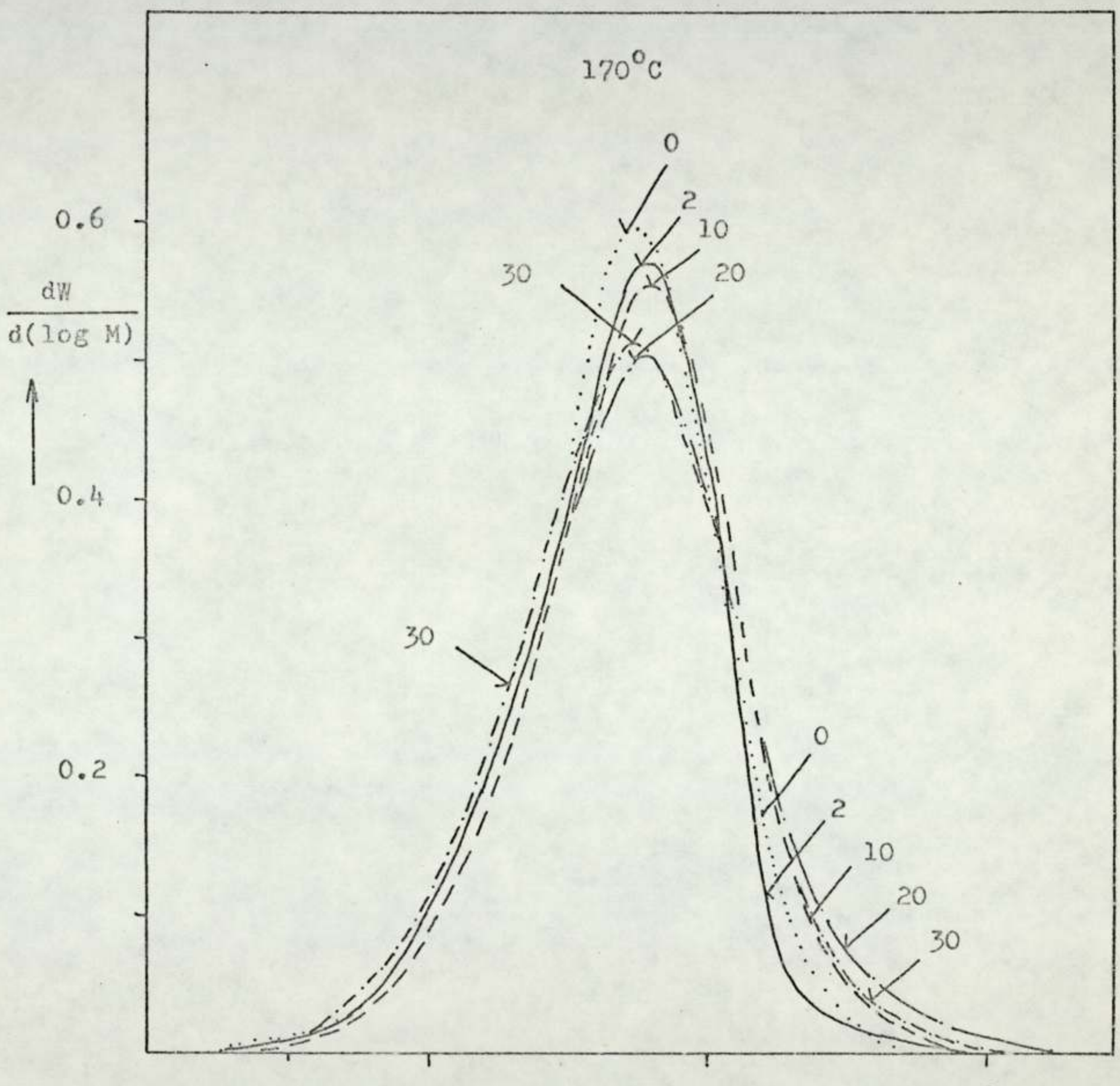


Fig.4-26a

Molecular weight distribution of PVC processed with Ca-stearate.Soluble phase in methylene dichloride.

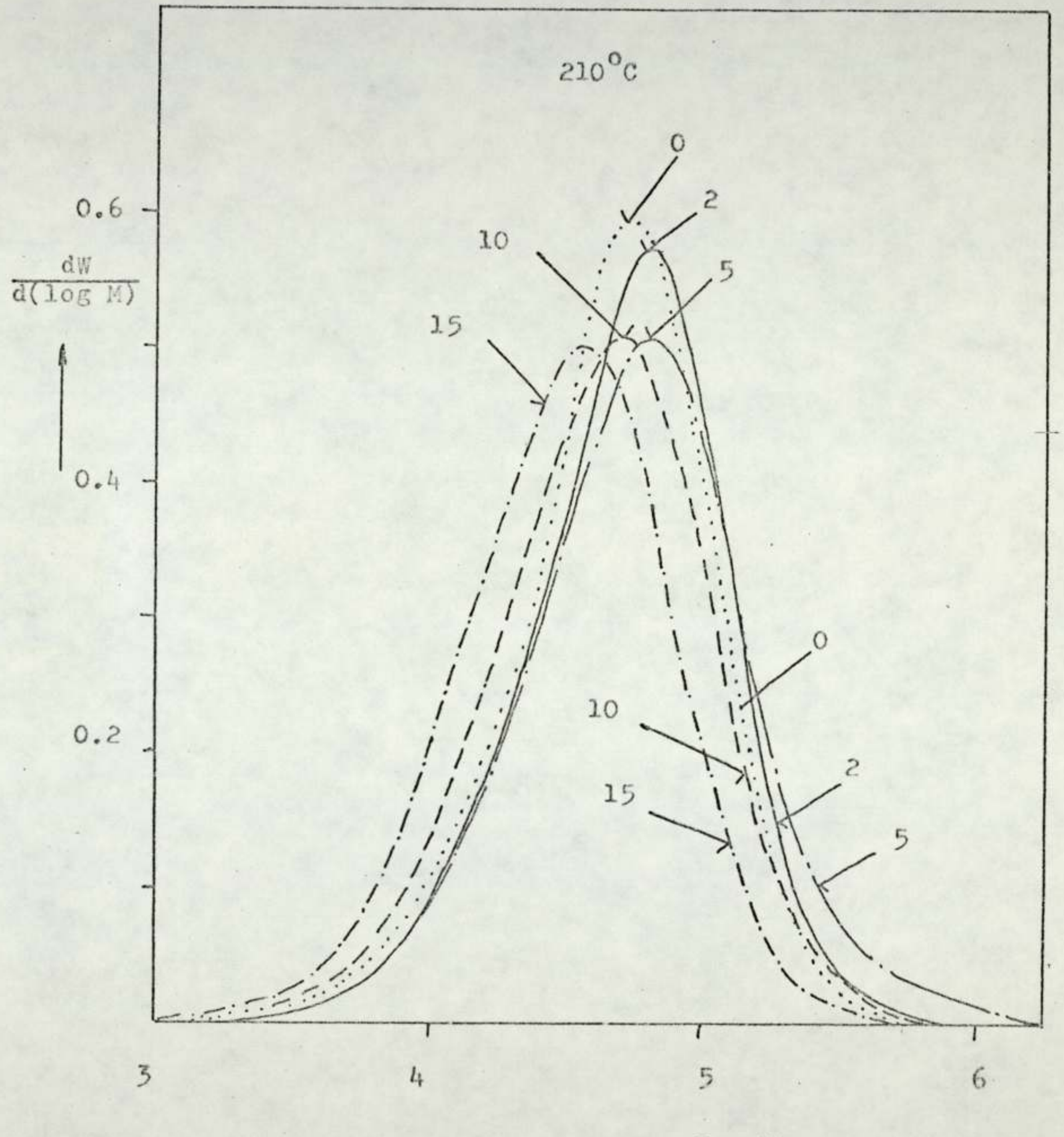


Fig.4-26b

4-3. PVC processed with Wax E

4-3.1. Results

4-3.1.1. The torque and the gel measurements

The change of torque during processing is plotted vs time in Fig. 4-27 for 210°C and 170°C temperatures. Also on the same figure the gel (the insoluble part in methylene dichloride) is plotted as a function of processing time. After the initial maxima the torque decreased due to the fusion of the polymer. It should be noted that the level of torque after 2min is lower for 170°C than for 210°C. When the polymer was processed without the additives, the torque in the initial period was higher at 170°C compared with 210°C (see chapter 3, Fig. 3-2) and therefore it appears that the lower torque at 170°C on Fig. 4-27 is due to the lubricating action of Wax E, which is regarded as an external lubricant[63,65]. The role of lubricants (internal and external) was discussed earlier in the section 4-2.2. Furthermore, the torque at 1min (viz following Table 1) was lower in the presence of Wax E than without the lubricant which also indicates the lubricating effect of Wax E.

Table 1. Comparison of the torque (units) at 1min of processing for PVC processed without additives and with Wax E.

No additives		Wax E	
210°C	170°C	210°C	170°C
0.875	1.9	0.5	1.1

The torque increased after 2-4min and for 210°C the rate of increase was considerably higher than at 170°C. The gel content also increased more rapidly at 210°C and reached 89.2% at 22min. It may be noted that the gel content at 210°C increased more rapidly in the initial stage than the gel content of PVC processed with no additives (see Fig. 3-2, chapter 3).

4-3.1.2. Colour change

Discolouration of the polymer during processing is shown in Fig. 4-28. On the same figure is the plot of the discolouration of the polymer processed without additives which was taken from Fig. 3-3, chapter 3. The total colour difference increased linearly from the beginning of processing for both temperatures and the rate of increase was higher at 210°C. At longer processing time the rate decreased for both temperatures. It is evident that there was no induction period of colour formation. Furthermore, the rate at 170°C was slower than the rate for the polymer processed without additives. At 210°C however, the rate appears to be similar.

The slower rate at 170°C in the presence of Wax E may suggest that the contribution of the pure mechanical process to the overall thermomechanical degradation was less at 170°C due to the presence of Wax E. At 210°C the rates were similar which may suggest that the thermal process predominates during the degradation in torque rheometer at this temperature.

4-3.1.3. Unsaturation

The unsaturation in processed polymer was determined by the method described earlier in the chapter 3, section 3.1.2. The result for both temperatures is shown in Fig. 4-29. Also on the same graph is the plot of the unsaturation of the polymer processed without additives. There is an initial rapid increase for both temperatures. For 170°C the unsaturation after 2min increased linearly up to 25min. For 210°C the unsaturation was higher already at 5min than at 170°C and continued to increase with further processing at the higher rate indicating the auto-accelerating character of the dehydrochlorination reaction. It appears that the rate at 210°C was similar to the rate of the polymer processed without additives but at 170°C the rate was lower.

4-3.1.4. IR-spectroscopy results

IR-spectra of processed polymer were obtained using pressed films of total sample and also of 7% solutions in methylene dichloride. The spectra of the total samples contained an absorption peak centred at 1730 cm^{-1}-1735 cm^{-1} but no change in this absorption was observed during processing. Wax E (trade name of Hoechst A.G.) belongs to the group of wax esters (montan acid ester)[63] and therefore the absorption at 1730 cm^{-1}-1735 cm^{-1} is attributed to the esteric carbonyl of Wax E. The esteric carbonyl peak, which was also present in the IR spectra of the soluble phase, contained a shoulder at 1720 cm^{-1}. The 1720 cm^{-1} carbonyl absorption was attributed to α- chloroketone carbonyl (see chapter 3, section 3.2.4.) and also to the α-chlorocarboxylic acid carbonyl. The plot of the 1720 cm^{-1} carbonyl peak, expressed as an index, is shown for both temperatures in Fig. 4-30. The index initially increased and at 170°C after 2min increased linearly with further processing. The increase was small when compared with 210°C processing temperature. At this temperature the carbonyl index increased more rapidly already after 2min.

The peroxide content, which was determined by the iodine-liberation method and described in the chapter 3, section 3.1.1., is also plotted on Fig. 4-30. For lower temperature the peroxide was not detected but the measurement was not made after 1min at which time the peroxide was present in the polymer processed without additives (see Fig. 3-7). At higher temperature the peroxide was detected after 2min and increased steadily with further processing. It can be seen that the gel content in Fig. 4-27 also continued to increase rapidly after 2min. This result is similar to that obtained with the polymer processed without additives where peroxide content again increased after 5min together with the gel content (see Fig. 3-2 and 3-7, chapter 3). However, the initial drop in the gel content on Fig. 3-2 was not observed here in Fig. 4-27.

Further examination of IR-spectra of soluble phase revealed the increase of the absorption peak at 2850 cm^{-1}. This absorption peak which also increased in the unstabilized polymer (see Fig. 3-6), was assigned to the C-H stretching of unsaturated -CH=CH- bond (see section 3.2.4., chapter 3) as a result of dehydrochlorination. The plot of the index $I_{2850\ cm^{-1}}$ is shown in Fig. 4-31. Here again there was rapid increase of the index initially followed by a slower rate at 170°C but at 210°C the rate was considerably higher.

4-3.1.5. UV-spectroscopy results

UV-spectra of processed polymer were obtained, after the removal of the insoluble gel in methylene dichloride, using 0.6% solutions in CH_2Cl_2 and 1mm silica glass cells. For 170°C absorptions centred at 230nm, 275nm and a small ill-defined band at 360nm - 375nm were observed and the absorbance increased with processing. Above 300nm there was no evidence of structure in the UV-absorption up to 600nm. The absorbance vs time for 170°C is plotted on Fig.4-32a. For 210°C the absorption band at 225nm-235nm was again observed and also an absorption centred at 260nm. Above 300nm no significant absorption bands were observed (only a small ill-defined band at about 370nm) and the absorbance again progressively decreased up to 600nm. The absorbance vs time for 210°C is shown in Fig. 4-32b. At 170°C the UV-absorbance increased with processing time (Fig.4-32a) and at 210°C the increase was faster (Fig. 4-32b) especially after 5min of processing.

A comparison of the absorbance at 310nm for both temperatures is shown in Fig. 4-32c. At 170°C the absorbance increased linearly up to 30min and at 210°C it was initially higher but increased more rapidly after 5min. It may be noted that this plot is similar to the plot of IR-peak at 2850 cm^{-1} (see Fig.4-31).

4-3.1.6. Molecular weight measurement

The MWD of the soluble phase of processed polymer is shown in Figs. 4-33a and 4-33b for 170°C and 210°C, respectively. The MWD of the polymer processed at lower temperature (Fig. 4-33a) contained a higher molecular weight tail up to 20min processing which indicates a crosslinking reaction. This higher molecular weight tail of the sample processed for 30min has shifted to the lower molecular weight region which suggests that apart from the crosslinking, chain scission also occurred at longer processing times. For 210°C (see Fig. 4-33b) the MWD of the samples processed up to 5min has broadened on both sides and therefore again initially both crosslinking and also chain scission took place. It may be noted here that after gelation the torque was higher than at 170°C and the gel content increased rapidly after 2min (see Fig. 4-27) together with the unsaturation (Figs. 4-29,31,32c). The MWD of the sample processed for 10min and especially for 15min had shifted to the lower molecular weight region which indicates more extensive chain scission. The increase of the carbonyl index and the peroxide content (see Fig. 4-30) indicated that this chain scission had an oxidative character.

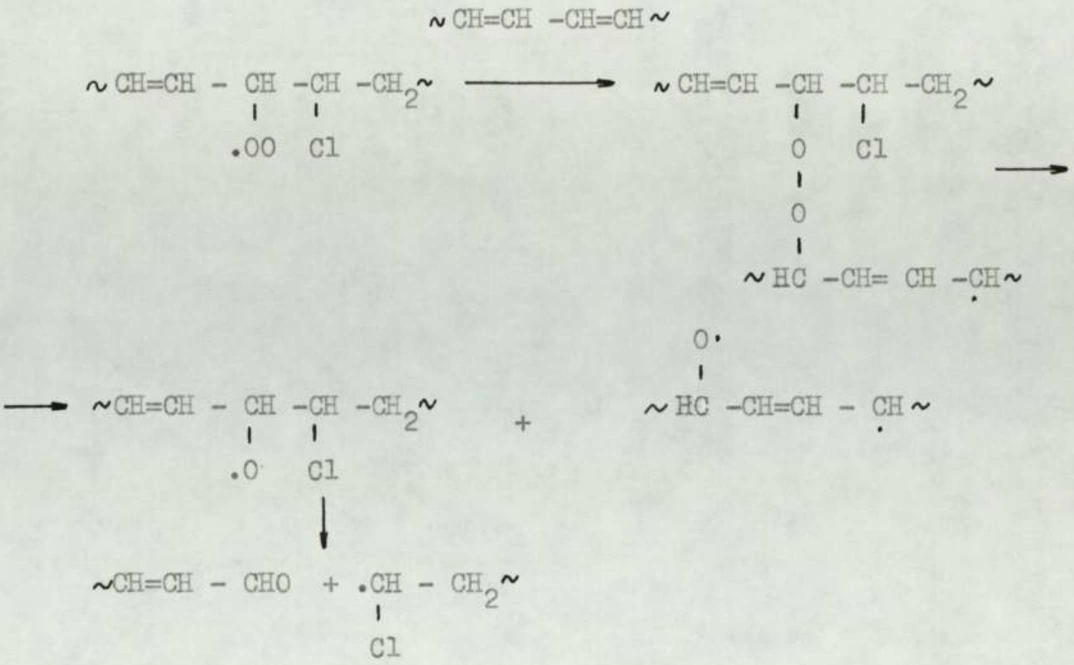
4-3.2. Discussion

The role of lubricants during processing of PVC was discussed in the section 4-2.2. of this chapter. It was shown that the lubricants have been classified according to their function during processing and that two main groups predominate, the internal and the external types. If the classification is done by chemical composition, Wax E belongs to the group of fatty acid derivatives (montan acid ester)[63]. Because of its chemical nature it collects at the surface of the polymer melt due to its low compatibility and forms a lubricating layer between the polymer and the metal surface of the processing equipment. This should result in lower mechanical work being exercised upon the polymer and in lower shear stresses (torque).

The level of torque in the fusion stage was lower than the torque which was observed during processing of PVC without additives (see e.g. Table 1, section 4-3.1.1.). Furthermore, the torque (Fig. 4-27) at 170°C was lower in the initial stage of processing than at 210°C whereas for the polymer processed without additives the torque at 170°C was higher than at 210°C (see Fig. 3-2, chapter 3). This result suggests that Wax E decreased the torque in the fusion stage due to its lubricating action and also that the mechanical work was lower immediately after the fusion at 170°C than at 210°C. The discolouration at 170°C increased at a slower rate (see Fig. 4-28) than the discolouration of the polymer processed without additives but at 210°C the rate was similar. The unsaturation increase (Fig. 4-29) at 170°C was also slower. It may be that the contribution of the pure mechanical process to the overall thermomechanical degradation was less at 170°C due to the presence of Wax E.

For 170°C the torque and the gel content started to increase after 2min (Fig. 4-27) and the discolouration increased linearly (Fig. 4-28) indicating no induction period. The unsaturation after the rapid initial increase (Fig. 4-29,31) increased linearly with further processing indicating a constant rate of dehydrochlorination. The carbonyl index (Fig. 4-30) after the initial increase continued to increase linearly with further processing but the increase was small. The presence of the carbonyl band indicates the formation of an in-chain ketone as a result of oxidation. The formation of higher molecular species (Fig. 4-33a) and also the increase of the gel and the torque (Fig. 4-27) indicates the existence of a crosslinking reaction. The exact mechanism of this reaction is not yet clear but the presence of the oxidation suggests the participation of alkoxy and also hydroxyl radicals formed by the decomposition of hydroperoxide with formation of ether and /or carbon-carbon crosslinks. This possibility was suggested in the discussion on the polymer processed without additives in the chapter 3.

At 210°C the torque and the gel content increased rapidly after 2min and also the discolouration increased at a higher rate (Fig. 4-28). The carbonyl index increased more rapidly than at 170°C especially after 5min and peroxide content increased steadily with further processing. The unsaturation (Fig. 4-29) increased at a higher rate than at 170°C and had an auto-accelerated character. These results suggest the catalytic action of the intermediate free radical species formed by the oxidation ($ROO^{\bullet}$, $RO^{\bullet}$,$OH^{\bullet}$), together with the thermal energy increased the rate of the dehydrochlorination reaction. These free radical species may also be involved in the competitive crosslinking reaction which resulted in the rapid increase of the gel content (Fig. 4-27). Furthermore, the chain scission occurred more extensively at this temperature, viz Fig. 4-33b. The chain scission reaction was also discussed in the section 3.3. of the chapter 3 where oxidative chain scission was associated with kinetic chain branching. It is also possible that the peroxy-crosslinks may be present in the crosslinked phase which would give rise to lower molecular weight species on thermal breakdown. This possibility was also referred to in the section 4-1.1. of this chapter and can be described by the following reaction:



$$\sim CH{=}CH-\underset{\cdot OO}{CH}-\underset{Cl}{CH}-CH_2\sim \xrightarrow{\sim CH=CH-CH=CH\sim} \sim CH{=}CH-\underset{\substack{|\\O\\|\\O\\|\\ \sim HC-CH=CH-\underset{\cdot}{CH}\sim}}{CH}-\underset{Cl}{CH}-CH_2\sim \longrightarrow$$

$$\longrightarrow \sim CH{=}CH-\underset{\cdot O}{CH}-\underset{Cl}{CH}-CH_2\sim \quad + \quad \sim\overset{O\cdot}{HC}-CH{=}CH-\underset{\cdot}{CH}\sim$$

$$\downarrow$$

$$\sim CH{=}CH-CHO + \cdot\underset{Cl}{CH}-CH_2\sim$$

Torque and the gel content of PVC processed with 0.65phr of Wax E at 170°C and 210°C.

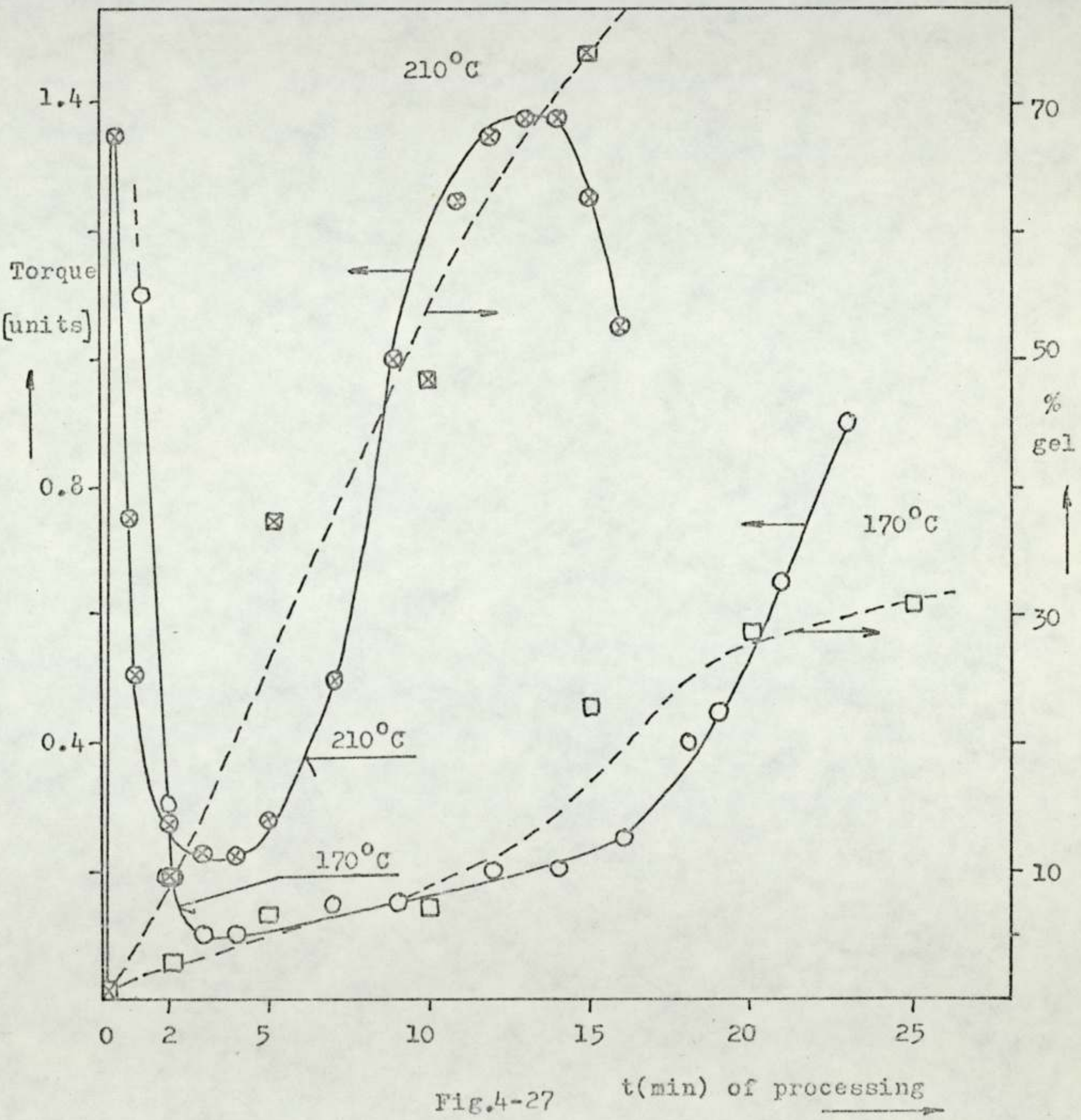


Fig.4-27

Comparison of discoloration of PVC processed in torque rheometer without additives and with Wax E at 170°C and 210°C.

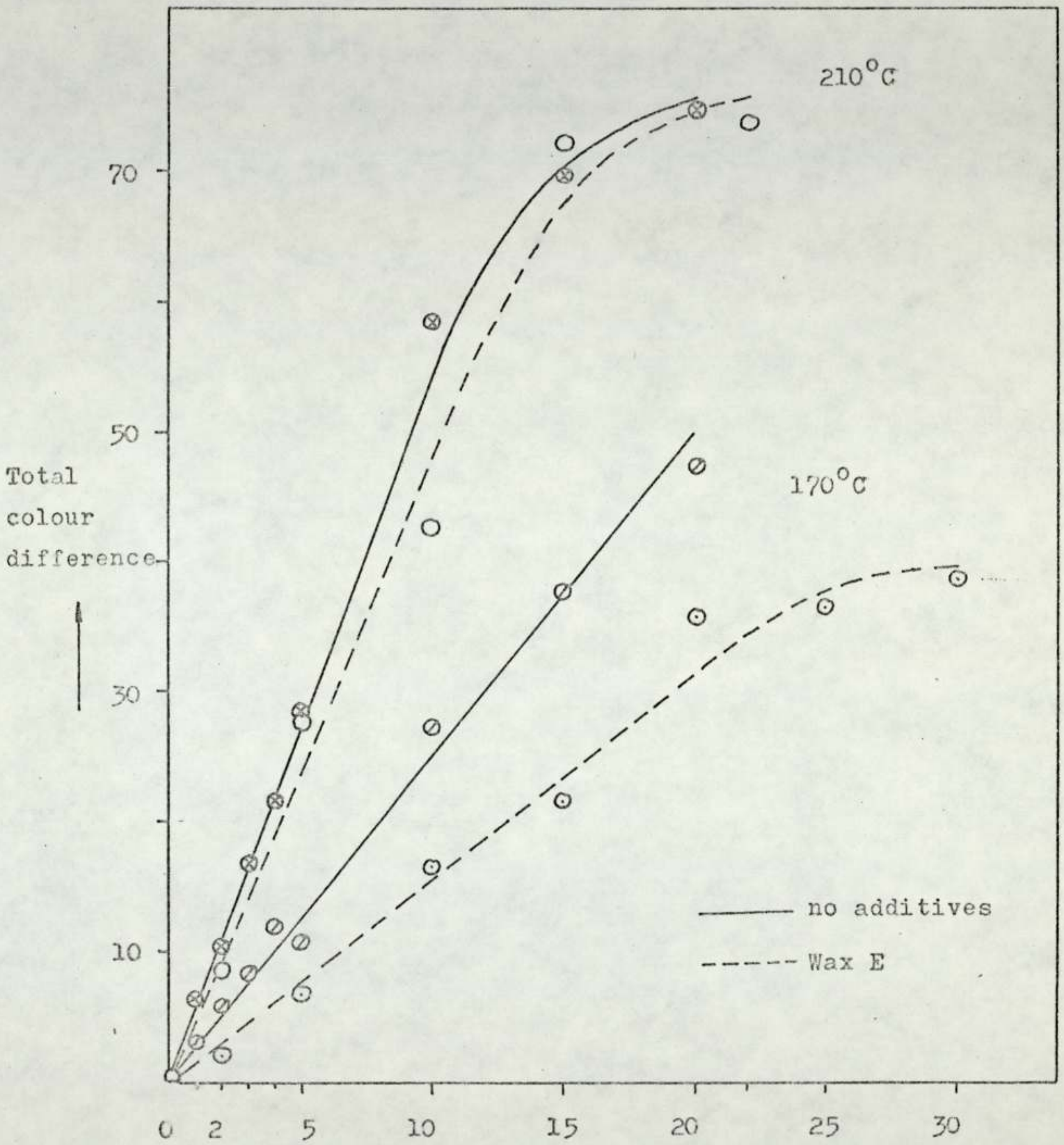


Fig.4-28

Unsaturation vs processing time of PVC processed with Wax E and also without the additives at 170°C and 210°C.

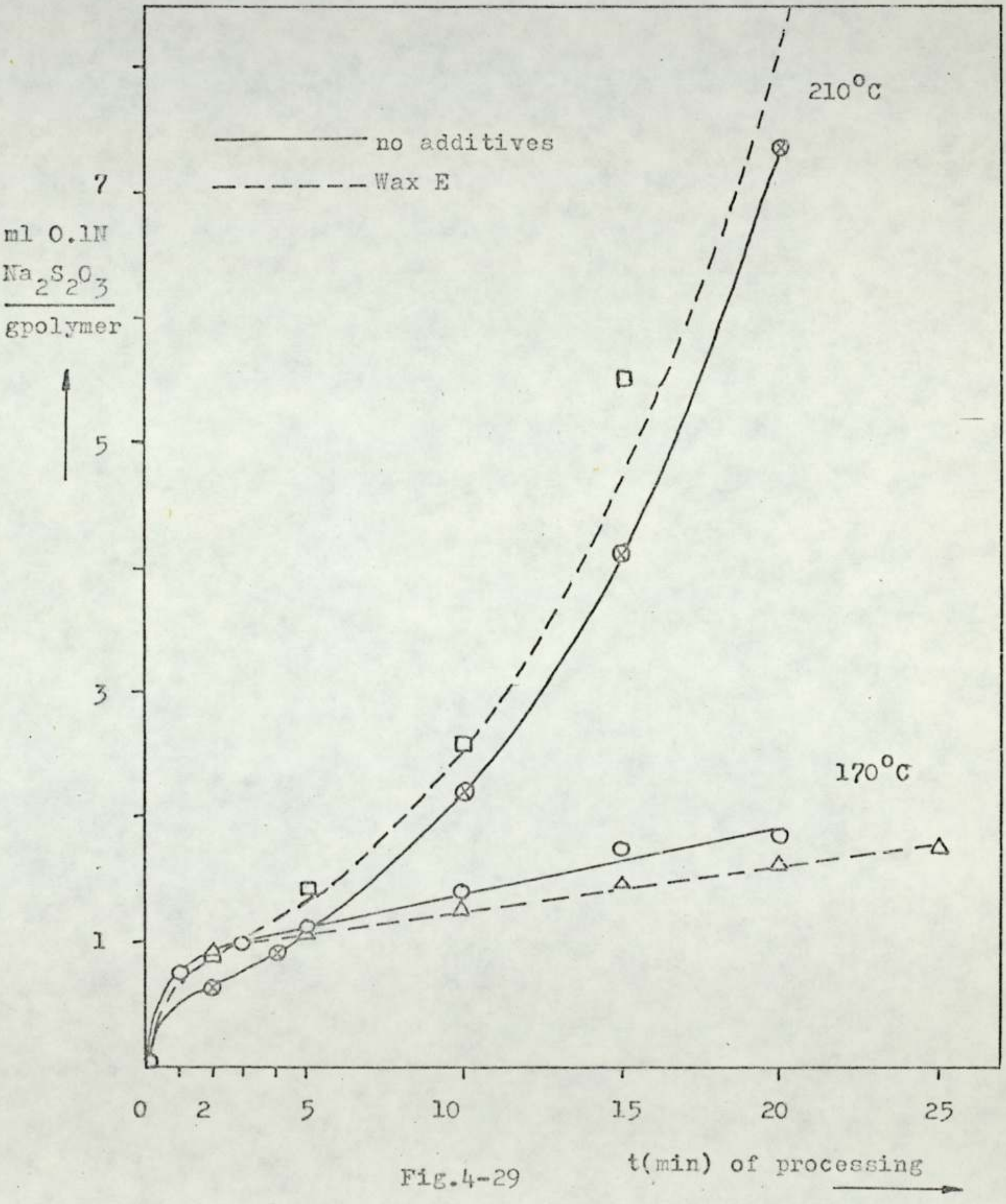


Fig.4-29

Carbonyl index $I_{CO}1720cm^{-1}$ and peroxide content of PVC processed with Wax E

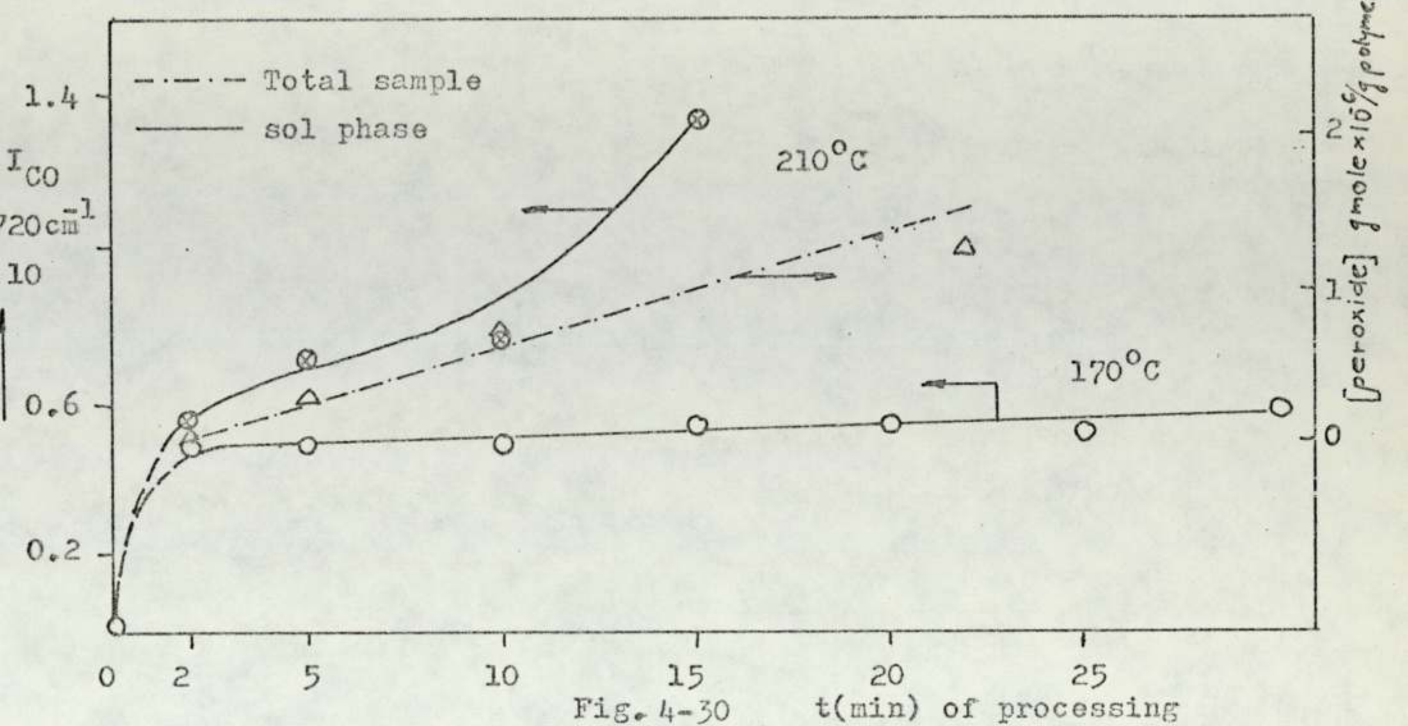


Fig. 4-30

$I_{2850cm^{-1}}$ index of PVC processed with Wax E at 170°C and 210°C, soluble phase

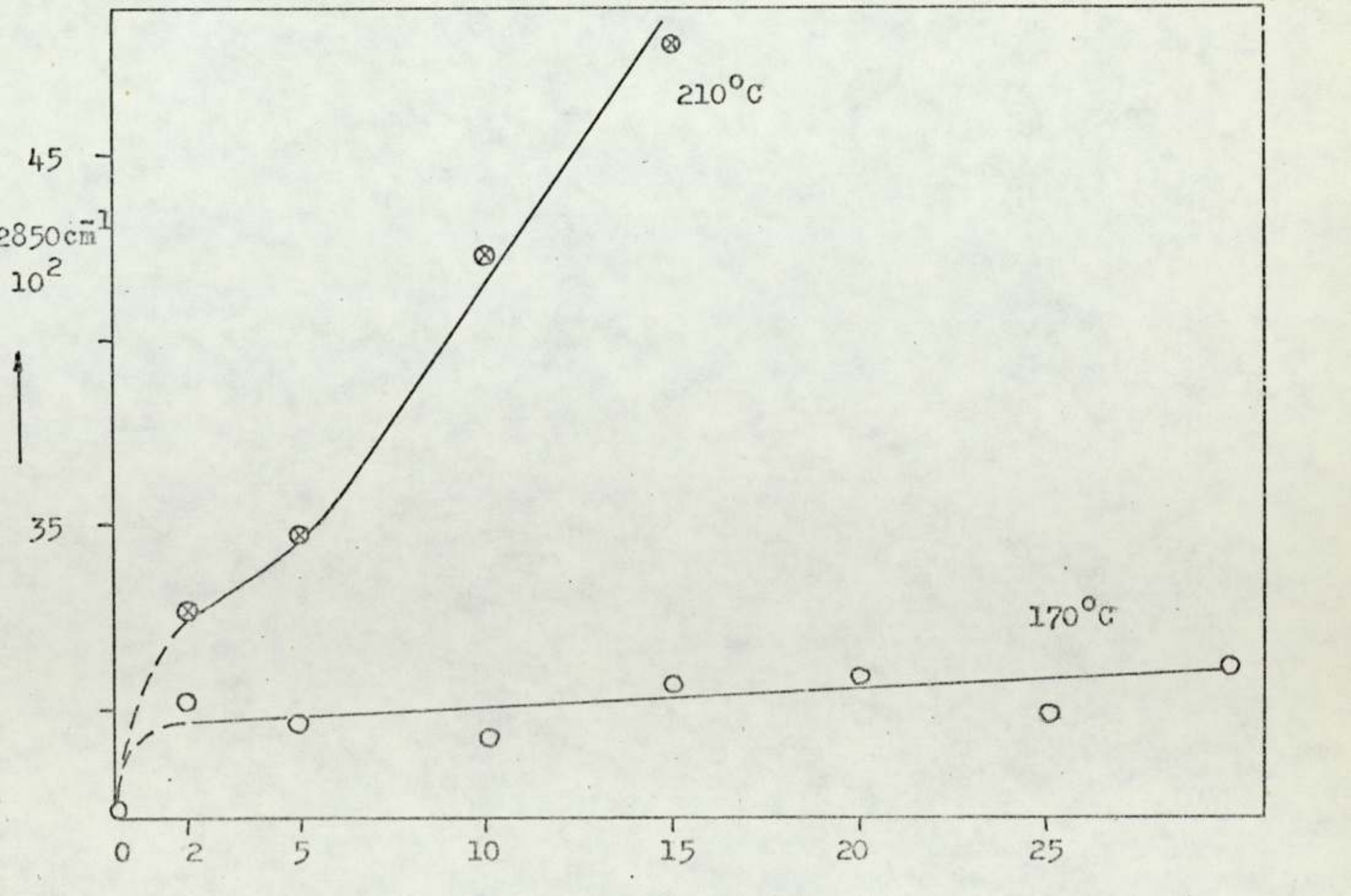


Fig. 4-31

UV-absorbance vs time of PVC processe~~e~~d with Wax E at 170°C and 210°C. (0.6% solution in CH_2Cl_2, 1mm cell used.)

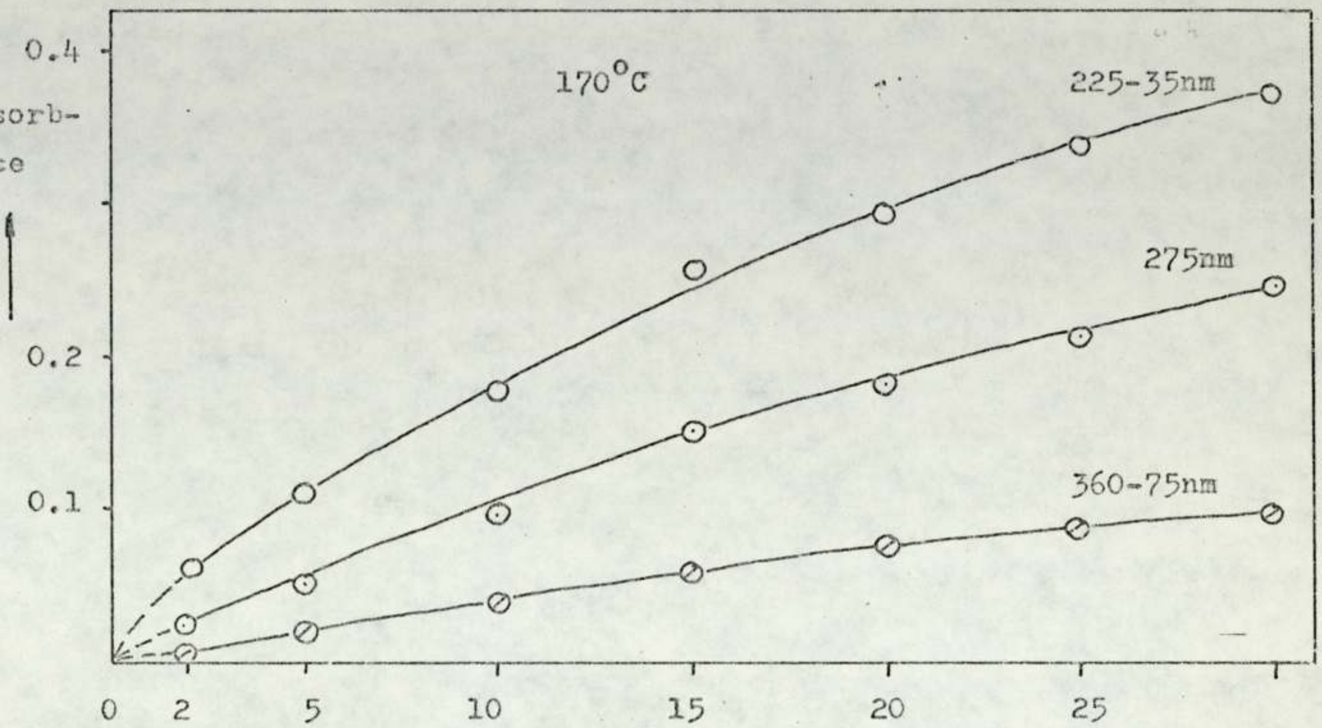


Fig. 4-32a

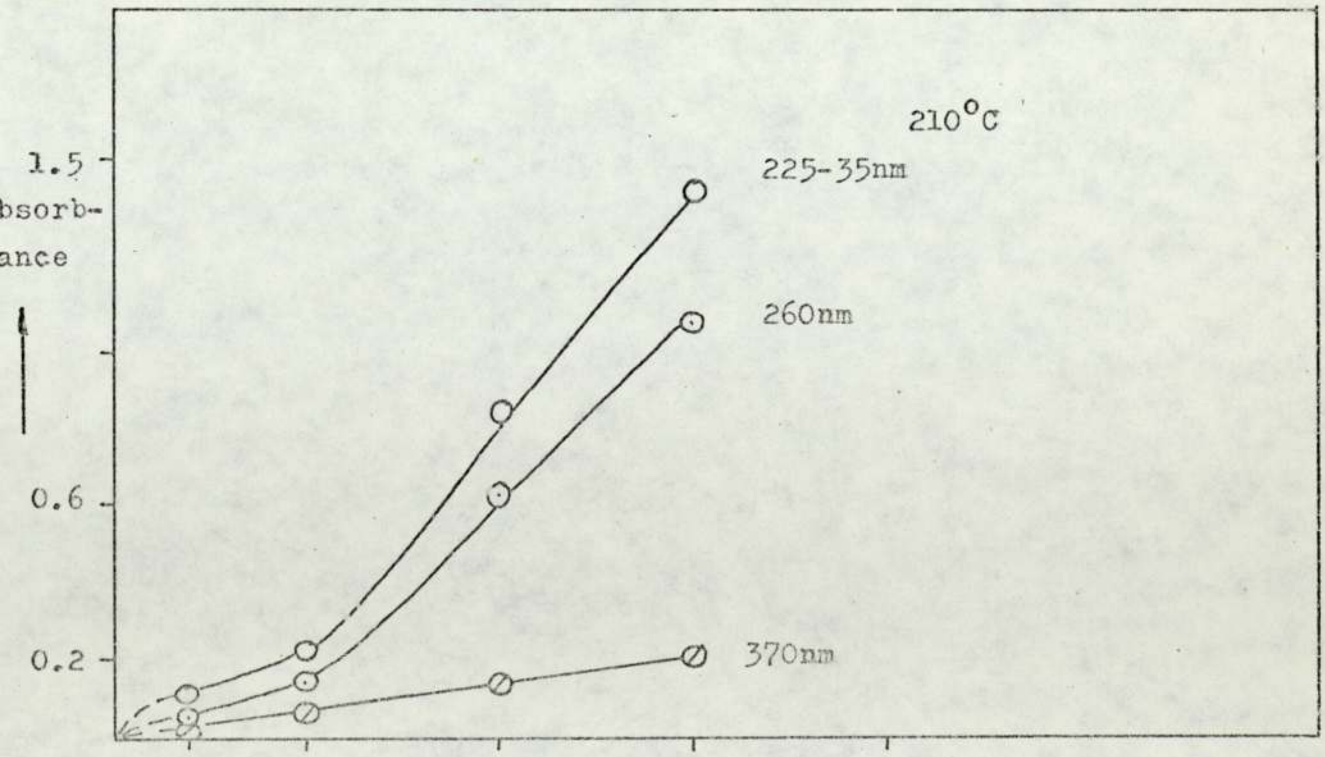


Fig. 4-32b

UV-absorbance at 310nm vs processing time of PVC processed with Wax E at 170°C and 210°C.
(0.6% solution in CH_2Cl_2,1mm cell used)

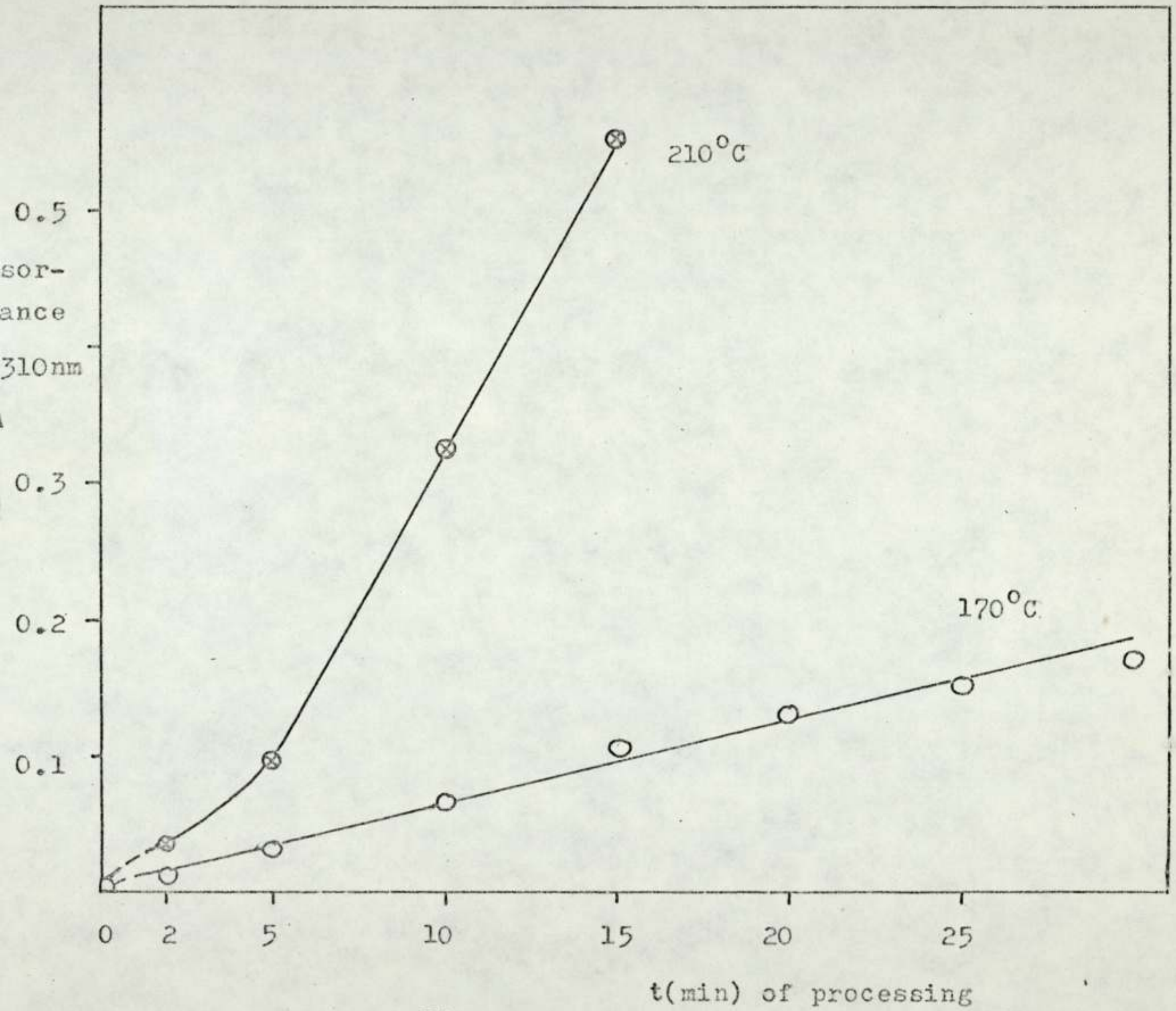


Fig.4-32c

Molecular weight distribution (MWD) of PVC processed with 0.65phr of Wax E (soluble part in CH_2Cl_2) at 170°C

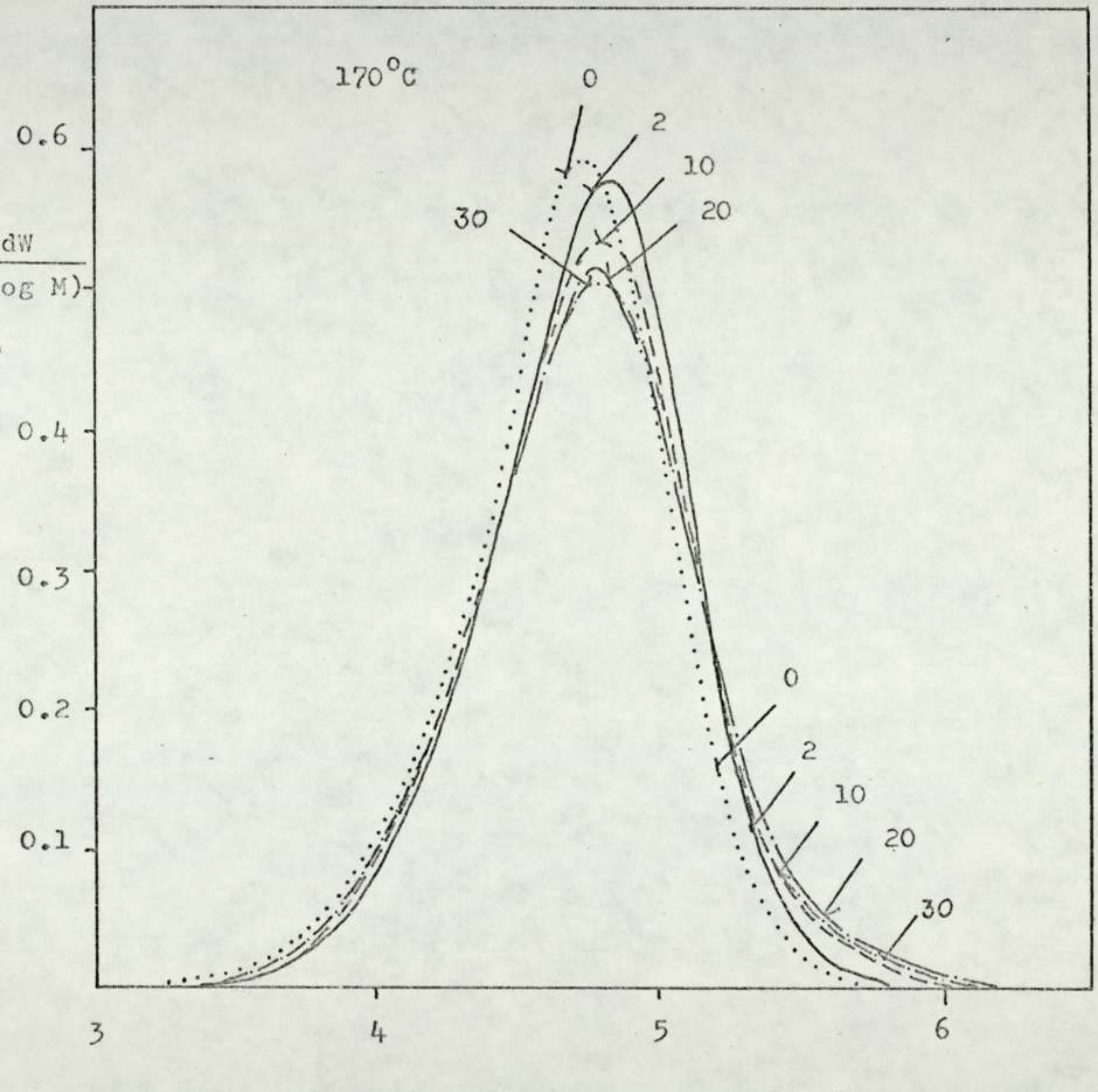


Fig. 4-33a

Molecular weight distribution (MWD) of PVC processed with 0.65phr of Wax E at 210°C (soluble part in CH_2Cl_2)

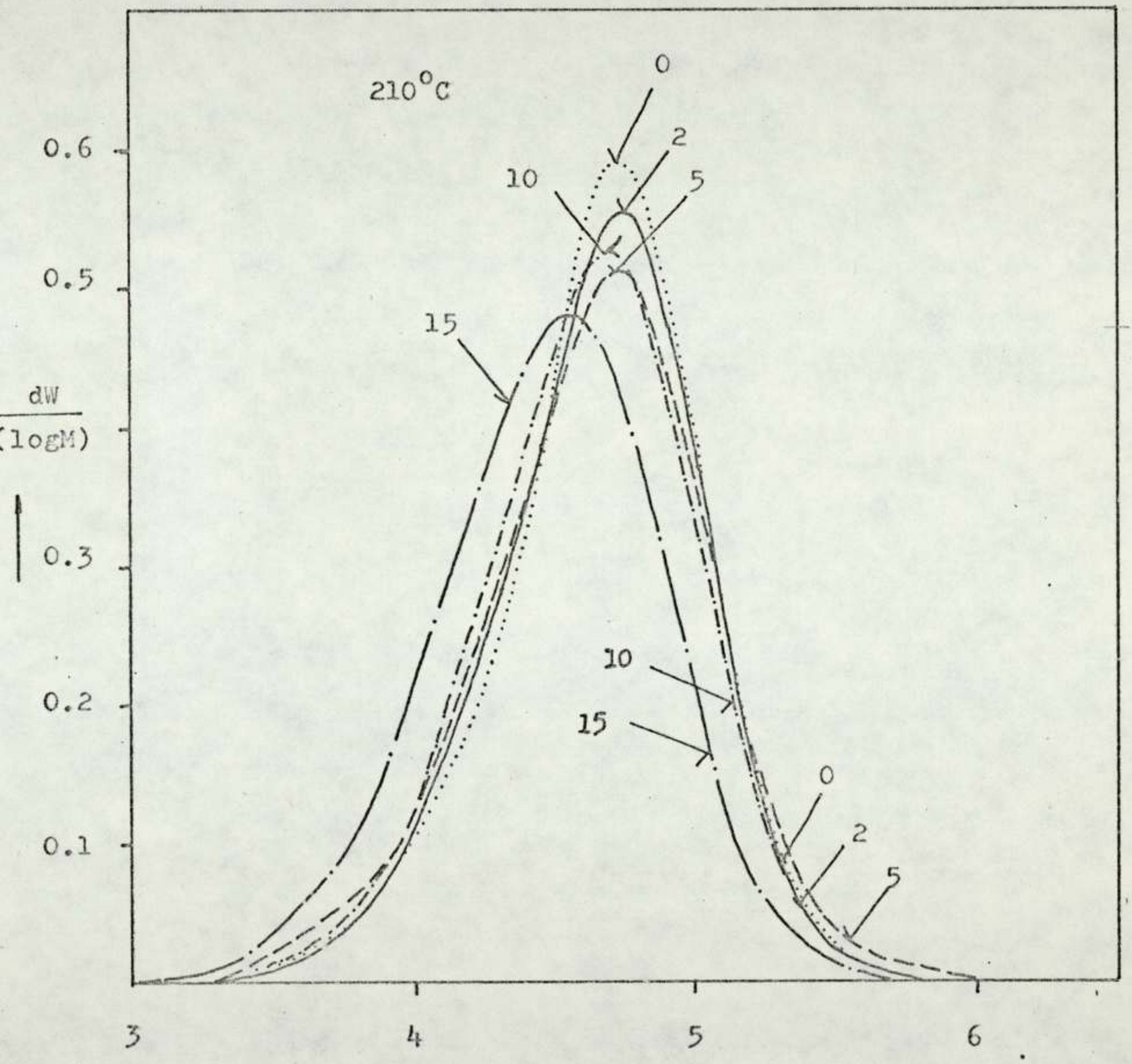


Fig.4-33b

4-4. PVC processed with 2.5phr of Irgastab T290, 0.8phr of Ca-stearate and 0.65phr of Wax E

The processing of PVC in the Rapra torque rheometer was described in previous section 1-3 of this chapter, with individual additives, namely dibutyltin maleate, Ca-stearate and Wax E. In this section the results obtained using these additives together are discussed. The experimental techniques used here were torque and the gel measurement, IR and UV-spectroscopy, colour change, unsaturation and peroxide content measurements, molecular weight determination. These were described earlier in the chapters 2 and 3.

4-4.1. Results

4-4.1.1. Torque and gel measurement

The torque and the gel content vs processing time for 170°C and 210°C are shown in Fig. 4-34. In both cases the torque increased to a maximum in the initial stage of processing and after the gelation decreased. At 170°C the torque slightly decreased within the 20min and with further processing it started to increase again. A small amount of gel (0.9-3.5%) was formed within this period. At 30min of processing the polymer contained 5.8% of the gel insoluble in CH_2Cl_2. It appears that there is an induction period of 20-25min for the increase of the torque and the gel formation.

At 210°C the torque started to increase again after 5-8min. The gel content was initially low (5-5.5%) but increased after 10min of processing and 74% was found at 22min. At this temperature it is apparent that the induction period of gel formation was 10min and 5-8min for the increase of the torque.

It should be pointed out that when the polymer was processed with Irgastab T290 without lubricants a similar induction period of the torque increase and also the gel formation (viz.Fig.4-1, section 4-1) was observed and therefore it appears that the presence of Ca-stearate here has no significant effect on the induction period, measured by the torque change and the gel increase.

4-4.1.2. Colour change

The total colour difference vs time for 170°C and 210°C is plotted in Fig. 4-35. It can be seen that there is a small initial increase within the first 2min for both temperatures. At lower temperature the colour remained constant up to 20min of processing. At 210°C, however, discolouration started to increase again especially after 10min and continued to increase with the higher rate up to 22min after which time processing was not continued. It is apparent that there is an induction period of 20min of colour formation at 170°C and 5-10min at 210°C. The observed induction period of colour formation is in good agreement with the induction period of the torque increase and the gel formation (viz. Fig. 4-34). Here again it may be pointed out that the induction period of colour formation is similar to the induction period which was observed when the polymer was processed with only the thermal stabilizer (viz. Fig. 4-2, section 4-1).

4-4.1.3. IR-spectroscopy results

Examination of the IR-spectra of processed polymer in the region of 1500-1900 cm^{-1} and which was previously shown (see section 4-1.1.3.) to be useful for following the changes during processing, revealed several absorption bands which were formed in the course of processing. An example of the observed absorption peaks is shown in Fig. 4-36 for the 210°C processing temperature.

The absorption peaks at 1778 cm^{-1} and 1848 cm^{-1} increased during processing as could be seen in Fig. 4-36. The formation of these peaks was also shown previously during processing of PVC with dibutyltin maleate alone (viz. Fig.4-3a, b and 4-8). They were attributed to the anhydride of maleic acid (see section 4-1.1.3.). The plot of the absorption at 1778 cm^{-1}, expressed as an index I_{CO}1778 cm^{-1} is shown in Fig. 4-37. Similar plots were obtained for the smaller absorption at 1848 cm^{-1} and therefore it is not shown here. The index increased at 170°C up to 20min after which time it increased more rapidly and reached a plateau at the longer processing time. At 210°C the rate by which it increased was considerably higher and reached the plateau at 10min. It should be noted that this plateau corresponds to the induction period of the gel formation and also to the increase of the discolouration (viz. Fig. 4-34,35).

Another absorption band formed during processing was centred at 1730-35 cm^{-1}. At 170°C this peak remained at this frequency within the 20-25min of processing. At 210°C this peak was also centred at 1730-35cm^{-1} within the induction period of 10min and with further processing the small shift towards 1740 cm^{-1} was observed. The plot of this absorption peak as an index I_{CO}1730-40 cm^{-1} is illustrated on Fig. 4-38. At 210°C the index rapidly increased immediately from the beginning of processing and reached the maximum at 10min. At 170°C the increase was slower up to 20min and at 25-30min the rate decreased. Similar peak was also observed when dibutyltin maleate was used alone (viz. section 4-1.1.3.) and also Ca-stearate (Fig. 4-19, section 4-2.1.2.). This absorption peak was attributed to the ester carbonyl peak and has been previously shown by other workers[43,60,61].

On Fig. 4-36 could also be seen a broad absorption peak centred at 1575 cm^{-1}. This peak decreased during processing significantly at 170°C and disappeared at 210°C. The similar behaviour was shown for the polymer processed with Irgastab T290 only (Fig. 4-3a, 4-5). The double peak at 1603 cm^{-1} and 1575 cm^{-1} was attributed to the carboxylate anion of the maleic moiety. When Ca-stearate was used alone, the double peak at 1572 cm^{-1} and 1535 cm^{-1} was observed (viz. Fig. 4-16). It is therefore apparent that the broad peak centred at 1575 cm^{-1} on Fig. 4-36 is of the carboxylate anion of dibutyltin maleate and Ca-stearate. The carboxylate absorption peak at 1575 cm^{-1} is plotted as an index $I_{COO}1575\ cm^{-1}$ in Fig. 4-39. At 210°C the index decreased rapidly within 10min and at 15min was not detected. At 170°C it decreased at the lower rate up to 20min and with further processing decreased more rapidly. It should be mentioned here that the carboxylate absorption was still present at 30-35min but the observed peak consisted of two bands centred at 1570-80 cm^{-1} and 1540 cm^{-1}. It was mentioned earlier that the carboxylate absorption of Ca-stearate exhibited double peak at 1572 cm^{-1} and 1535 cm^{-1} and therefore the carboxylate absorption which was still present after 30min at 170°C is considered to be of the unreacted Ca-stearate. This result suggests that the maleic carboxylate reacted preferentially over the carboxylate of Ca-stearate.

In the carbonyl region, besides the anhydride and esteric carbonyls, another absorption peak was detected at 1705 cm^{-1}. This peak could be seen on Fig. 4-36 and is also shown in Figs. 4-40a,b. This peak was not present within the induction period but it appeared at both temperatures towards the end of the induction period. This is illustrated in Figs. 4-40a,b. The formation of this absorption was described in the section 4-2 (viz. Fig. 4-17, 4-18) and was considered to be of the acid carbonyl of stearic acid which was formed by the reaction of Ca-stearate with HCl. From this result it may be suggested that during processing dibutyltin maleate is more reactive towards evolved HCl than Ca-stearate and is similar to the view mentioned above that maleate carboxylate is more reactive than the carboxylate of Ca-stearate.

IR-spectra of the total sample and especially of the gel phase also contained a broad absorption centred at 3450 cm^{-1}. This absorption was observed in the initial gel of the unstabilized processed polymer (see Fig. 3-8a, chapter 3) and this corresponded well with the initial peroxide maxima (see Fig. 3-7) found in the polymer using chemical method of determination. However, the same absorption peak was observed when the polymer was processed with Irgastab T290 (see Fig. 4-7a) and also with Ca-stearate (Fig. 4-20, 21), but the chemical analysis failed to identify the peroxide.

The peroxide was not found within the induction period, which will be described later (e.g. Fig. 4-43) and therefore it may be that the observed broad absorption at 3450 cm^{-1}, especially in the gel phase, is not of the OH stretching mode of the hydroperoxide.

4-4.1.4. Unsaturation and UV-spectroscopy results

Chemically measured unsaturation is shown in Fig. 4-41. The unsaturation increased initially for both temperatures and at 170°C it remained constant up to 20min. With continued processing, further increase was observed again after 20min. At 210°C the unsaturation increased at the higher rate after 5-10min and continued to increase at the higher rate up to 22min of processing.

The UV-spectra of 0.66% solutions in CH_2Cl_2 were obtained using 10mm and 1mm silica glass cells. For 170°C a broad absorption bands at 225-235nm, 275-285nm and a small ill-defined band centred at 375nm were observed. For 210°C above 300nm the ill-defined band was centred at 340nm. No significant absorption bands were observed between 300nm and 650nm, within which range the absorbance progressively decreased. The observed absorption bands are plotted vs processing time in Fig. 4-42a and 4-42b for 170°C and 210°C, respectively. At 170°C after the initial increase the absorbance remained constant up to 20min and with further processing again increased. At 210°C the absorbance increased significantly after 10min. It is apparent that there is an induction period for the UV-absorbance increase. These results are in a good agreement with observed induction period of the unsaturation measured chemically

(Fig. 4-41), gel formation and the torque increase (Fig.4-34), and discolouration (Fig. 4-35). Furthermore, it should be mentioned, that the results obtained above are similar to the results obtained with dibutyltin maleate. These were described in the section 4-1 (and see Figs. 4-11a,b).

Comparison of the absorbance at 310nm for both temperatures is shown in Fig. 4-42c. It should be pointed out that the plot of the unsaturation, measured chemically, is similar to the plot of the UV-absorbance on Fig. 4-42c. At 210°C the concentration of the gel phase increased rapidly after 10min (see Fig. 4-34). It is apparent that the rapid increase of the UV-absorbance especially after 10min comes from the smaller portion of the sample examined which was readily soluble in CH_2Cl_2. This result suggests the existence of a chain scission reaction. It is of interest to note that the similar increase of the UV-absorbance at 210°C was observed in the unstabilized polymer and the polymer processed with individual additives.

4-4.1.5. Peroxide determination

The peroxide content in the polymer was determined by the iodine-liberation method which was described in the section 3.1.1. The results are shown in Fig. 4-43. At lower temperature peroxide was not detected and at 210°C no peroxide was found up to 5min. With further processing the peroxide content increased up to 22min. after which time processing was not continued. It appears that there was no peroxide formed within the induction period. The similar results were obtained with the polymer processed with Irgastab T290 without the lubricants (see e.g. Fig.4-13).

4-4.1.6. Molecular weight distribution (MWD) results

MWD of the soluble phase are illustrated on Fig. 4-44a for 170°C and on Fig. 4-44b for 210°C, respectively. Soluble phase for 170°C represents between 99.1%-94.2% (2-35min) of the total sample and for 210°C between 97.5-26% (2-22min).

At lower temperature MWD contained higher molecular weight tail up to 35min. This results suggest that the molecular enlargement took place even within the induction period. At 210°C the higher molecular weight tail was present up to 10min and with further processing the shift of MWD towards the lower molecular weight region was observed. It appears that up to 10min the crosslinking or a chain extension reaction predominates and at the longer processing time also chain scission occurred.

Summary of the results

The torque and the gel measurement showed the existence of the induction period of 20min at 170°C and 5-10min at 210°C. The same induction period was demonstrated by the measurement of discolouration of the polymer during processing and by the unsaturation, measured chemically and also by the UV-absorbance results. The IR-spectroscopy results showed that during the induction period an anhydride was formed as a result of the reaction between Irgastab T290 and evolved HCl and also an ester was formed by the exchange of a labile chlorine atom with the carboxylate moiety of the thermal stabilizer. It was shown that the maleate carboxylate was more reactive than the carboxylate of the Ca-soap, which was found to be present even at 30-35min at 170°C. Stearic acid was formed only at the end of the induction period. The extent of the induction period was the same as the induction period observed with dibutyltin maleate alone. It is suggested that the role of Ca-stearate in the presence of Irgastab T290 is predominantly of the lubricant with more pronounced effect at the longer processing time. Molecular enlargement was observed within the induction period at both temperatures. The peroxide was observed at 210°C after the induction period and it increased with further processing. At the higher temperature the chain scission occurred after longer processing time.

Torque and the gel content vs time of PVC processed with 2.5phr Irgastab T290,0.8phr Ca-stearate and 0.65phr Wax E at 170°C and 210°C

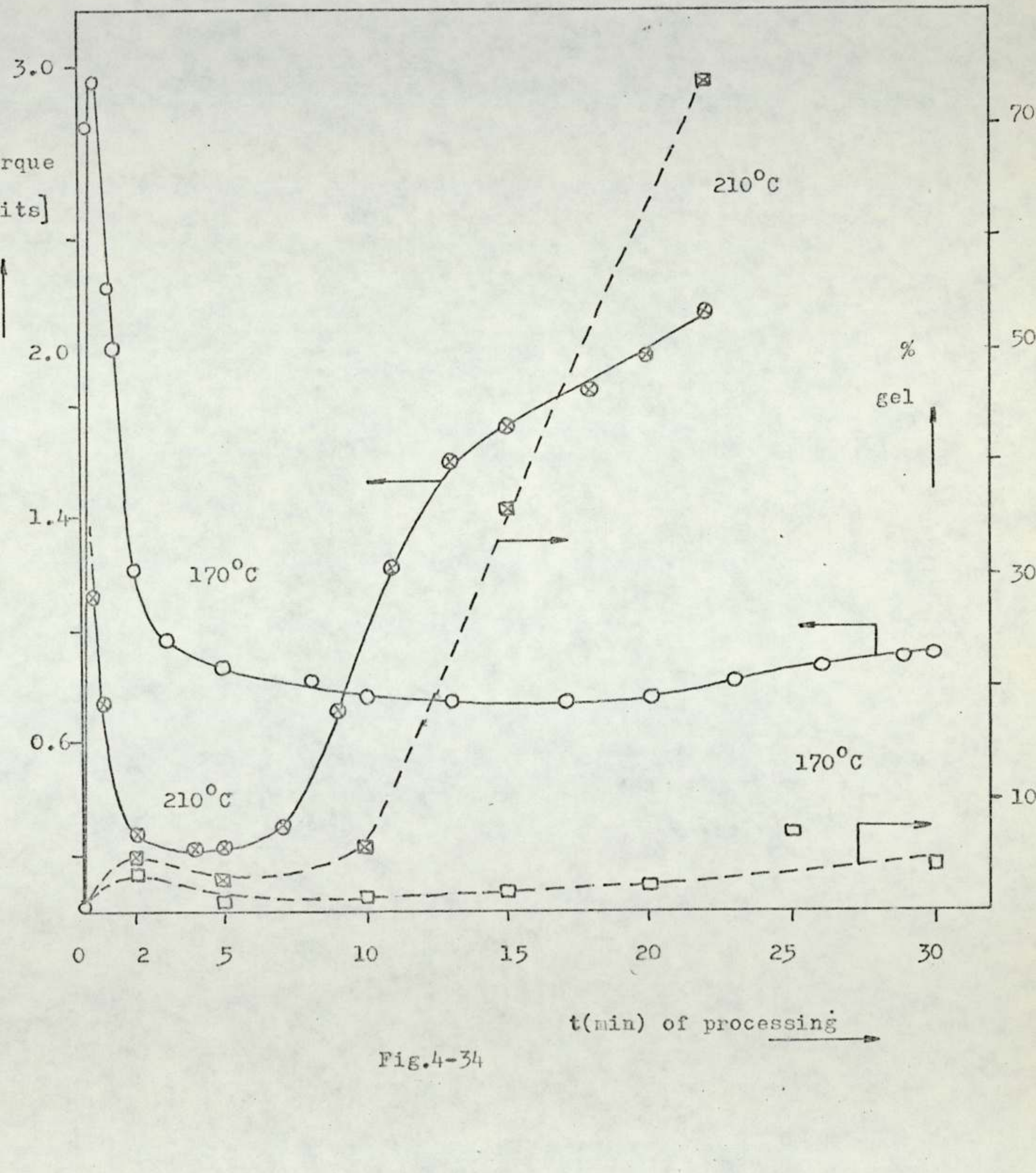


Fig.4-34

Colour change of PVC processed with Irgastab T290, Ca-stearate, and Wax E

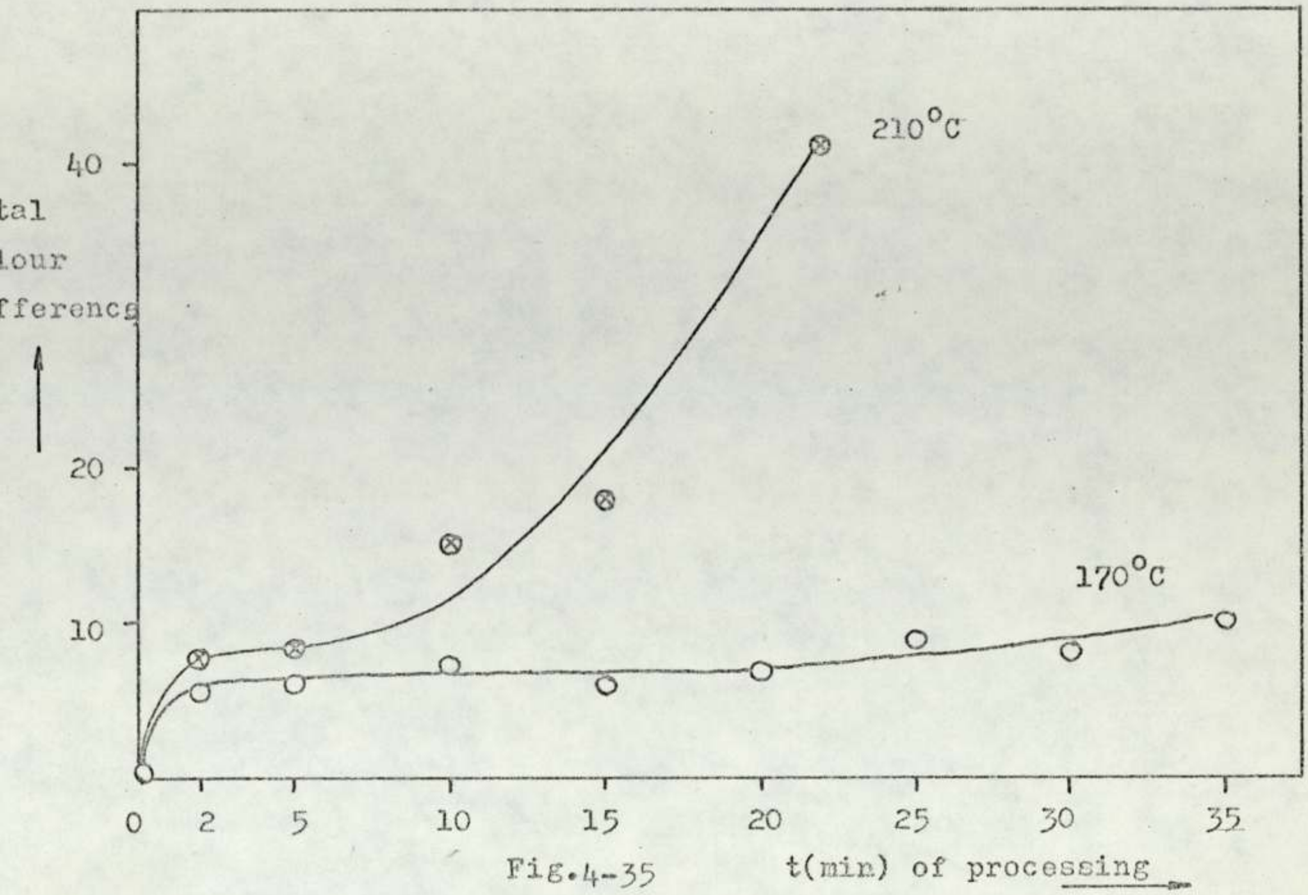


Fig.4-35

Carbonyl index $I_{CO}1778cm^{-1}$ of PVC processed with Irgastab T290, Ca-stearate and Wax E

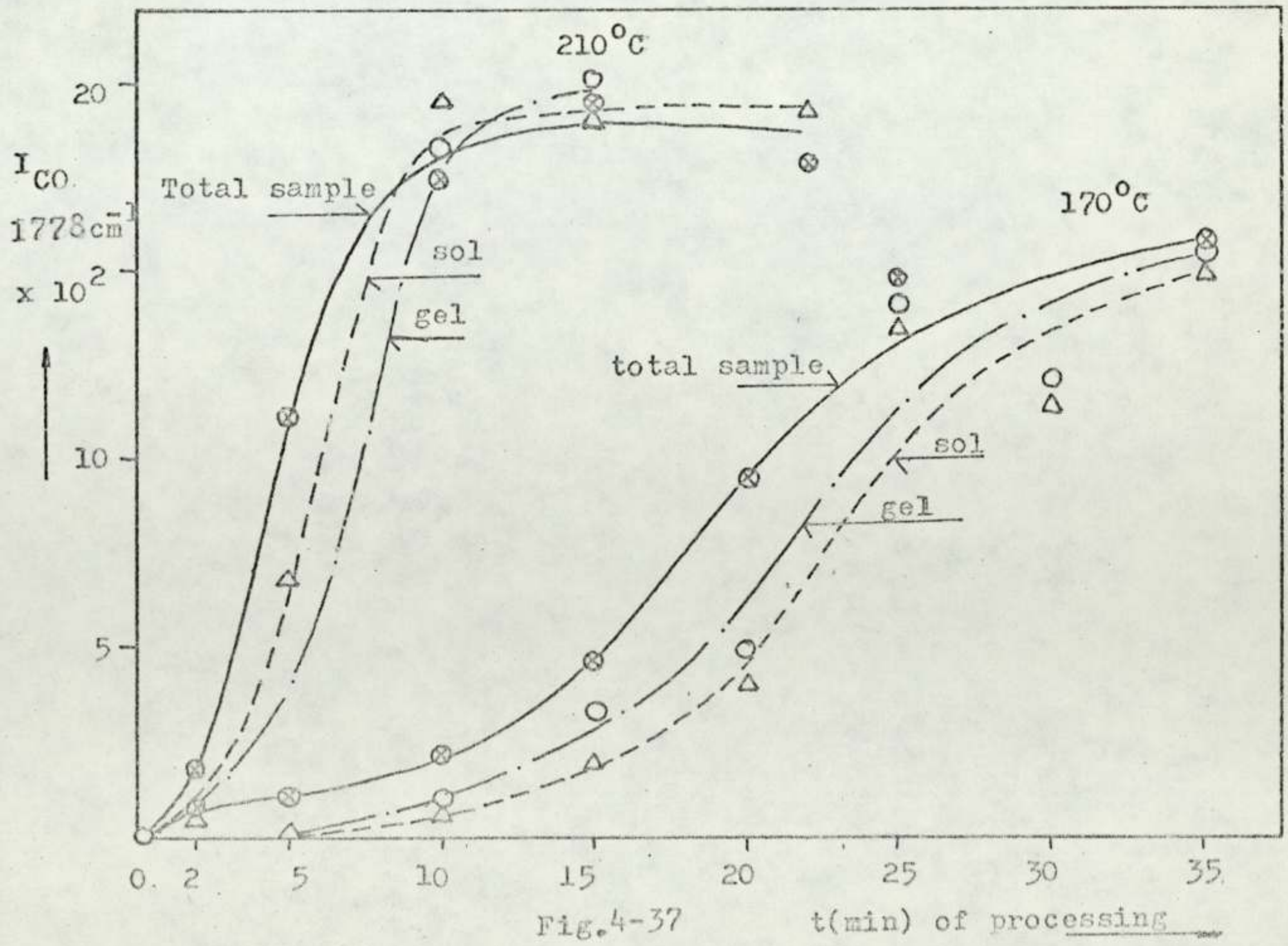


Fig.4-37

IR-spectra of PVC processed with 2.5phr of Irgastab T290, 0.8phr of Ca-stearate, 0.65phr of Wax E at 210°C, total sample

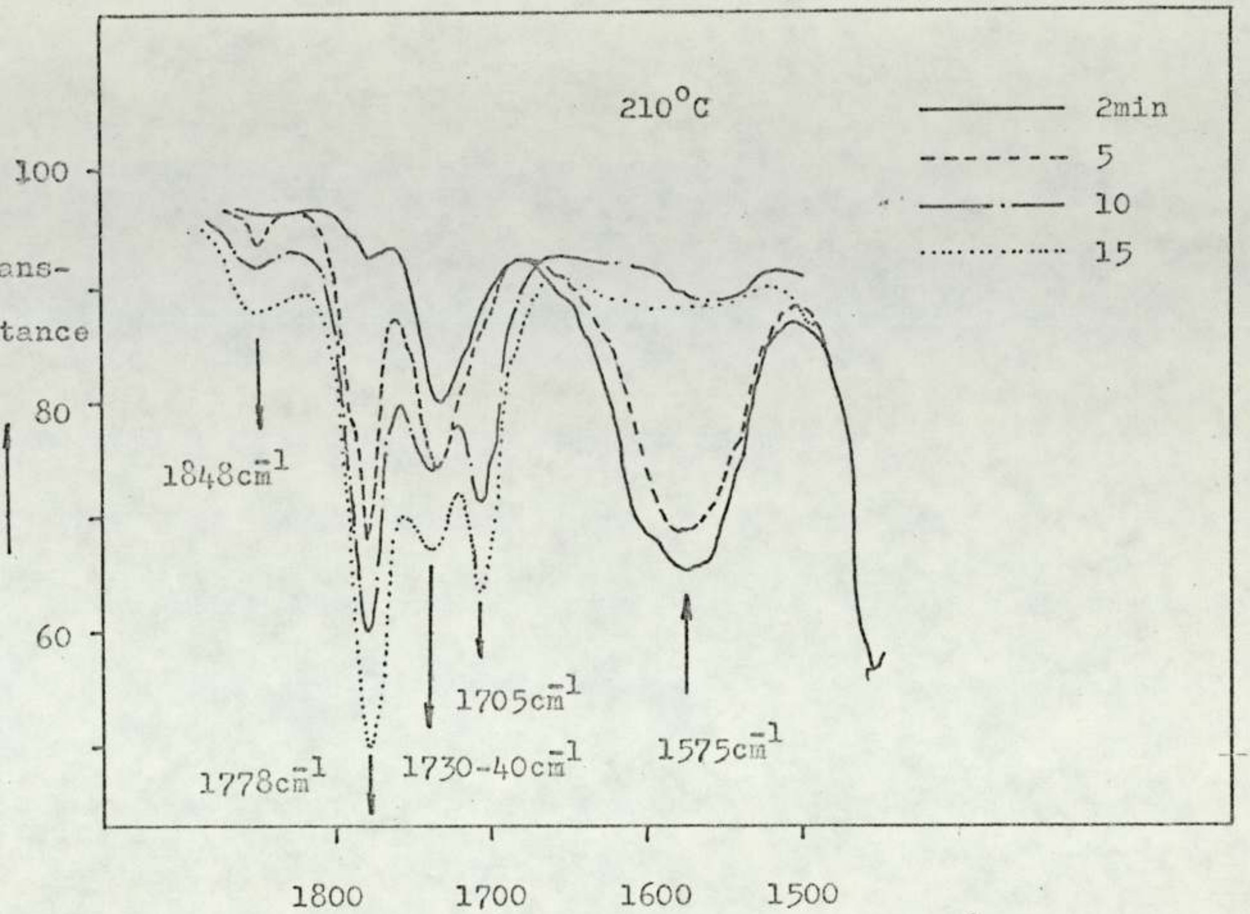


Fig.4-36

Carbonyl Index I_{CO} 1730-40cm^{-1} of PVC processed with Irgastab T290, Ca-stearate and Wax E

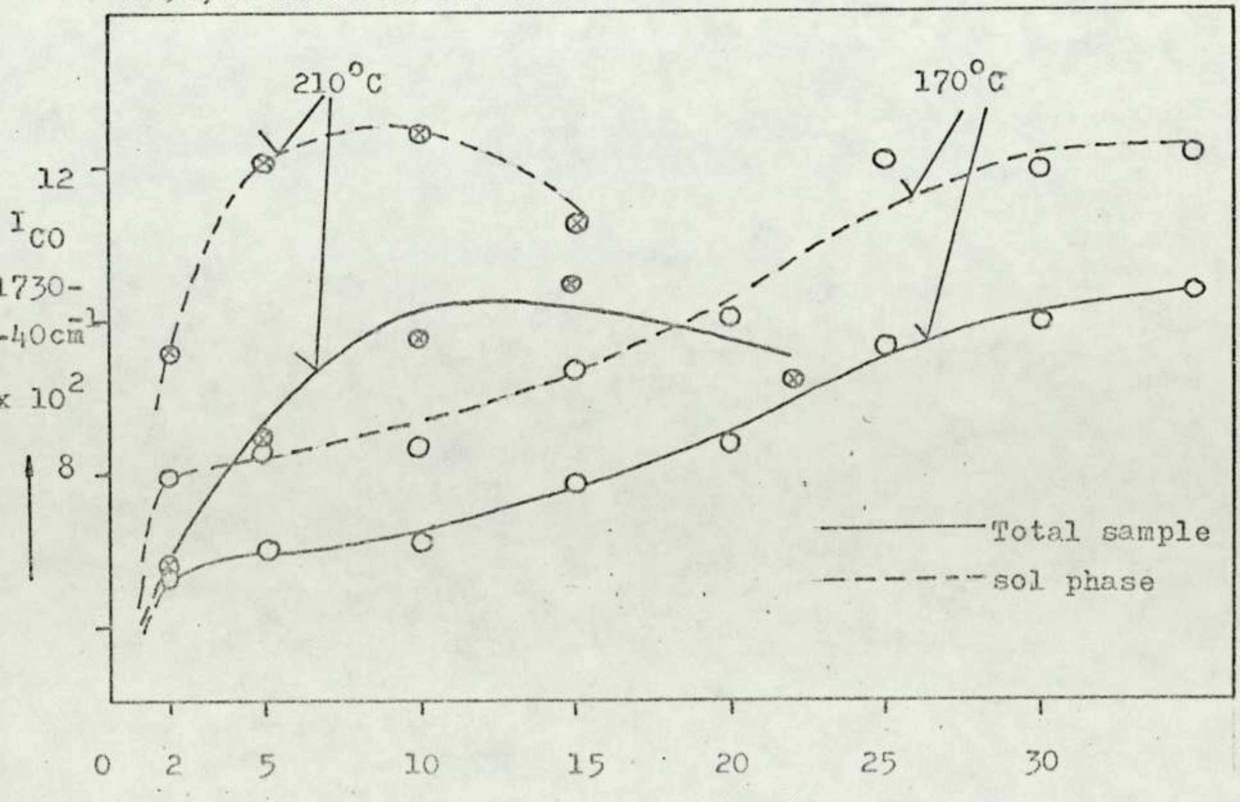


Fig.4-38

Carboxylate index I_{COO} 1575cm^{-1} of PVC processed with Irgastab T290, Ca-stearate and Wax E

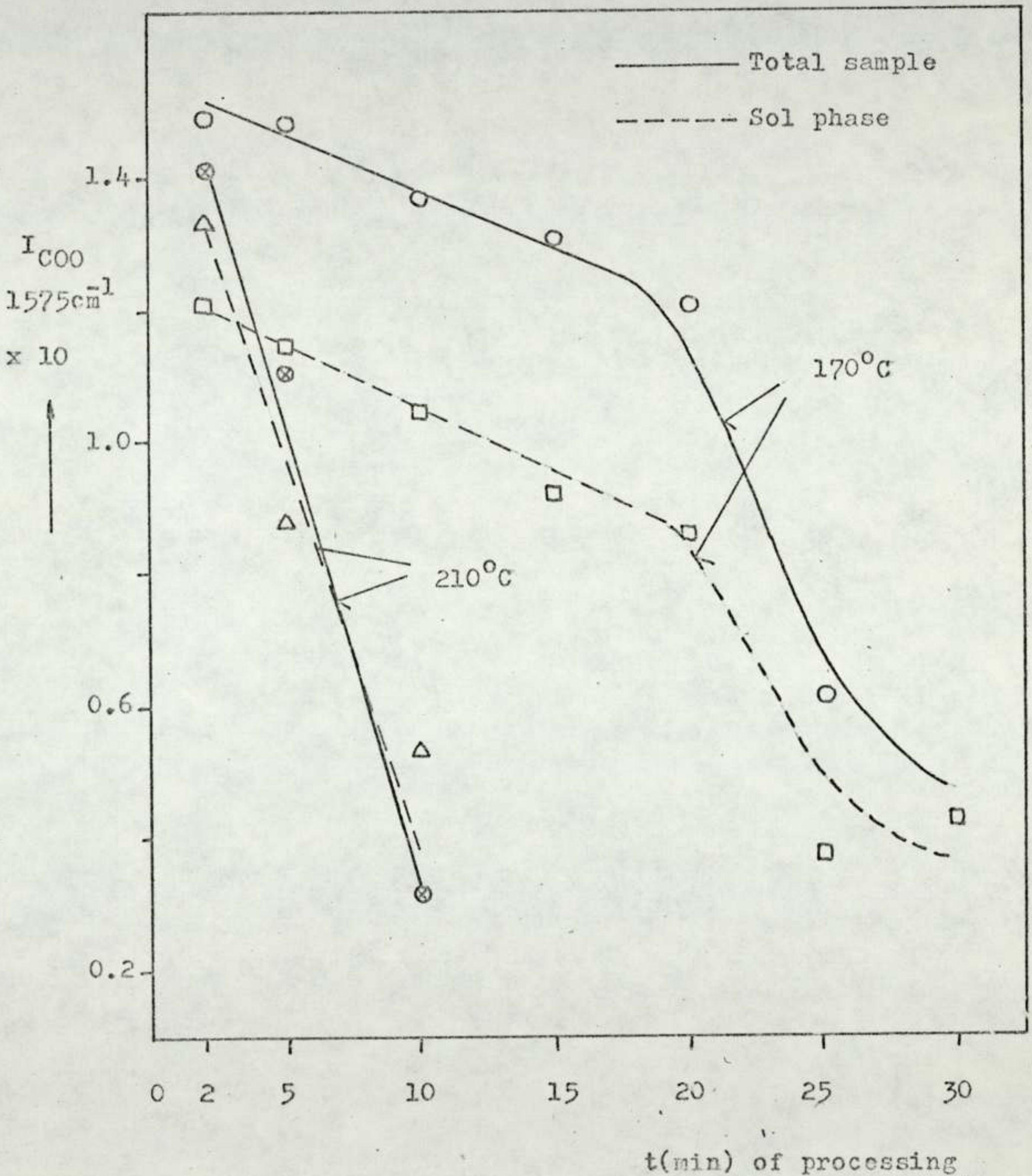


Fig. 4-39

IR-spectra of PVC processed with Irgastab T290, Ca-stearate and Wax E at 210°C and 170°C; formation of the absorption band at 1705cm^{-1}.

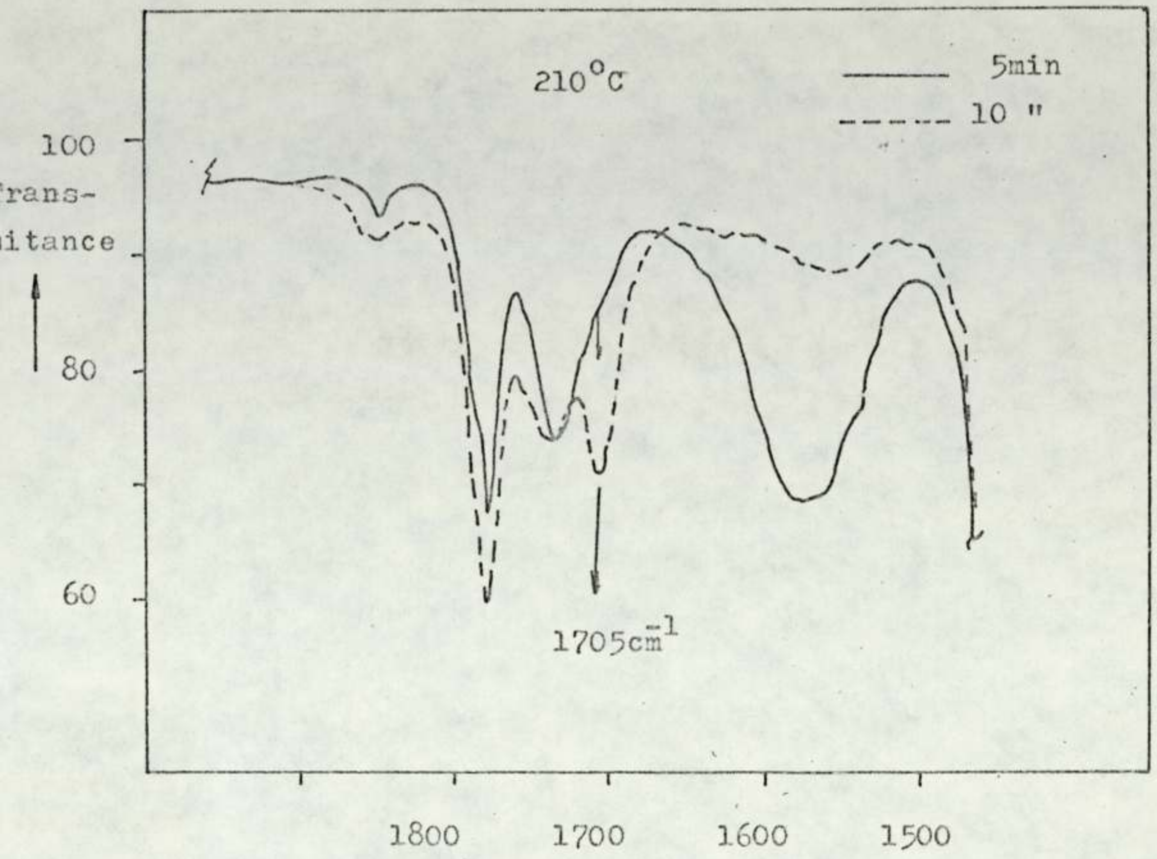


Fig. 4-40a

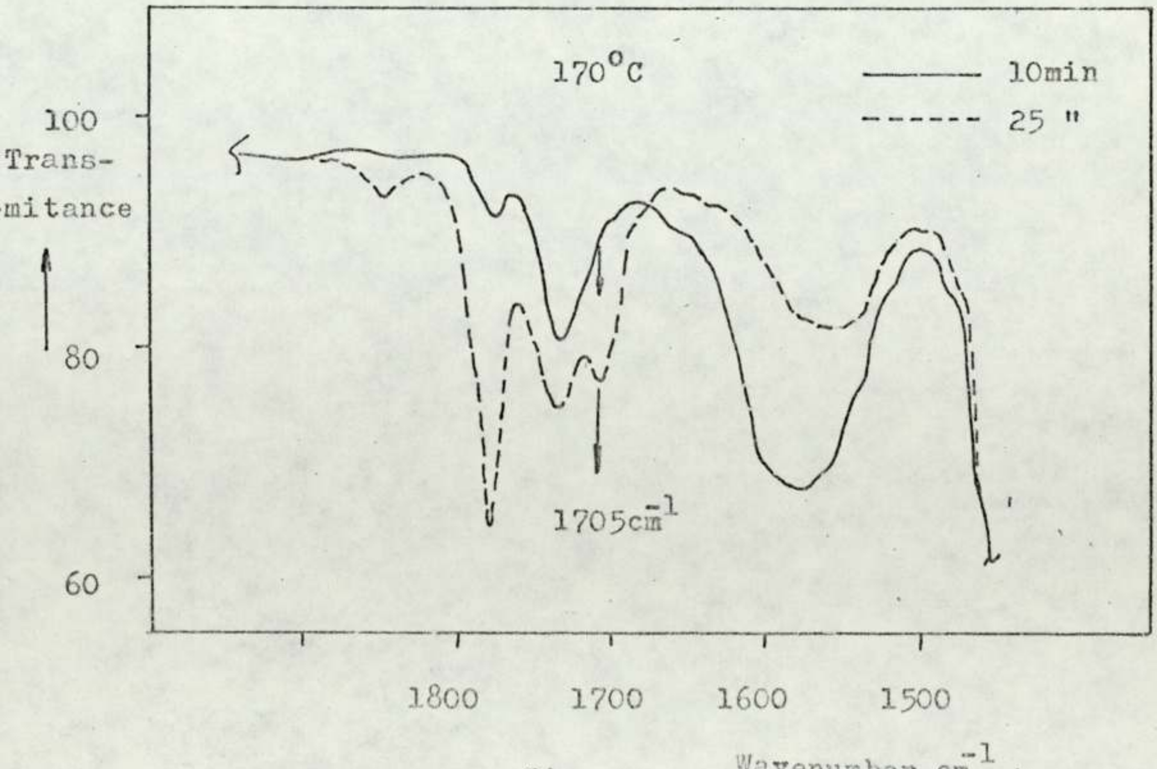


Fig.4-40b

Unsaturation in PVC processed with Irgastab T290, Ca-stearate, and Wax E

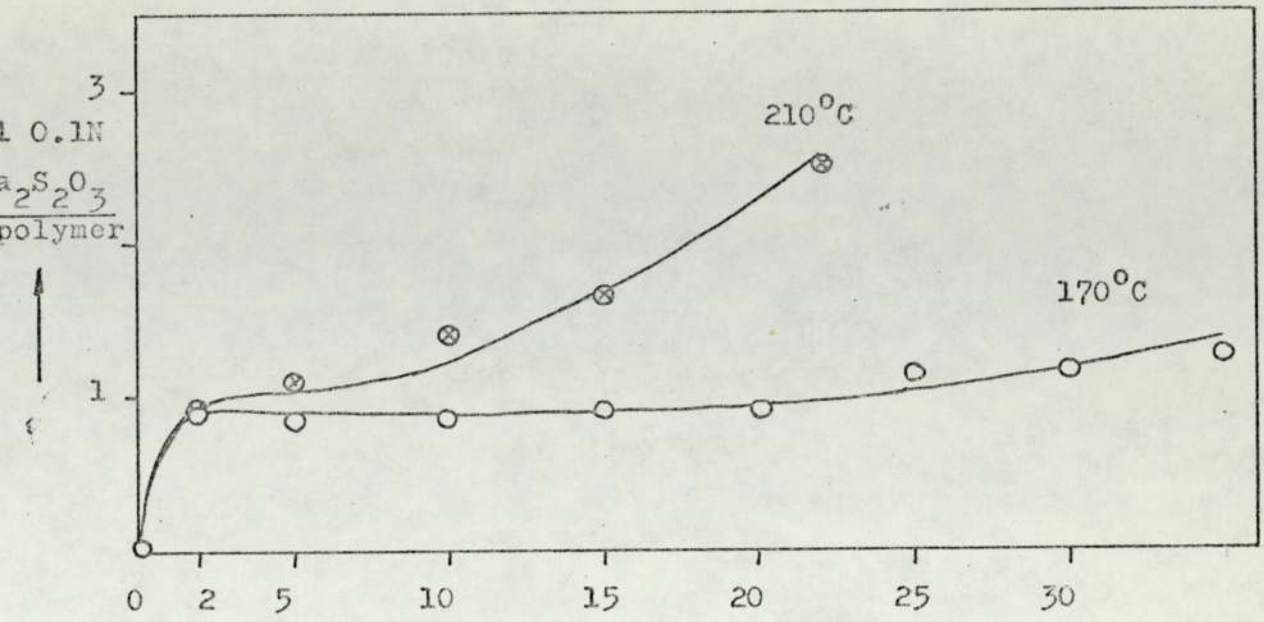


Fig. 4-41

UV-absorbance vs time of PVC processed with Irgastab T290, Ca-stearate and Wax E (0.6% solution in CH_2Cl_2), 1 & 10mm cell used

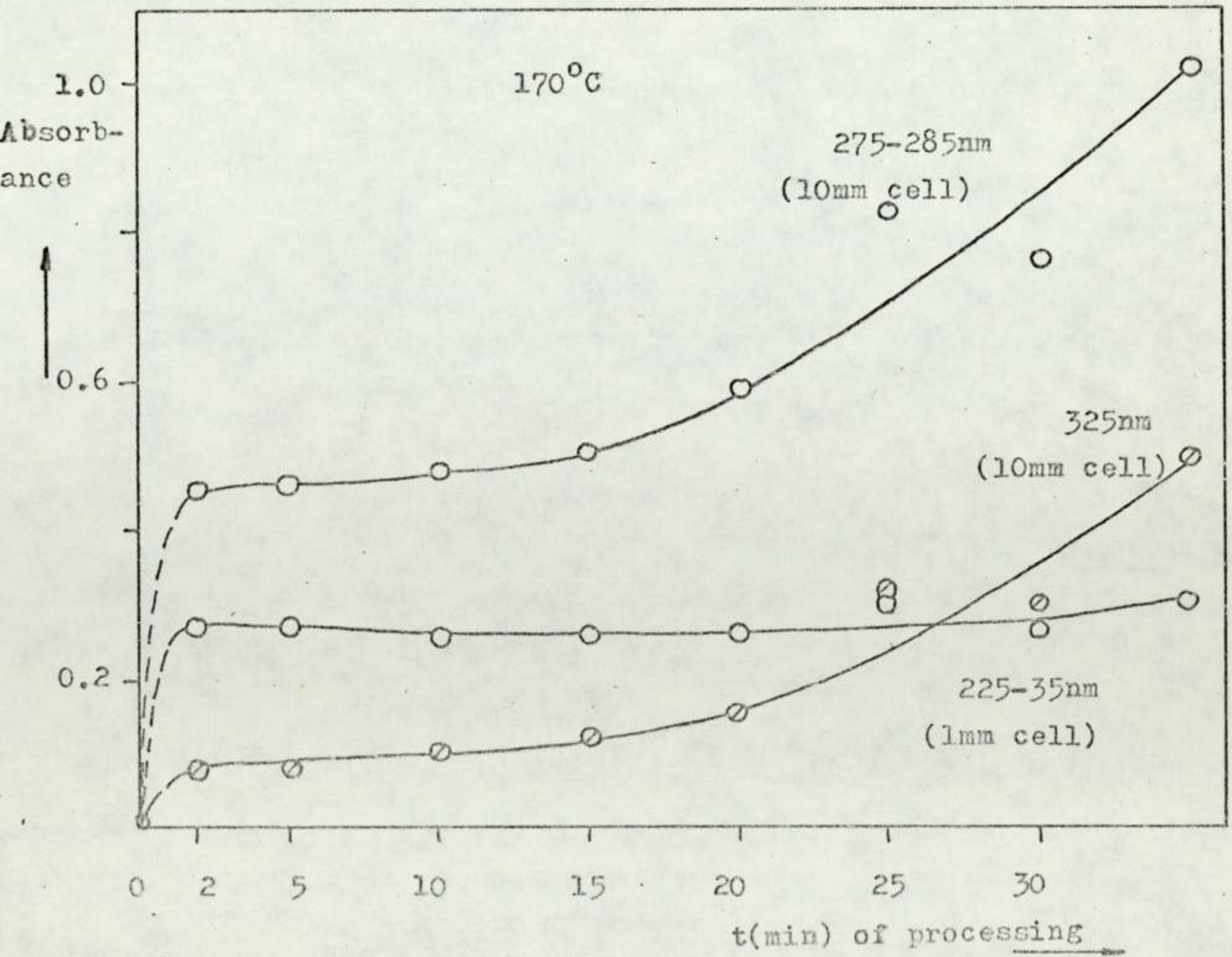


Fig.4-42a

UV-absorbance vs time of PVC processed with Irgastab T290, Ca-stearate and Wax E (0.6% solution in CH_2Cl_2), 1mm cell used.

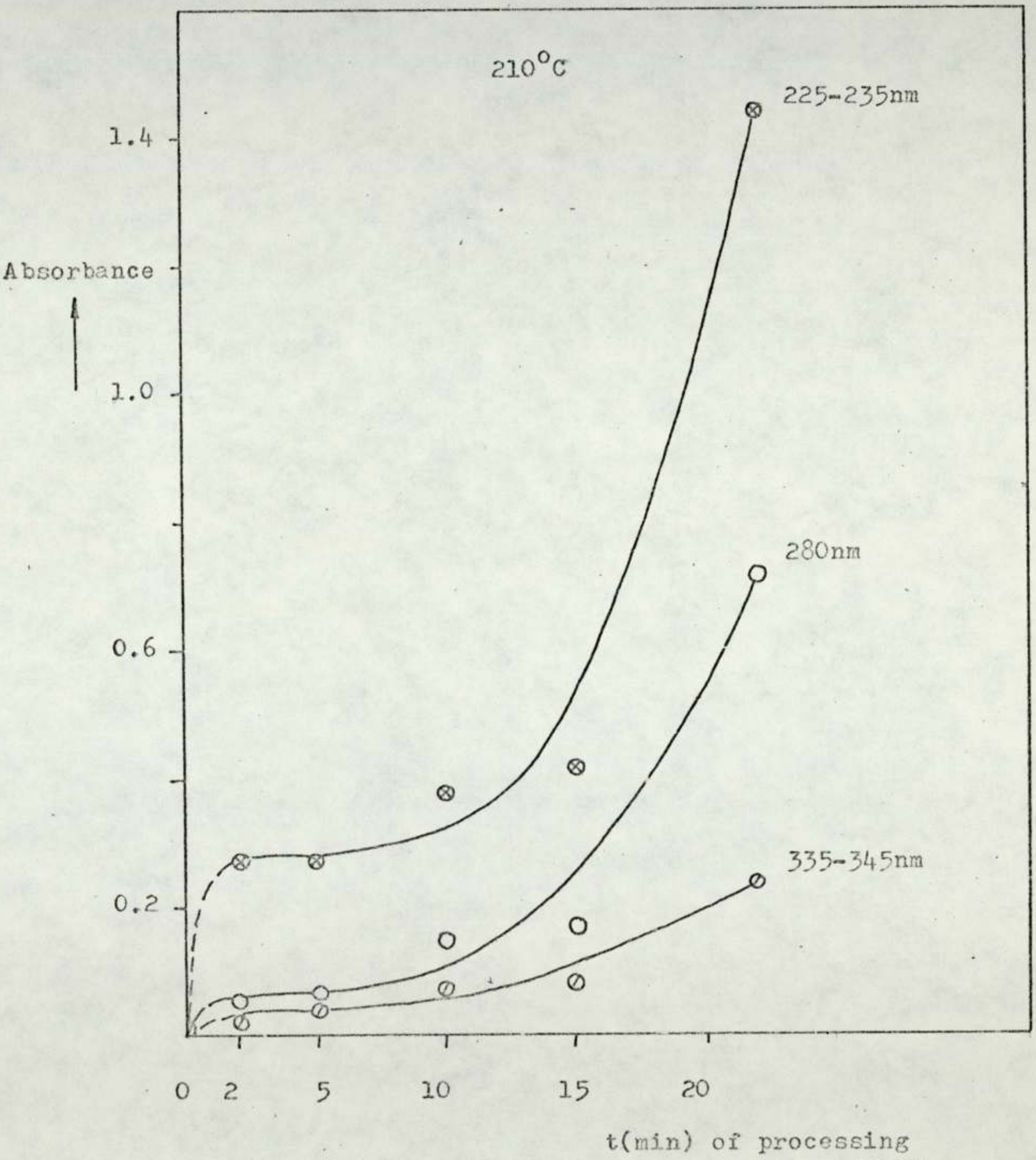


Fig.4-42b

UV-absorbance at 310nm vs time of PVC processed with Irgastab T290,Ca-stearate and Wax E.(0.6% solutions in CH_2Cl_2, 1mm cell used)

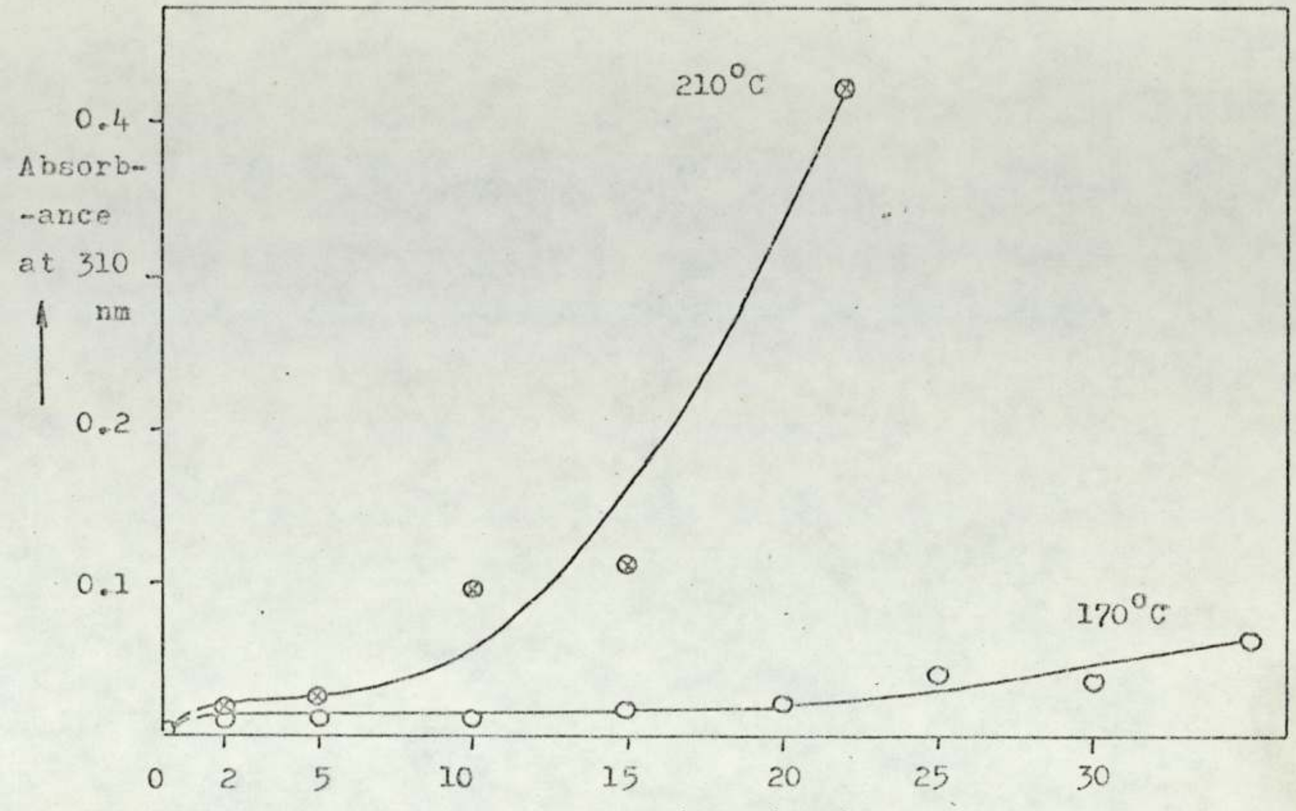


Fig. 4-42c t(min) of processing

Peroxide content of PVC processed with Irgastab T290,Ca--stearate and Wax E at 210°C and 170°C.

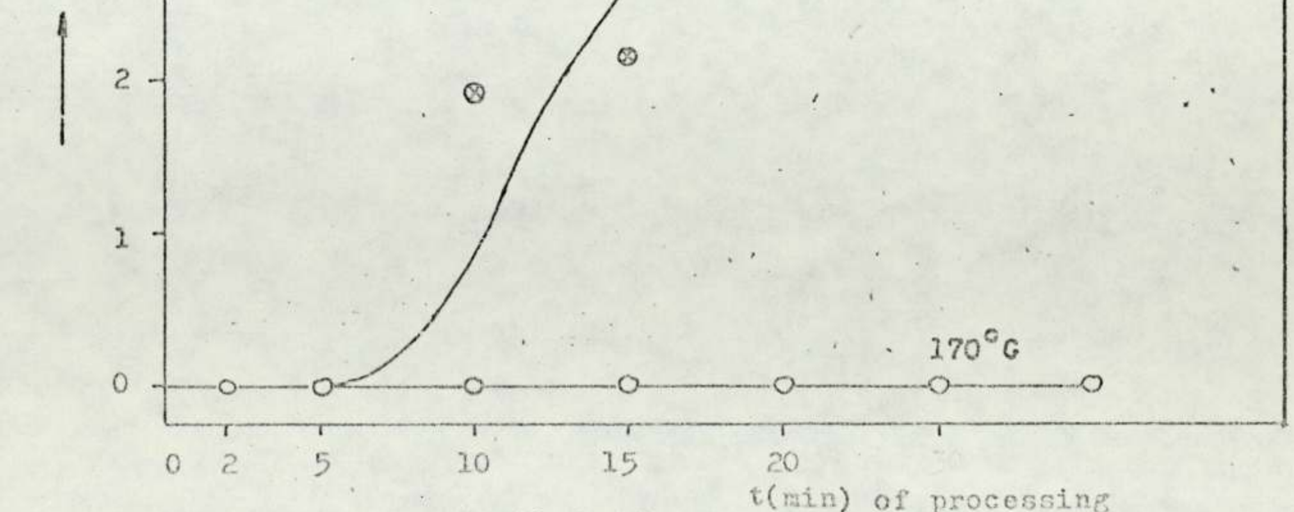


Fig.4-43

Molecular weight distribution (MWD) of PVC processed with Irgastab T290, Ca-stearate and Wax E at 170°C. (Soluble phase in CH_2Cl_2)

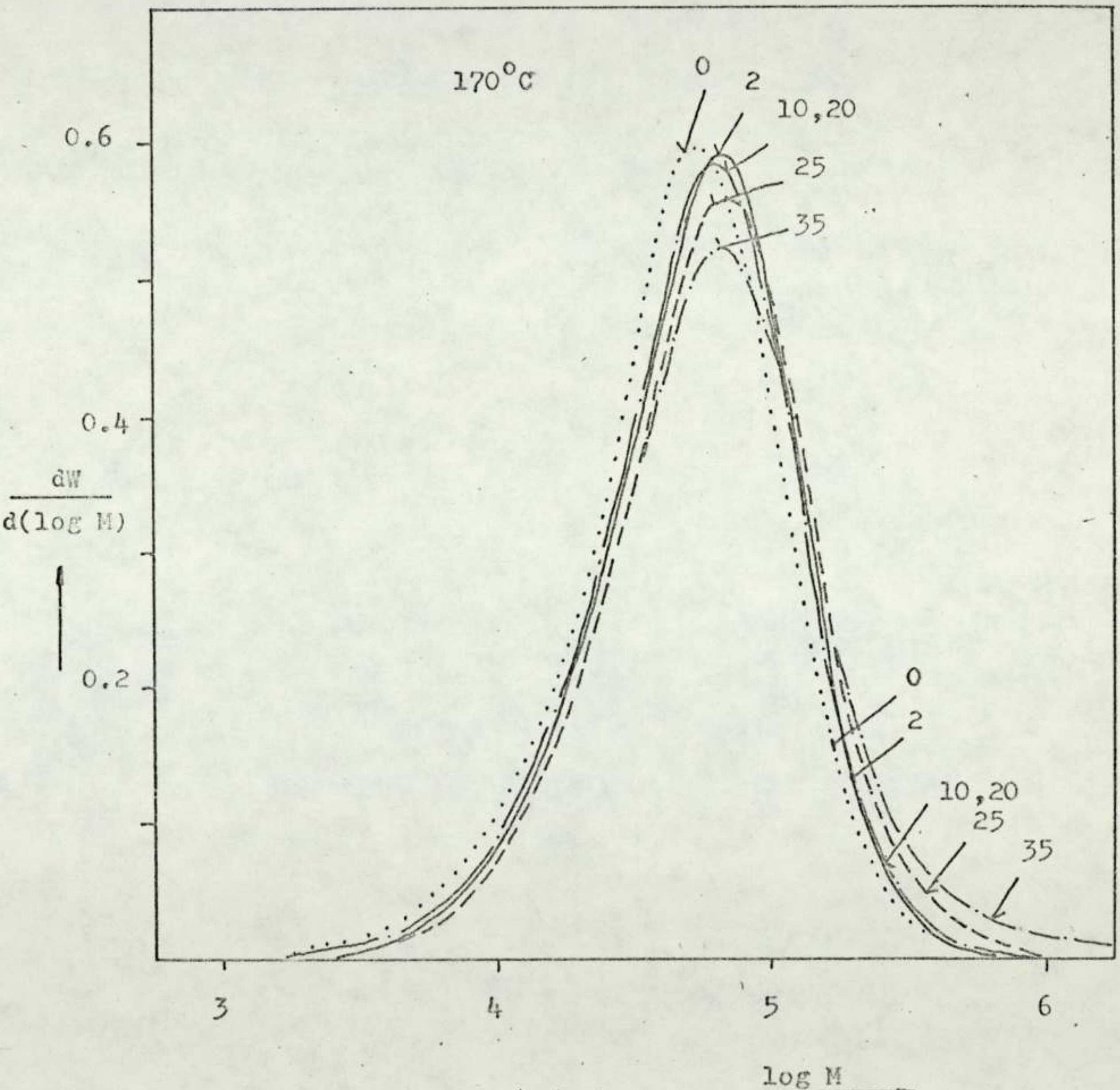


Fig. 4-44a

Molecular weight distribution (MWD) of PVC processed with Irgastab T290, Ca-stearate and Wax E at 210°C. (Soluble phase in CH_2Cl_2)

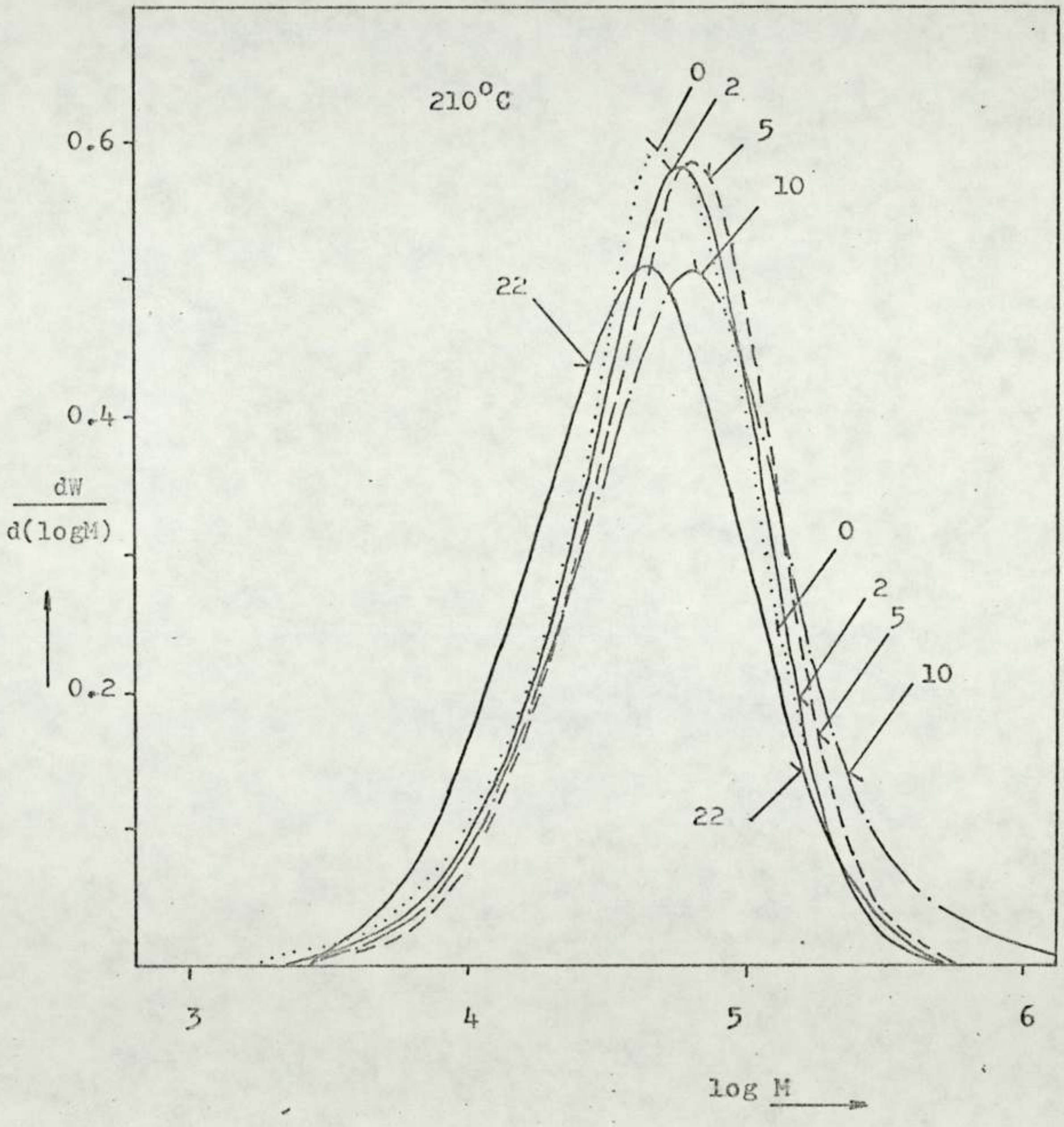


Fig.4-44b

CHAPTER 5. Mechanical properties of PVC processed without additives

The mechanical properties, namely elastic modulus and the dynamic mechanical loss ($\tan\delta_m$) were studied over the temperature range -100°C to +95°C-100°C. Also ~~an~~ impact strength data at room temperature were obtained. The apparatus and the sample used are described in the following experimental sections. It was shown in the chapter 3 that several chemical changes took place in the course of processing in the torque rheometer. Some of these were crosslinking, dehydrochlorination and chain scission and therefore it was of interest to study the effect of these structural changes on the mechanical (impact strength and elastic modulus) and dynamic mechanical properties (temperature dependance of $\tan\delta_m$ and elastic modulus). The samples chosen were those in which the structural changes were most pronounced, e.g. polymer processed without the additives at higher temperature. No difficulties were encountered during sample preparation even with higher gel content polymer and therefore the crosslinking density of samples examined was considered to be low.

5.1. Experimental methods

5-1.1. Dynamic mechanical properties

From dynamic mechanical test it was possible to obtain simultaneously an elastic modulus and the mechanical damping. They are ~~one of~~ the basic parameters which are used to study molecular motions in solid polymers. In this work "Rheovibron" model DDV-II (Toyo Measuring Instruments Co. Ltd.) dynamic viscoelastometer was used. This apparatus belongs to the group of forced vibration, non-resonance instruments. The purpose of this apparatus is to measure the temperature dependance of the complex modulus E^* of high polymers at a definite frequency. If sinusoidal tensile strain is applied on one end of the sample, the sinusoidal stress is generated at the other end of the sample and the phase angle δ is found between the strain and the stress. By use of this apparatus tan δ_m was read off directly on the meter and the dispersion curves (tan $_m$ vs temperature) can be plotted over the wide range of temperatures in a very short time. The storage modulus E' and the loss modulus E" can be calculated from the amplitude of stress and strain and δ value.

5-1.1.1. Sample preparation, test procedure and calculating equation

The processed polymer in the form of a powder was pressed for 1min at 170°C in an electric press and the sheets of processed samples were obtained. From these sheets the samples in the form of ~~a~~ strips were prepared. The dimensions of the strip samples were as follows: length 6cm, breadth 0.32 cm and the average thickness was 0.018 cm. The samples were then placed between two chucks in the temperature controlled chamber of the instrument and the procedure described in[66] the instruction manual was adopted. It is known[67] that the secondary transitions are more easily determined at lower frequencies and therefore the measurement was carried out at the oscillating frequency of 3.5Hz. The elastic modulus and the dissipation factor tan δ was measured in the temperature range -100°C to + 95°C-100°C.

The complex modulus E^*, which is given by the ratio of the maximum stress to the maximum strain, is expressed by the following equation[67]:

$$E = E^* = \sqrt{E'^2 + E''^2}$$

where E' = storage modulus

E'' = loss modulus

For the non-resonance forced-vibration instruments, the ratio of the loss and the storage modulus is equal to the damping term sometimes called dissipation factor (or loss tangent):

$$\tan\delta = \frac{E''}{E'}$$

The dissipation factor tan δ is proportional to the ratio of energy dissipated per cycle to the maximum potential energy stored during the cycle and, using Rheovibron viscoelastometer, is obtained directly[66]. The value of the modulus of elasticity measured by the Rheovibron was calculated using the following equation[66]:

$$E^* = \frac{2}{A.D-K} \times \frac{L}{S}$$

where L = sample length

S = sample cross-section area

A = amplitude correction factor

D = dynamic force

K = error constant due to the modulus of elasticity and displacement in the chuck rod and stress gauge (value of K = 28 was used)

The tensile storage modulus E' and loss modulus E'' can be obtained as follows:

$$E' = E^* \times \cos\delta \quad \text{and} \quad E'' = E' \times \tan\delta$$

In the region of the dynamic mechanical spectra, where the damping is low and therefore the value of $\cos\delta$ is near 1, the storage modulus E' is equal to the measured modulus E^*.

5-1.2 Impact strength measurement by Charpy impact tester

The principle of the Charpy notched impact test is to measure the absorbed energy during the fracture of polymer samples. Breaking energy is applied on the sample by the pendulum-type weight which strikes the specimen in the form of a simply supported cantilever beam of rectangular cross-section and known dimensions, in the middle. In order to encourage the specimen to break, it is provided in the middle with the notch.

The energy of fracture is equal to the energy stored in the weight less the energy remaining in the weight after the fracture:

$$\text{I.S.} = E - e/A$$

where E = energy stored in the pendulum
e = residual energy
A = fracture surface area

Residual energy is indicated by the height the pendulum ascends after the fracture and to avoid the necessity of subtraction, the "e" dial is graduated backwards. The following equation was used for the calculation:

$$\text{CH.N.I.S.} = \frac{\text{K x scale reading}}{t}$$

where K = constant depending on the pendulum weight used

t = thickness of the sample

Samples were prepared by the compression moulding and were notched by a cutter of a tip radius 0.25mm. The specimen size of the rectangular cross-section was 50mm x 6mm x 3mm and the depth to the tip of the notch was 3.5mm. At least 10 samples were used for each measurement.

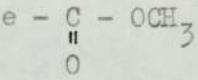
5-2. Results and discussion

The dynamic mechanical loss data (E' and tan δ at different temperatures) were obtained for the unprocessed PVC and for the series of processed polymer samples without additives with known gel content: 40.8%, 66.2% and 88.9%. The samples were processed for 10min, 15min and 20min at 210°C (viz Fig. 3-2, chapter 3). It should be pointed out that these samples may be regarded as being the polymers containing two distinct phases, namely crosslinked phase, which progressively increases, and the soluble phase (solvent CH_2Cl_2). Because of their identical chemical nature, they are intrinsically compatible.

The plot of tan δ_m and elastic modulus E' vs temperature is shown in Fig.5-1. Tan δ curve exhibited a broad peak between -110°C - +30°C and was centred at about -40°C and another peak of higher magnitude in the temperature region of +30°C - 96°C centred at 85°C - 95°C. The detailed illustration of the higher temperature peak is in Fig. 5-2. Previous mechanical and also dielectric studies have shown[68,69,70] that at least two relaxation processes, α and β occur in PVC. The higher temperature loss peak, viz e.g. Fig. 5-2, is designated as α-relaxation and is associated with glass-transition temperature (Tg). The smaller secondary transition at lower temperature, frequently found in other polymers, was first reported in the dynamic mechanical spectra of PVC by Schmieder and Wolf[71] and was described as β-relaxation (or transition). It should be noted that the magnitude of the β - transition (Fig.5-1) was not significantly affected by the processing and only a slight enlargement especially of the right side of the peak was observed. However, the minimum in tan δ between the α and β- peaks (further referred to as tan δ_{min}), which was situated at 30°C - 35°C, had changed when compared with the unprocessed polymer and is further illustrated in Fig. 5-3. The tan δ_{min} goes through the maximum at 10min of processing and its magnitude for all the samples examined is higher than that of unprocessed PVC.

Pezzin et al[69] have shown that tan δ_{min} was affected by thermal treatment (annealing and quenching) and cold drawing, but the β-peak was not affected by this treatment as well as by the increase of the crystallinity[69,70] and the changes in the local distribution of chlorine atoms[69] along the chain (for instance in the head-to-head structure of chlorinated polybutadiene). It has been shown to be influenced by the plasti~~z~~ciation, copolymerization and post-chlorination[69].

The secondary transitions in linear polymers are sometimes explained[75] by the motion of the small groups attached to the main chain, for example



$-\underset{\underset{O}{\|}}{C}-OCH_3$

side group in poly (methyl methacrylate), which has a broad secondary transition around 40°C or to the phenyl side group in poly (styrene).

The β-transition of PVC is most often explained[72,73,74] by the motion of short chain-sections of the main chain about two colinear bonds, in the manner of crankshaft. The interpretation of secondary transitions by Andrews[76,77] is based on the loosening of various types of intermolecular cohesive bondings (e.g. dipolar or hydrogen bonds) in the solid state. The chlorination of PVC was shown[69] to broaden the β-peak and displaced it ~~at~~ to higher temperature. This was explained to be due to ~~by~~ the decrease of the chain flexibility and it was concluded, in accordance with Andrews' theory, that the β-transition is due to a co-operative motion or to an association-dissociation process which was considered to be the breakdown of intermolecular bonding between C-Cl dipoles. Heidingfeld et al[78] interpreted the β-transition as a loosening of the weaker bonds between polarized methylene groups.

The magnitude of the β-peak (viz Fig.5-1) did not change by the processing and only the tan δ_{min} had changed as shown in Fig.5-3 where maximum at 10min was observed. Tan δ_{min} then decreased and therefore it is apparent that the β-peak became more pronounced. It was shown earlier in chapter 3 (see Fig. 3-13) that the MWD of the samples processed for 10min and especially for 15min and 20min contained low molecular species as the result of the chain scission. It may be that the mobility of the short-chain segments of the lower molecular weight species is higher than the high molecular weight species initially present and the more pronounced β-peak, as described above, was observed.

The decrease of the modulus E' in the α- transition region was slower (see Fig. 5-1) for the polymer containing higher amount of the gel and therefore for more crosslinked polymer. Furthermore, the α-peak (see Fig. 5-2) was shifted from 85.8°C to 95.5°C and appeared to be broadened especially for 20min sample.

The α-relaxation (Tg) was attributed[74] to co-ordinated motion of a large number of carbon atoms (perhaps 50-100) and attached pendant groups about the chain axis. It has previously been shown[69,78] that chlorination increased the glass transition temperature and Tg was connected[78] with the presence of bonds between the C-Cl dipoles which tend to dissociate in the Tg region. It has been also previously demonstrated[69,70,78] that the increase of the crystallinity increased the Tg. The effect of MWD on the mechanical α-relaxation has been discussed by Buchdahl and Nielsen[79] who found that the temperature and the shape of the α- peak was essentially the same for the total sample and for the fractionated polymer. It is also known[80] that crosslinking raises the glass transition temperature and broadens the transition region.

It is therefore probable that the increase of Tg by about 10°C (viz Fig.5-2) is the result of the presence of crosslinks, formed during processing. These crosslinks will restrict to a degree the motion of large segments of the main chains and as a consequence of this restriction the increase of the modulus and the Tg is observed.

The results of the impact strength measurement on the samples previously examined by the dynamic mechanical test is shown in the following Table 5-1:

TABLE 5-1

Sample	% gel	CH.N.I.S. (KJ/m^2)	E'(GN/m^2)R.T.
PVC (unprocessed)	0.45	3.3	2.29
10min/210°C	40.8	2.39	2.53
15min	66.24	2.92	2.62
20min	88.9	2.60	2.72

It can be seen that the impact strength is not significantly affected by the thermal treatment. In the right-hand column of Table 5-1 are listed elastic moduli E' at room temperature taken from the Fig.5-1. It can be seen that the modulus increased steadily with the crosslinking but the increase was small (18.7%).

It was previously suggested[74,81] that the room temperature impact strength of PVC arises because of molecular motion in the β-process. It may be that the room temperature impact strength (see Table 5-1) is connected with the β-transition because insignificant change was observed in the magnitude of the β-peak during processing. On the other hand, the correlation between the β-relaxation and the impact strength might me fortuitous because physical properties such as impact strength (or tensile strength) involve large deformations whereas deformations during dynamic mechanical testing, especially at low frequencies, are very small.

VARIATION OF TENSILE MODULUS E' AND $TAN\delta_M$ FOR PVC PROCESSED WITHOUT ADDITIVES AT 210°C

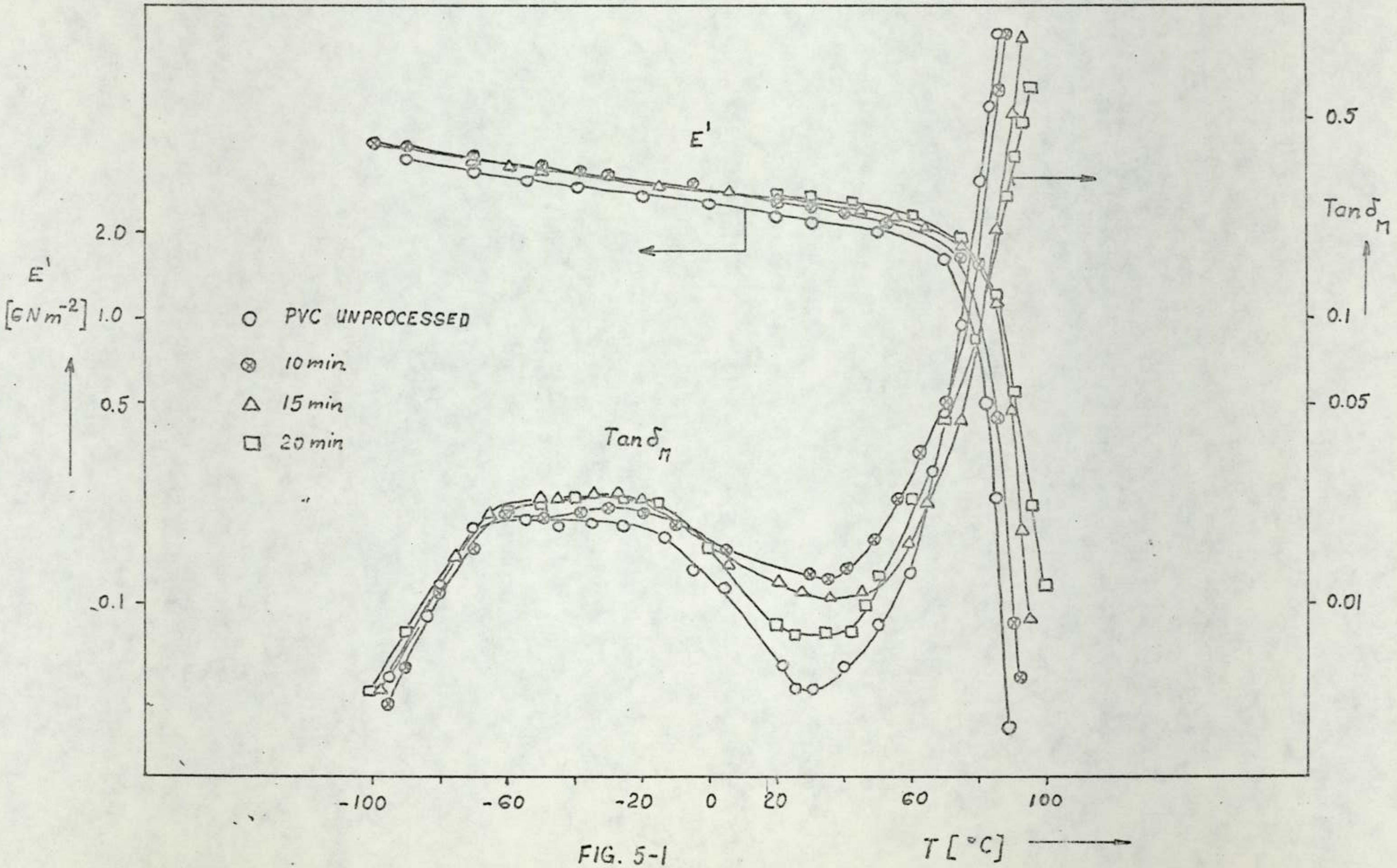


FIG. 5-1

Loss tangent ($\tan\delta_m$) as function of temperature for PVC processed without additives at 210°C.

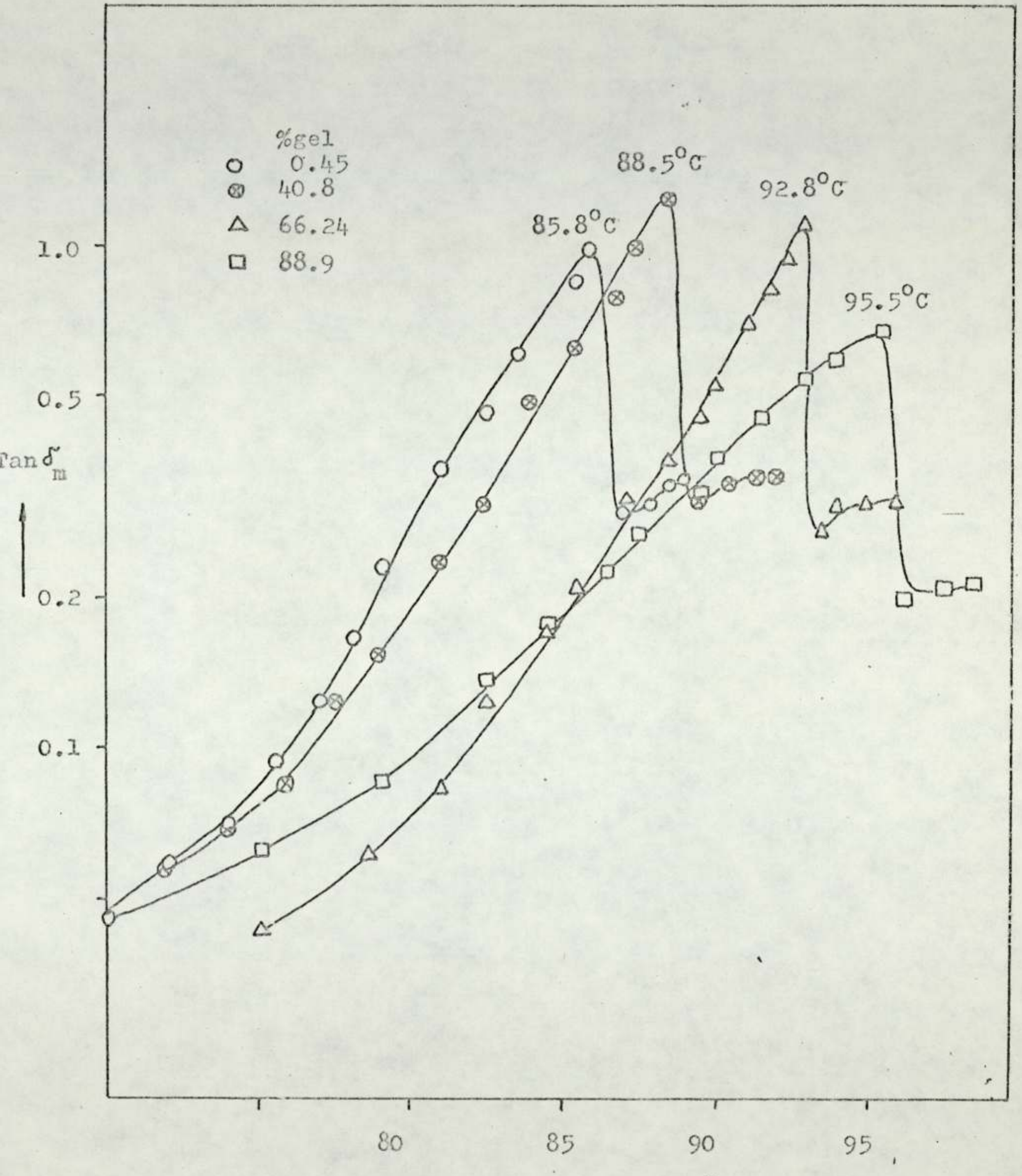


Fig.5-2

Loss tangent ($\tan\delta_{min}$ at 30°C-35°C) as function of time for PVC processed without additives at 210°C.

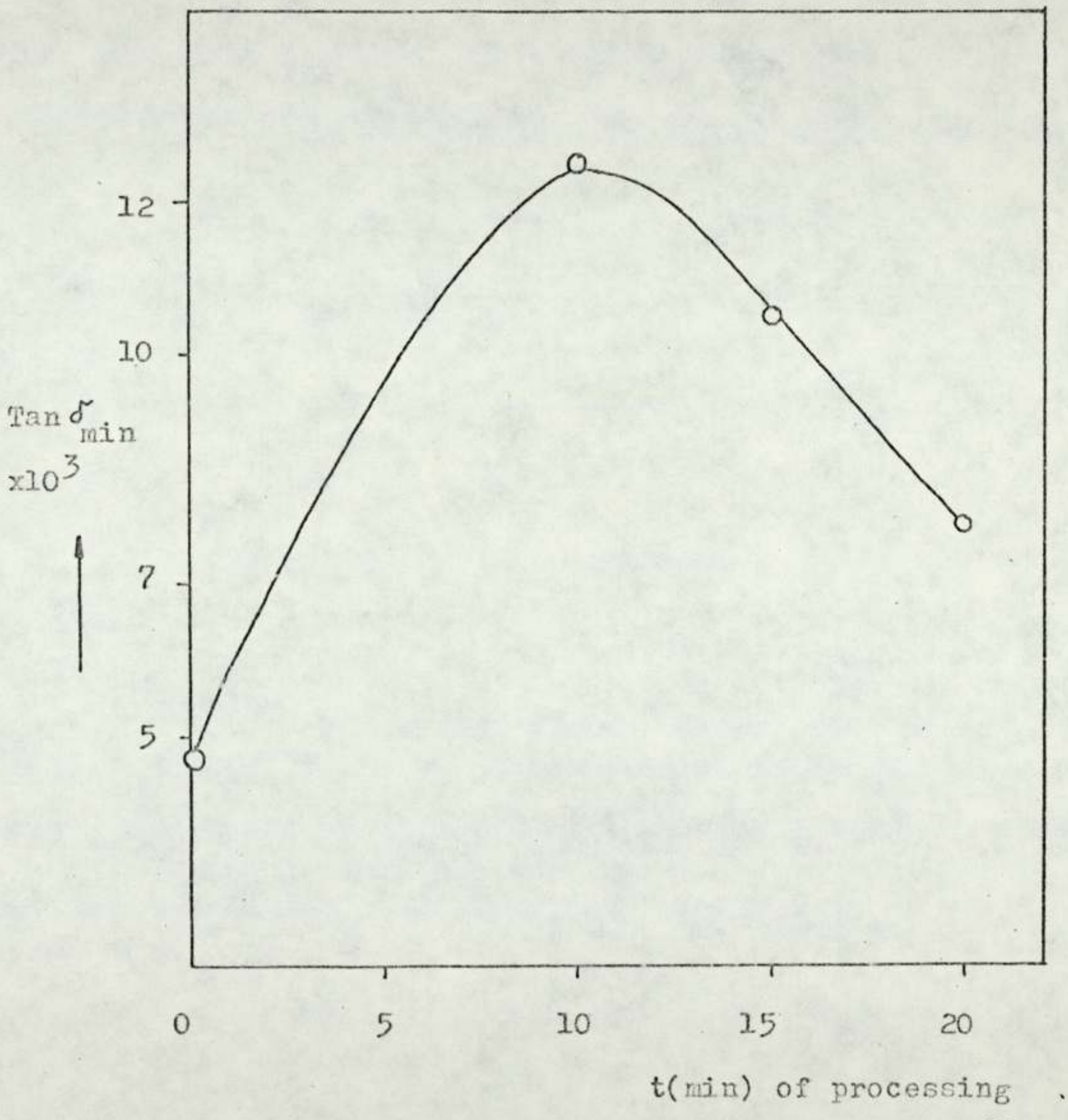


Fig.5-3

CHAPTER 6. Photodegradation of PVC processed in torque rheometer without additives

6-1. Experimental

6-1.1. Apparatus for UV-irradiation

Irradiation was carried out in the cylindrical enclosure (cabinet) which contained an inner cylindrical frame. The frame carried specimens round the cylindrical array of 32 fluorescent tube-lamps. The tubes were spaced so that the samples passed at the distance of 10cm from the outermost points on the tubes. The cylindrical cabinet was opened to the atmosphere on both, the lower and upper sides, and the circulation of air in the cabinet was ensured by the driven ventilator situated under the rotating frame. The temperature in the cabinet during exposure was between 36°C - 40°C.

6-1.1.1. Radiation source

The source consisted of the cylindrical array of 20W fluorescent tube-lamps, positioned on the inner side of the cylindrical cabinet. 24 lamps type C (Phillips actinic blue 05) and 8 lamps type A1 (Westinghouse sunlamps FS20) were used and these were symmetrically distributed so that the combination was one lamp type A1 for every three lamps of type C. The spectral distribution of both types of lamps used is shown[82] in Fig. 6-1a 6-1b for the lamp C and lamp A1 respetively. The maximum in the relative intensity of the lamp C is at 374nm and of the lamp A1 at 317nm, the available wavelength was between 280nm - 500nm and the radiation intensity I_o at the sample surface was I_o=44.3 W/m^2.(82)

To minimize the problem of decline in lamp output, the tubes were replaced sequentially every 2000 hrs of exposure.

6-1.1. Sample preparation

Samples were used in the form of the films of the thickness near 0.05mm. The films were prepared by compression moulding of the processed polymer in the form of the powder. Hydraulic, electrically heated press was employed and the polymer was pressed at 170°C for 1min. The polymer films were then placed in a specimen holder which had dimensions suitable for the Perkin-Elmer IR-spectrophotometer, model 257. The film of unprocessed polymer was prepared by evaporation of 1% solution in methylene dichloride (b.p.39.5°C) on mercury surface at room temperature with subsequent drying of the film in vacuum at 39°C-40°C to constant weight. The gels, obtained by the centrifugation method (see experimental chapter 2), were mostly in the form of thin films and were used without further modification. Similar samples as described above, were prepared for the measurement of colour change during UV-exposure.

6-1.3. Measurement of IR-spectra and discolouration

IR-spectra of irradiated polymer samples were obtained using Perkin-Elmer spectrophotometer Model 257. The spectra were obtained before the irradiation and then after various durations of exposure to UV light. Because of the use of the specimen holders, the possibility of scanning different portions of irradiated samples was minimized. Furthermore, the spectral changes observed during photodegradation are expressed as an index of a particular absorption and therefore the possible small variation in the sample thickness is eliminated.

The change of colour during exposure was measured using Colormaster model V and the procedure described in the experimental chapter 2 was used. The measurement of the same portion of the samples after various exposure times was ensured by the use of the sample holders as described earlier. The total colour difference was calculated (see chapter 2) using the readings obtained after each particular time of exposure and the reading obtained for the unirradiated and unprocessed polymer film. Therefore, obtained total colour difference at zero-irradiation time represents the colour change after processing.

6-2. Results of photodegradation of processed PVC using total samples

6-2.1. IR-spectroscopy results

The examination of the spectra showed the significant growth of several absorption bands in the region of 1600 cm^{-1}- 1850 cm^{-1} and 3000 cm^{-1}- 3600 cm^{-1}. An illustration of IR-spectra of the polymer processed for 2min at 210^{o}C and irradiated up to ~ 1000 hours is shown in Fig. 6-2. Three carbonyl peaks have developed during the exposure. These were centred at 1785 cm^{-1}, 1745 cm^{-1} and 1720 cm^{-1}. The growth of the peak at 1720 cm^{-1} was fastest and the two peaks at 1785 cm^{-1} and 1745 cm^{-1} became shoulders of the main carbonyl peak at 1720 cm^{-1} during the course of exposure. In the 1600 cm^{-1}- 1700 cm^{-1} region no distinct peaks were observed but the broadening of the main carbonyl peak occurred and a broad shoulder was observed.

The broad hydroxyl peak contained two distinct absorptions centred at 3450 cm^{-1} and 3200 cm^{-1}. The changes in the IR-spectra of the unprocessed polymer were similar as for the processed PVC, but the main carbonyl peak was centred at 1715 cm^{-1}.

The formation of carbonyl peak at 1725 cm^{-1} has been previously observed[10] together with the peak at 1775 cm^{-1}. 1725 cm^{-1} absorption was assigned to β-chloroketone and 1775 cm^{-1} peak was attributed to peracid[10]. The carbonyl peaks observed after irradiation of pressed PVC films in air, using xenon-arc irradiation, were attributed[9] to α-chloroketones (1725cm^{-1}- 1745cm^{-1}) and aliphatic aldehydes (1720cm^{-1}- 1740cm^{-1}). Carbonyl peaks at 1720cm^{-1} and 1770cm^{-1} were also observed[83] after irradiation of PVC in the oxygen atmosphere, using medium pressure mercury lamp. Other workers[11] attributed the carbonyl peak at 1715cm^{-1} and at 1735cm^{-1}-1745 cm^{-1} to β-chlorocarboxylic acid carbonyl and α-chlorocarboxylic acid carbonyl, respectively. The presence of the hydroxyl peaks centred at 3460 cm^{-1} and 3200 cm^{-1} have also been previously observed[11] and the latter was assigned to the acidic hydroxyl. OH-absorption peak centred at 3400 cm^{-1} has been previously shown[84] to be formed during photo-oxidation of polypropylene and was attributed[84] to hydrogen-bonded OH groups (both alcohol and hydroperoxide).

The broadening of the main carbonyl peak in the region of 1600 cm^{-1} - 1700 cm^{-1} (viz Fig.6-2) may suggest[13] the presence of conjugated (1600 cm^{-1}) and unconjugated unsaturation (1640 cm^{-1} - 1660 cm^{-1}) and also the presence of conjugated carbonyl (1660 cm^{-1} - 1700 cm^{-1}).

The growth of the carbonyl peak at 1720 cm^{-1} and hydroxyl peak at 3450 cm^{-1} as a function of exposure time for the samples processed for different time at 210°C was expressed as an index $ICO_{1720\ cm^{-1}}$ $\left(\frac{A1720\ cm^{-1}}{A2915\ cm^{-1}}\right)$ and $I_{OH}3450\ cm^{-1}$ $\left(= \frac{A3450\ cm^{-1}}{A2915\ cm^{-1}} \right)$. The plot of the carbonyl index is shown in Fig. 6-3 and the hydroxyl index in Fig.6-4, respectively.

The plots for the unprocessed PVC are also included. The indices of the control (0) initially increased with slow rate but with continued exposure the rate increased and the photo-oxidation had an autoaccelerating character. For the processed samples, however, the initial rate of carbonyl and hydroxyl formation was fast, but later the rate decreased and photo-oxidation was slower. Furthermore, the extent of photo-oxidation was higher for the samples processed up to 5min (viz Fig. 6-3 and 6-4, curves 1-5). It appears that the photo-oxidation proceeded in two distinct stages viz the first stage with relatively high rate and the second stage with the slower rate. It should be noted that the duration of the first fast-rate reaction of the samples processed for 10, 15 and 20min was about 200 hrs. It may also be noted that these samples contained progressively higher percentage of the gel phase formed during processing (see e.g. Fig.3-2 chapter 3).

Similar kinetic behaviour, e.g. initial fast rate of photo-oxidation followed by the slower rate, was also observed for the samples processed at 170°C. This is illustrated in Fig. 6-5 and 6-6 by the plots of carbonyl index and hydroxyl index, respectively. Comparison of the rates and also the extent of the formation of carbonyl peak with the hydroxyl peak (for example comparison of the Fig. 6-3 with Fig. 6-4 and 6-5 with Fig. 6-6) indicates, that the carbonyl and hydroxyl species were formed simultaneously during the photo-oxiation reaction. This comparison is illustrated in Fig. 6-7, where carbonyl and hydroxyl indexes are plotted in the same figure.

6-2.2. Colour change

Discolouration of the polymer, processed at 210°C for different times, during UV-exposure is illustrated in Fig. 6-8 and for the polymer processed at 170°C in Fig. 6-9, respectively. For 210°C samples (see Fig. 6-8, curves 1-5) discolouration increased initially at higher rate than for the unprocessed sample and with further exposure the rate decreased. The discolouration of the samples processed for 10min, 15min and 20min, however, was small.

Similar results were obtained with the samples processed at 170°C (viz Fig.6-9) where again initial rapid increase was followed by the slower rate. It would appear that the discolouration during exposure proceeded in two stages, viz the initial stage with the higher rate followed by the second stage with the slower rate. This kinetic behaviour appeared to be similar to the carbonyl and hydroxyl formation as it was discussed in the previous section 6-2.1. The relation between the extent of oxidation and discolouration is illustrated in Fig.6-10 and Fig. 6-11 for 210°C and 170°C processed samples, respectively. These results suggest that the discolouration is related to the carbonyl group formed during exposure. Similar results were obtained by Martin and Tilley[85] and also by Martin[86], who attributed discolouration during photo-oxidation of PVC to carbonyl group.

6-2.3. Air permeability measurement

Permeability of air through the polymer film at room temperature was measured using apparatus, procedure and calculation, described in the experimental chapter 2. The samples were prepared by compression moulding of processed polymer in the form of the film and the discs of 6cm in diameter were prepared from the pressed polymer films. The thickness of the discs was near 0.025cm.

The plot of the permeability constant P against the gel content of the samples processed without additives is shown in Fig. 6-11a. The permeability constant decreased with the increased gel content in the polymer samples. This result suggests that the diffusion of air at room temperature through the progressively more crosslinked polymer decreased.

6-3. Results of photo-oxidation of gel phase of processed PVC

IR-spectroscopy results

Examination of IR-spectra of the gel phase after UV-irradiation revealed significant changes in the 1600 cm^{-1} - 1850 cm^{-1} and 3000 cm^{-1}- 3600 cm^{-1} region of the spectra. An example of the changes in these spectral regions is shown in

Fig.6-12 of the gel phase of the sample, processed for 3min at 210°C and irradiated up to ~1100 hrs. In the carbonyl region broad absorption peak centred at 1715 cm^{-1}-1720 cm^{-1} developed. Also the peak centred at 1600 cm^{-1} was observed. It may be noted that the total sample contained only a broad shoulder in the 1600 cm^{-1} - 1700 cm^{-1} region.

In the hydroxyl region of 3000 cm^{-1} - 3600 cm^{-1} the hydroxyl peak contained two absorption peaks centred at 3200 cm^{-1} and 3420 cm^{-1} - 3450 cm^{-1}. These two peaks were also observed in the total sample (Fig.6-2) and were discussed in the section 6-2.1. The position of the peak at 1600 cm^{-1} suggests the formation of conjugated unsaturation[13] during UV-irradiation as a result of dehydrochlorination.

The plots of carbonyl (I_{CO}1715 cm^{-1} - 1720 cm^{-1}) and hydroxyl (I_{OH}3420 cm^{-1} - 50 cm^{-1}) indices of the gels of PVC processed at 210°C for various time vs UV-irradiation time are shown in Fig. 6-13 and 6-14, respectively. The carbonyl index increased initially with high rate and on continued exposure the rate considerably decreased. For 1-3min gels a plateau was observed (see curves 1-3, Fig.6-13). The magnitude of the carbonyl index (and therefore the extent of photo-oxidation) of the initial gels was higher than the gels of samples processed for longer time. Furthermore,the hydroxyl index (see Fig. 6-14) increased considerably faster than the index of longer processed samples. The hydroxyl index of 4-20min gels also initially increased at fast rate but continued to increase with slower rate. The plot of of the $I_{1600\ cm^{-1}}$ is shown in Fig. 6-15. The extent of unsaturation is higher for the initial gels than for the gels processed for longer time. It should be noted (viz Fig.6-13) that the magnitude of carbonyl indices of 4-20min gels at the onset of the second (slower rate) stage of photo-oxidation is between 0.4-0.5. The carbonyl index was plotted against processing time and the result is shown in Fig.6-16. The carbonyl index exhibited a maximum at 2min but after 4min remained constant.

The plots of carbonyl and hydroxyl indices of the gel phase, present in PVC processed at 170°C are shown in Figs. 6-17 and 6-18, respectively. The index $I_{1600\ cm^{-1}}$ vs UV-exposure time is illustrated in Fig.6-19. The high rate of hydroxyl and unsaturation formation was observed for 1min gel and also the extent of carbonyl formation was higher than the gels of samples processed for longer time. The rate considerably decreased for 15min and 20min samples.

It appears that the samples processed for 1-3min at 210°C and 1min at 170°C contained very efficient promoter of UV degradation. It should be pointed out that peroxide was found to be present (see Fig.3-7, chapter 3) in these samples and thus it is probable that the peroxidic moiety is responsible for the observed high rate of photo-oxidation.

6-4. Photodegradation of PVC containing soluble phase of processed polymer.

Photodegradation of unprocessed PVC film samples containing various concentrations of soluble phase (in methylene dichloride) was carried out. The soluble phase was obtained from the polymer processed without additives at 210°C for

15min and 20min. The soluble phases are described in Table 6-1:

SOLUBLE PHASE	PROCESSING TIME(MIN)	UNSATURATION (ABSORBANCE AT 310nm, 0.07% SOLUTION, 10mm CELL)	CARBONYL INDEX $I_{1720cm^{-1}} \times 10^2$
Sample A	15	0.53	5.9
Sample B	20	1.035	12.46

The polymer films for UV-degradation were prepared by dissolution of unprocessed PVC with various concentrations (5-95%) of sample A or B (see Table 6-1). Obtained 1% w/w solutions in methylene dichloride were evaporated at room temperature and obtained polymer films were then dried in vacuum at 40°C to constant weight.

The plots of carbonyl index vs UV-exposure time of PVC containing sample A and B are shown in Figs. 6-20 and 6-21, respectively. The carbonyl index increased at high rate immediately from the beginning of exposure and even for low concentrations (5%) the rate was relatively high. The sample A (see Fig. 6-20, curve 100%) disintegrated after about 350hrs. The sample which contained 95% of sample B (see Fig. 6-21, curve 95%) disintegrated at about 600hrs. The 100% sample B could not be used since it was too brittle to handle. The unsaturation and the carbonyl index of both samples used are shown in the Table 6-1.

Carbonyl absorption formed in the total sample, gel and soluble phase of PVC processed for 15min at 210°C (gel concentration before exposure was 66.2%) is shown in Fig. 6-22. It can be seen that the initial stage of photo-oxidation is identical for the gel phase and total sample and the subsequent rate of photo-oxidation was lower for the gel phase. The soluble phase degraded very rapidly and disintegrated after 350hrs.

6-5. Discussion

The thermal degradation of PVC has been a focus of extensive studies in the past [15,18,19] but the photo-degradation of PVC received less attention.

It was previously stated[87] that PVC is degraded with light of wavelength 300nm and the wavelength of incident radiation at 310nm[88], described as "activation spectrum" was most effective for discolouration of PVC. Kenyon has shown[89] that HCl was liberated from PVC upon irradiation with light at wavelength 280nm to visible and the rate of evolution was wavelength dependent. Higher rate was observed with light of 253nm to visible wavelength. On the other hand, HCl was not detected [10] when PVC was irradiated by GE germicidal lamp, emitting at a wavelength of 253nm. HCl was obtained only when PVC was heated at higher temperature and it was concluded[10] that HCl was a product of thermal decomposition rather than photolysis. Kwei[10] has also shown, using IR-spectroscopy, formation of absorption bands at 1725 cm^{-1} and 1775 cm^{-1}. The integral intensity of the two absorption bands was plotted against the square root of time and the linear plot was obtained. Also the total oxygen consumption, calculated as the sum of the oxygen content in the polymer and in the gaseous products (CO_2 and CO), increased linearly with the square root time. From these results it was concluded[10] that the photo-oxidation of PVC was diffusion-controlled. Martin and Tilley[9] have shown formation of IR-absorption bands centred at 1730 cm^{-1} during photo-oxidation of PVC using xenon-arc irradiation, but no unsaturated aldehydes and ketones were observed. They concluded that dehydrochlorination has not preceded oxidation. Mack stated[87] that oxidation seems to be the main mechanism in light degradation and also that oxidative attack depends on an initial dehydrochlorination to provide points on the chain susceptible to oxidation. Similar views were expressed by Scarbrough et al[90]. HCl elimination was considered[11] to occur during UV-exposure, which gives rise to allylic hydroperoxide. It is generally known[89,90,31,91] that the rate of HCl evolution is higher for irradiated PVC than for unirradiated during thermal treatment. This was interpreted[18] by the presence of thermally labile structures as a result of photochemical oxidation.

IR-results in this work, using total sample (see Fig. 6-2) showed the formation of broad carbonyl absorption centred at 1720 cm^{-1} and broad hydroxyl peak with two distinct absorptions at 3450 cm^{-1} and 3200 cm^{-1}. Formation of these species manifests the extensive photo-oxidation of the polymer during UV-irradiation. Furthermore, significant broadening of the main carbonyl peak in the 1600 cm^{-1} - 1700 cm^{-1} region may suggest formation of unsaturation as a result of HCl elimination and also the formation of conjugated carbonyl. The IR-spectra of the gel phase revealed a distinct absorption at 1600 cm^{-1} (see Fig. 6-12) which again demonstrates the formation of unsaturation as a result of HCl elimination during UV-exposure.

The carbonyl and hydroxyl indices of total samples (Fig. 6-3,4,5,6) increased initially at a higher rate than the control and with continued degradation the rate decreased. Similar kinetic behaviour was observed during the exposure of the gel phase (Figs. 6-13,14,15,17-19). It appears that the photo-oxidation proceeded in two distinct stages viz a relatively fast first stage followed by a slower second stage. It has been previously demonstrated[92] that HCl was evolved from PVC films, irradiated in nitrogen, initially at high rate followed by a slower rate and the rate was independent of sample thickness. The amount of HCl was also proportional to the surface area. The optical photographs revealed that the degraded material was confined to the surface layer of 2000nm thick and it was concluded[92] that photodegradation took place in a thin surface layer. The slow rate reaction has been also shown[93] to be independent of radiation intensity and temperature. It was argued[93] that this second stage is controlled not by a chemical process but by an "availability" of HCl and that polyenes formed initially on the surface acted as a protective barrier against light[92]. It has been previously pointed out[97] that the major degradation will take place near the surface for a strongly absorbing polymer whereas for a weakly absorbing material the destructive action will be uniform through the polymer. When polyenes were formed in PVC film by pre-irradiation in nitrogen it was found[83] that subsequent photo-oxidation le~~a~~d to further increase of polyene concentration and reached a maximum. The possible explanation put forward to explain this[83] was that the thin layer of polyenes formed initially restricted the diffusion of oxygen through this layer and its replacement was controlled by the rate of diffusion through the array of rigid polyene structures. However, no oxygen diffusion data in the pre-irradiated PVC film were given. It is known[94] that the rate of oxidation of a polymer in the solid state depends upon the rate of oxygen supply by diffusion as the oxidation rate is proportional to the concentration of oxygen in the polymer phase.

Figures 6-13 and 6-14 show that the time of duration of the initial fast reaction was between 100hrs and 200hrs for all the gels except for the first three. Also the rate of the second stage (Fig.6-13) reaction was similar. The extent of photo-oxidation as a result of the first stage reaction was smaller for 4-20min gels than for the first three gels (see Fig. 6-13) and ~~was~~ became constant (see Fig. 6-16). Furthermore, the permeability constant decreased with increased gel content (see Fig. 6-11a). From these results it may be concluded that the decrease of the rate of photo-oxidation of the highly crosslinked samples is predominantly the result of slower diffusion of oxygen through the crosslinked structure.

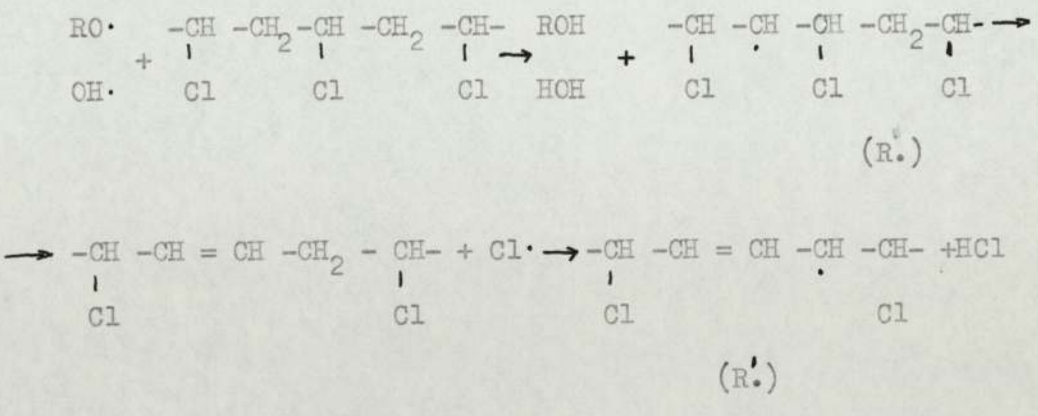
It has been previously shown[100] that crosslinking occurred during irradiation of PVC film by UV light emitted mainly at

254nm and that the radiation affected only the surface. It is likely that crosslinking which has been shown[101] to occur during irradiation also retards the photo-oxidation. Further experimental evidence is needed to verify this possibility.

The hydroxyl index of gels obtained from PVC processed for a short time (see Figs. 6-14 and 6-18) increased at much higher rate than the index of gels from samples processed for longer time. Also the extent of carbonyl formation (Figs. 6-13,6-17) and unsaturation (Figs. 6-15,6-19) was higher. It is known[84,95] that hydroperoxide photolyses very efficiently at ambient temperatures and it is therefore probable that the rapid photo-oxidation of the initial gels is due to the catalytic action of intermediate free radicals ($RO^{\bullet}, OH^{\bullet}$) formed by the photolysis of peroxide:

$$ROOH \xrightarrow{h\nu} RO. + OH. \qquad (1)$$

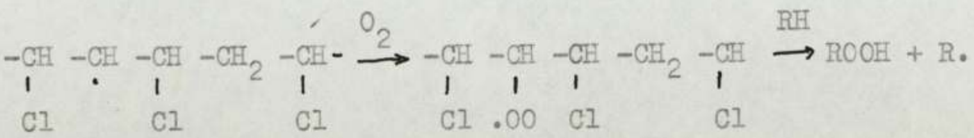
These intermediate free radicals by suitable H-atom abstraction (e.g. methylenic) are initiators for dehydrochlorination and photo-oxidation:



$$\begin{matrix}RO\cdot\\OH\cdot\end{matrix} + -\underset{Cl}{CH}-CH_2-\underset{Cl}{CH}-CH_2-\underset{Cl}{CH}- \longrightarrow \begin{matrix}ROH\\HOH\end{matrix} + \underset{(R\dot{})}{-\underset{Cl}{CH}-\dot{C}H-\underset{Cl}{CH}-CH_2-\underset{Cl}{CH}-} \longrightarrow$$

$$\longrightarrow -\underset{Cl}{CH}-CH=CH-CH_2-\underset{Cl}{CH}- + Cl\cdot \longrightarrow \underset{(R'\dot{})}{-\underset{Cl}{CH}-CH=CH-\dot{C}H-\underset{Cl}{CH}-} + HCl$$

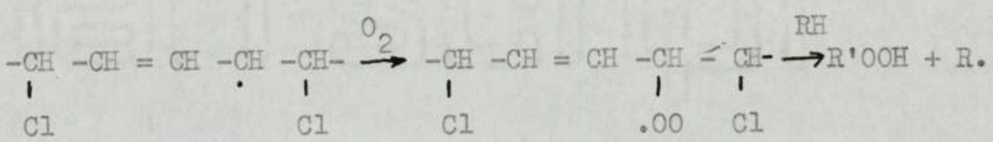
Alkyl radicals ($R^{\bullet}$, $R^{!}$) in the presence of oxygen will react to give peroxy radicals and so propagate oxidation chain:



$$-\underset{Cl}{CH}-\underset{\cdot}{CH}-\underset{Cl}{CH}-CH_2-\underset{Cl}{CH}- \xrightarrow{O_2} -\underset{Cl}{CH}-\underset{.OO}{CH}-\underset{Cl}{CH}-CH_2-\underset{Cl}{CH} \xrightarrow{RH} ROOH + R.$$

(R.)

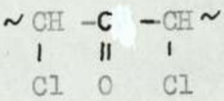
and



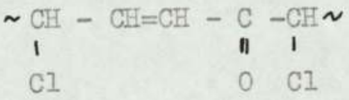
$$-\underset{Cl}{CH}-CH=CH-\underset{\cdot}{CH}-\underset{Cl}{CH}- \xrightarrow{O_2} -\underset{Cl}{CH}-CH=CH-\underset{.OO}{CH}-\underset{Cl}{CH}- \xrightarrow{RH} R'OOH + R.$$

(R'.)

Intermediate secondary hydroperoxides (ROOH,R'OOH) then undergo further photolysis (reaction 1) with formation of alkoxy ($RO^{\bullet}$, $R'O^{\bullet}$) and hydroxyl radicals $OH^{\bullet}$. Rearrangement of alkoxy radicals will lead to formation of chloroketone and conjugated ketone:



$$\sim\underset{Cl}{CH}-\underset{O}{\overset{\|}{C}}-\underset{Cl}{CH}\sim$$



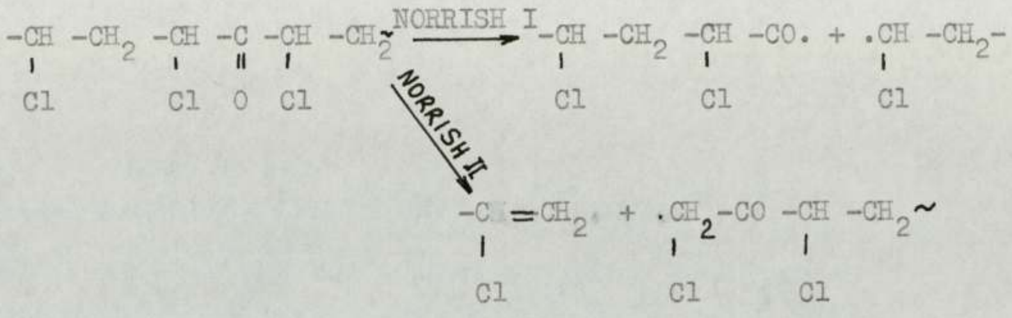
$$\sim\underset{Cl}{CH}-CH=CH-\underset{O}{\overset{\|}{C}}-\underset{Cl}{CH}\sim$$

Reactive $OH^{\bullet}$ radicals can abstract hydrogen atom from the polymer chain with formation of polymeric alcohol:

$$OH. + RH \longrightarrow ROH + R.$$

The carbonyl and hydroxyl indices increased during UV-exposure with similar rates (see Fig.6-7) which might indicate the similar rates of formation of polymeric alcohol and ketone as a result of photolysis of intermediate hydroperoxides.

Furthermore, carbonyl groups when exposed in the range of 270nm-330nm are easily excited to singlet and triplet states[95] and can undergo photochemical reactions, classified as Norrish type I and type II[95,96]:

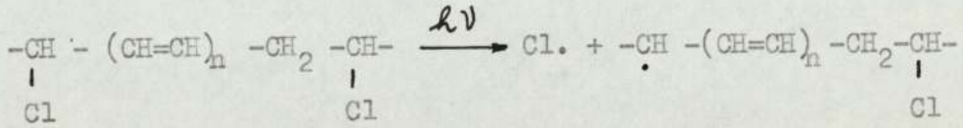


$$-\underset{Cl}{\underset{|}{CH}}-CH_2-\underset{Cl}{\underset{|}{CH}}-\underset{O}{\underset{\|}{C}}-\underset{Cl}{\underset{|}{CH}}-CH_2\sim \xrightarrow{\text{NORRISH I}} -\underset{Cl}{\underset{|}{CH}}-CH_2-\underset{Cl}{\underset{|}{CH}}-CO\cdot + \cdot\underset{Cl}{\underset{|}{CH}}-CH_2-$$

$$\xrightarrow{\text{NORRISH II}} -\underset{Cl}{\underset{|}{C}}=CH_2 + \cdot\underset{Cl}{\underset{|}{CH_2}}-CO-\underset{Cl}{\underset{|}{CH}}-CH_2\sim$$

As a result of Norrish I and II reactions, a scission of the main backbone chains occurs. It has been shown previously[11] that the embrittlement of PVC during photo-oxidation is the result of a predominantly chain scission process which resulted in the decrease of molecular weight[11].

The initial rates of photo-oxidation are higher for all the ~~all~~ processed samples when compared with the cast unprocessed PVC film. It was shown earlier that these samples contained unsaturation as a result of thermal dehydrochlorination (see e.g. Fig. 3-9,10, chapter 3) and therefore they absorb in the wavelength region of the incident light, used in this study. Unsaturation structures formed by the thermal treatment were considered[18,97] to act as sensitizers, because they absorb sufficient proportion of high energy necessary for the initiation of C-Cl bond scission[30]:



$$-\underset{Cl}{\underset{|}{CH}}-(CH{=}CH)_n-CH_2-\underset{Cl}{\underset{|}{CH}}- \xrightarrow{h\nu} Cl\cdot + -\underset{\cdot}{CH}-(CH{=}CH)_n-CH_2-\underset{Cl}{\underset{|}{CH}}-$$

The initial high rate of photo-oxidation of processed polymer can be accounted for by the presence of unsaturation, as discussed above. The photo-oxidation of PVC which contained various amounts of soluble phase (see Fig.6-20,21) proceeded with higher rate than that of control. The soluble phase contained unsaturation and carbonyl (see Table 6-1). Ketonic species were suggested[89] as initiators of photodegradation and the initiation of dehydrochlorination by benzophenone has been previously demonstrated[98]. It is therefore reasonable to suggest that the high rate of photodegradation is due to the unsaturation and the carbonyl species present in the samples examined.

Discolouration of PVC during UV-exposure is shown in Figs. 6-8 and 6-9 for the samples processed at 210°C and 170°C, respectively. The colour formation proceeded with similar pattern as photo-oxidation, measured by carbonyl and hydroxyl formation. It was also found that the carbonyl absorption peak was related to discolouration (see Figs.6-10,6-11). This result may suggest that the discolouration of PVC during photo-oxidation is a result of presence of chromophore (probably conjugated carbonyl),formed during photo-oxidation.

Spectral distribution of fluorescent lamp type C
(Philips Actinic Blue 05)

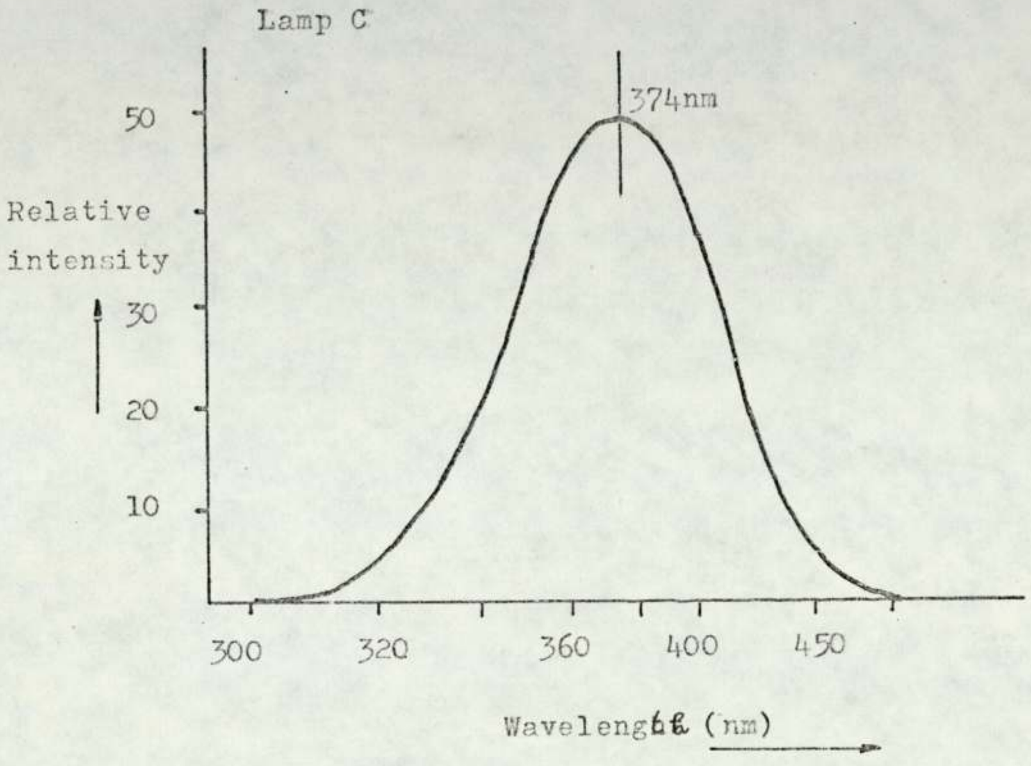


Fig. 6-1a

Spectral distribution of fluorescent lamp type A1
(Westinghouse sunlamp FS20)

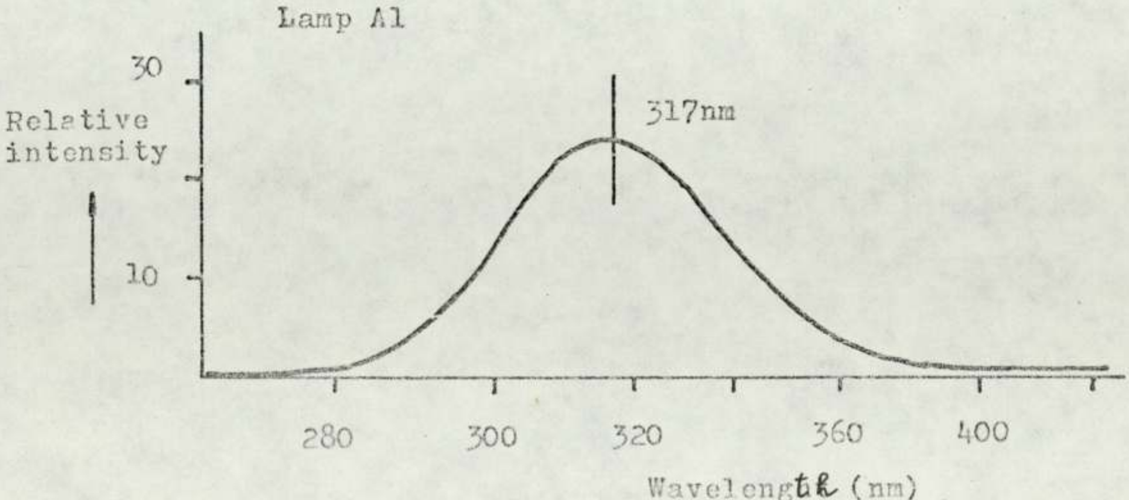


Fig. 6-1b

Carbonyl absorption (centred at $1720cm^{-1}$) and hydroxyl absorption ($3450cm^{-1}$) formation during UV-irradiation in PVC, processed for 2min at 210°C without the additives. (Total sample)

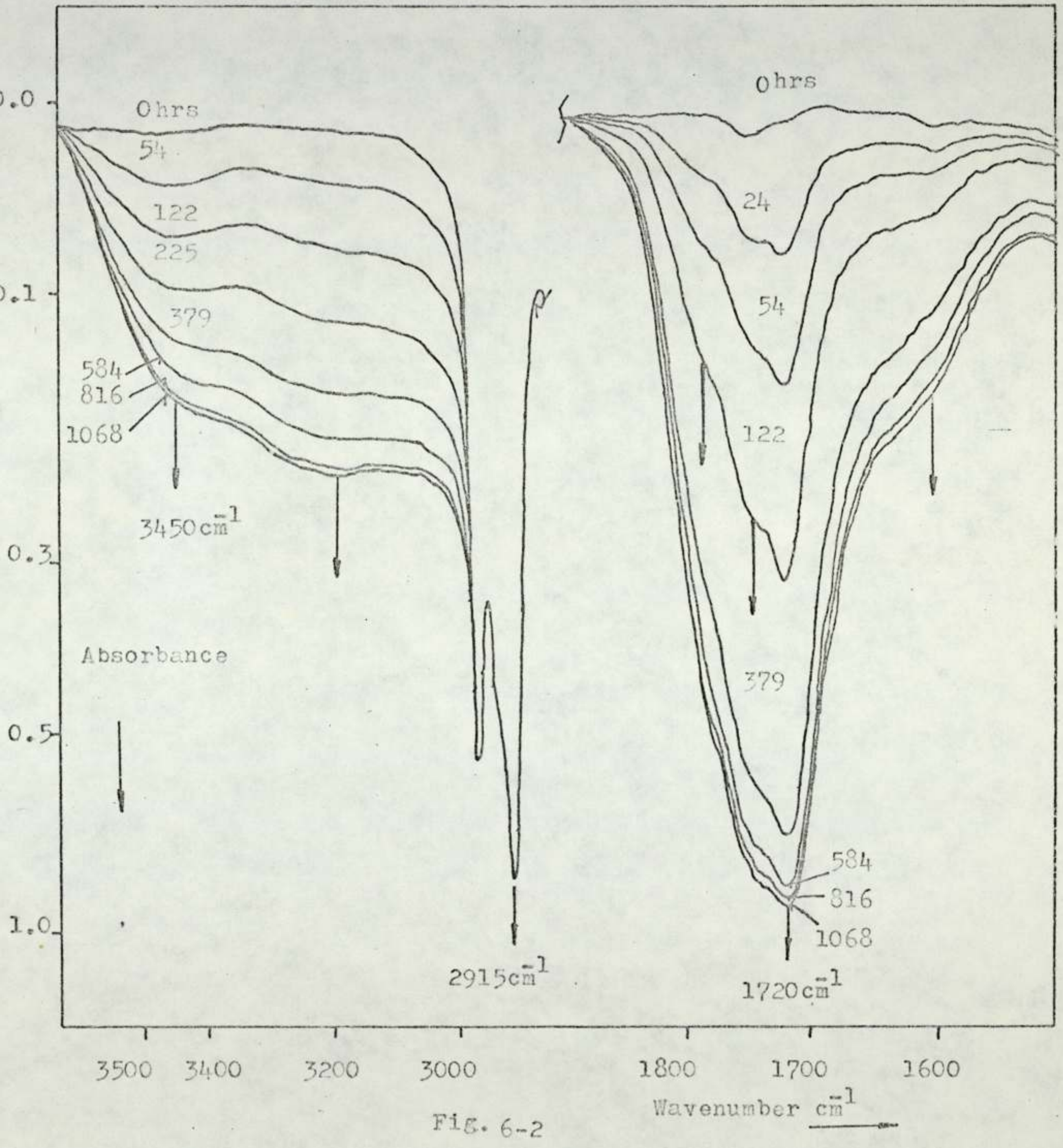


Fig. 6-2

Carbonyl Index I_{CO} 1720 cm^{-1} vs UV-irradiation time of PVC processed at 210°C without the additives (Total sample)

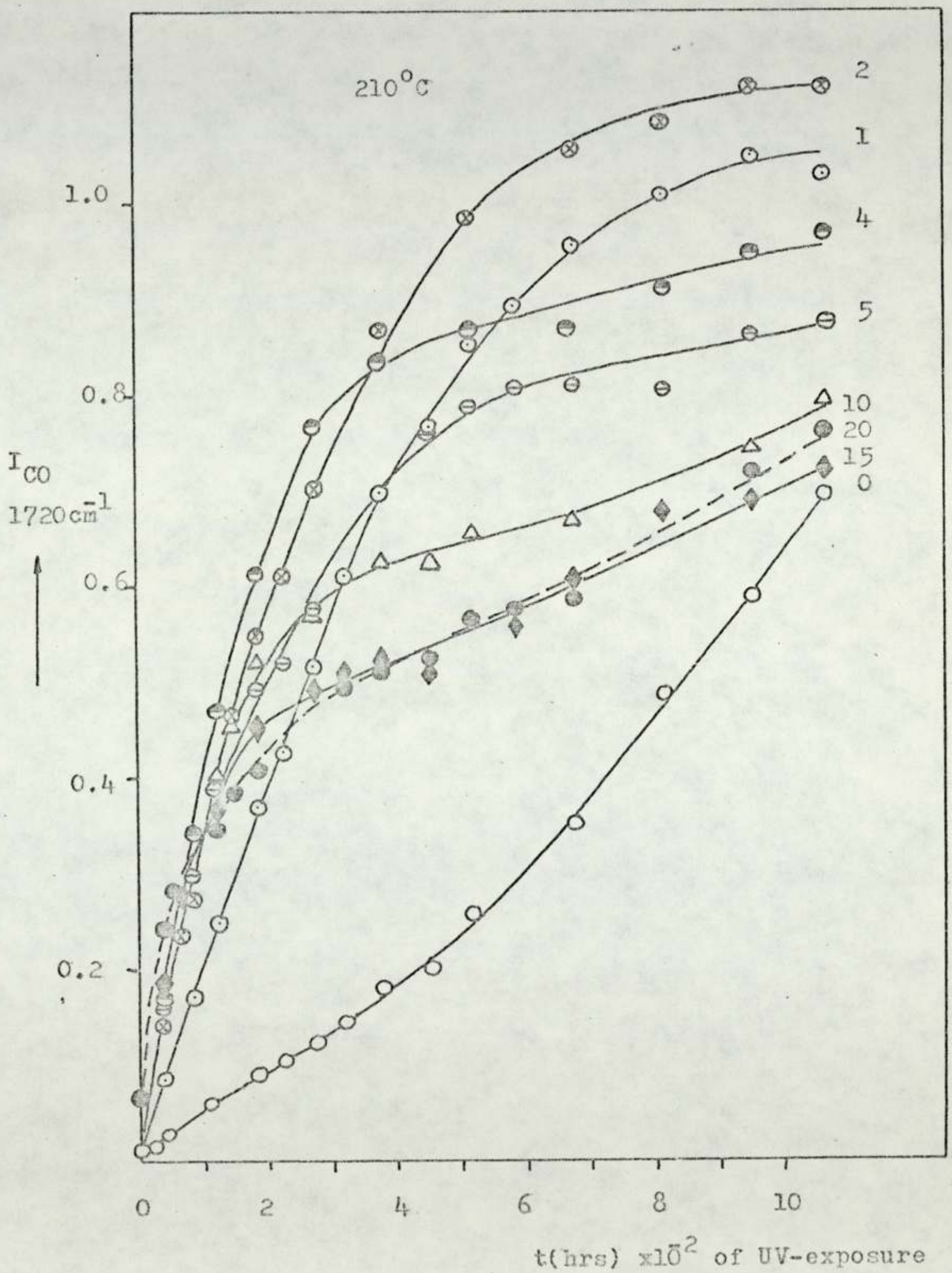


Fig. 6-3

Hydroxyl Index I_{OH} 3450 cm^{-1} vs UV-irradiation time of PVC processed at 210°C without additives. (Total sample)

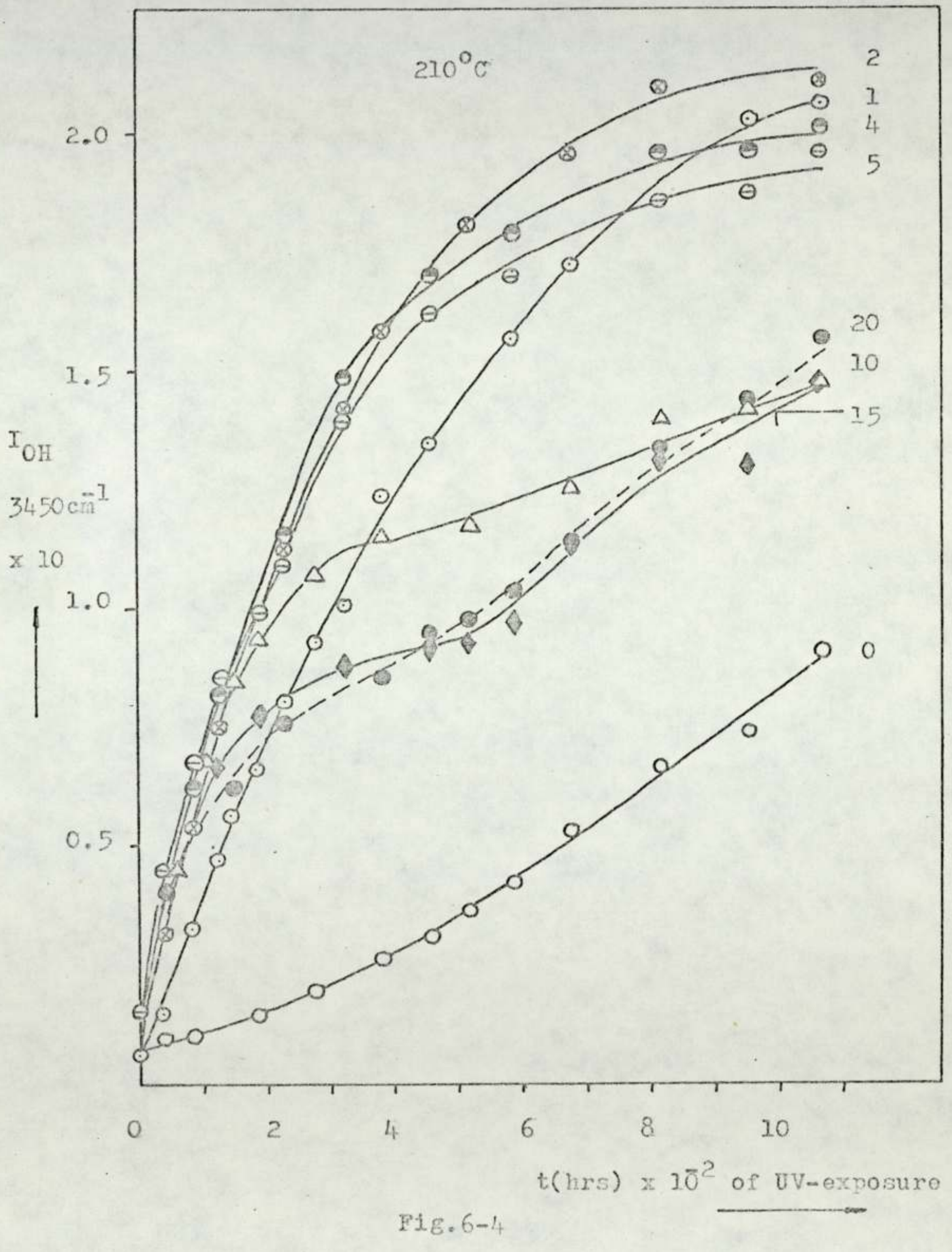


Fig.6-4

Carbonyl Index I_{CO} 1720 cm^{-1} vs UV-irradiation time of PVC processed at 170°C without additives. (Total sample)

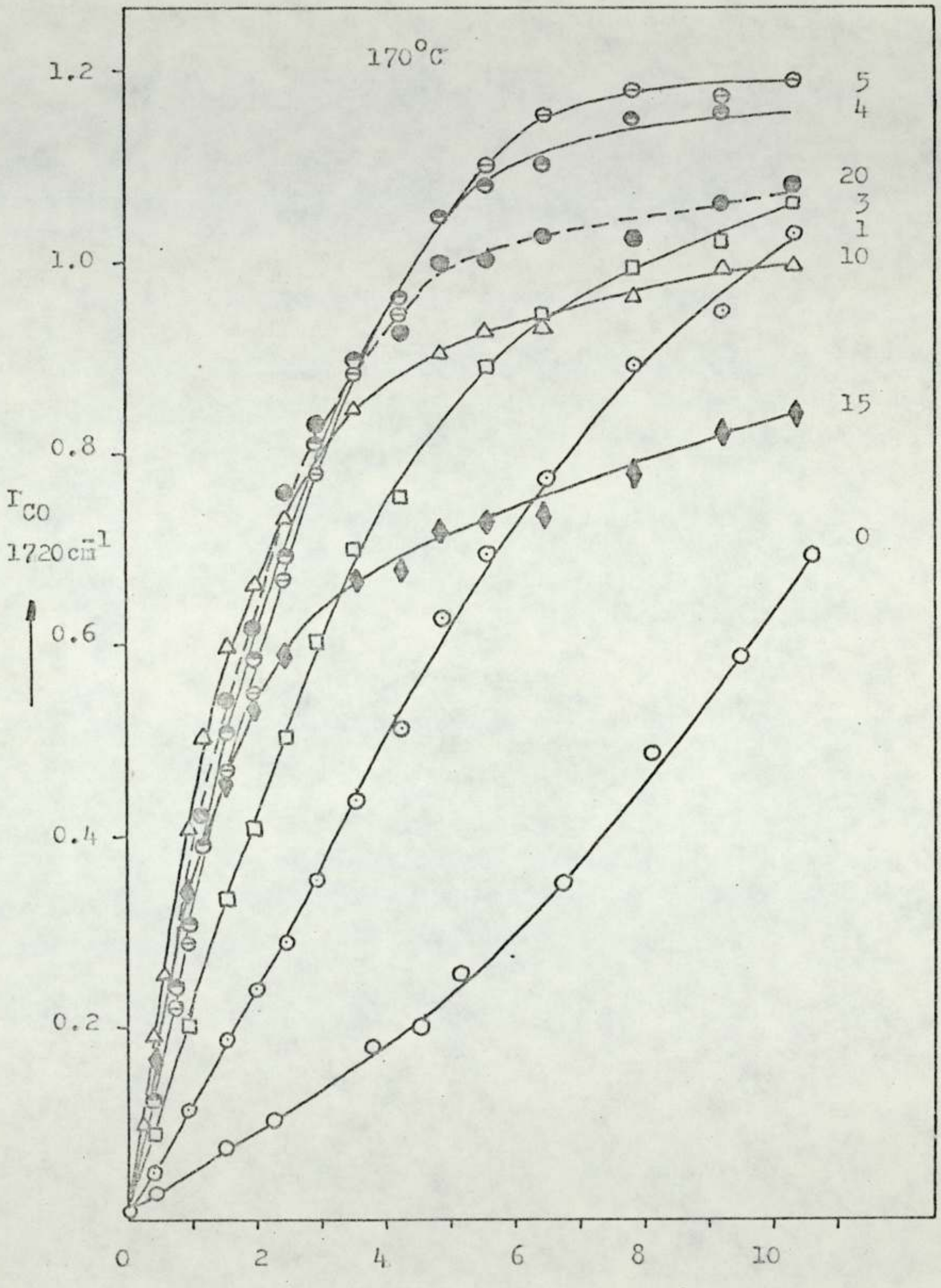


Fig. 6-5

Hydroxyl Index I_{OH} $3450cm^{-1}$ vs UV-irradiation time of PVC, processed at 170°C without additives. (Total sample).

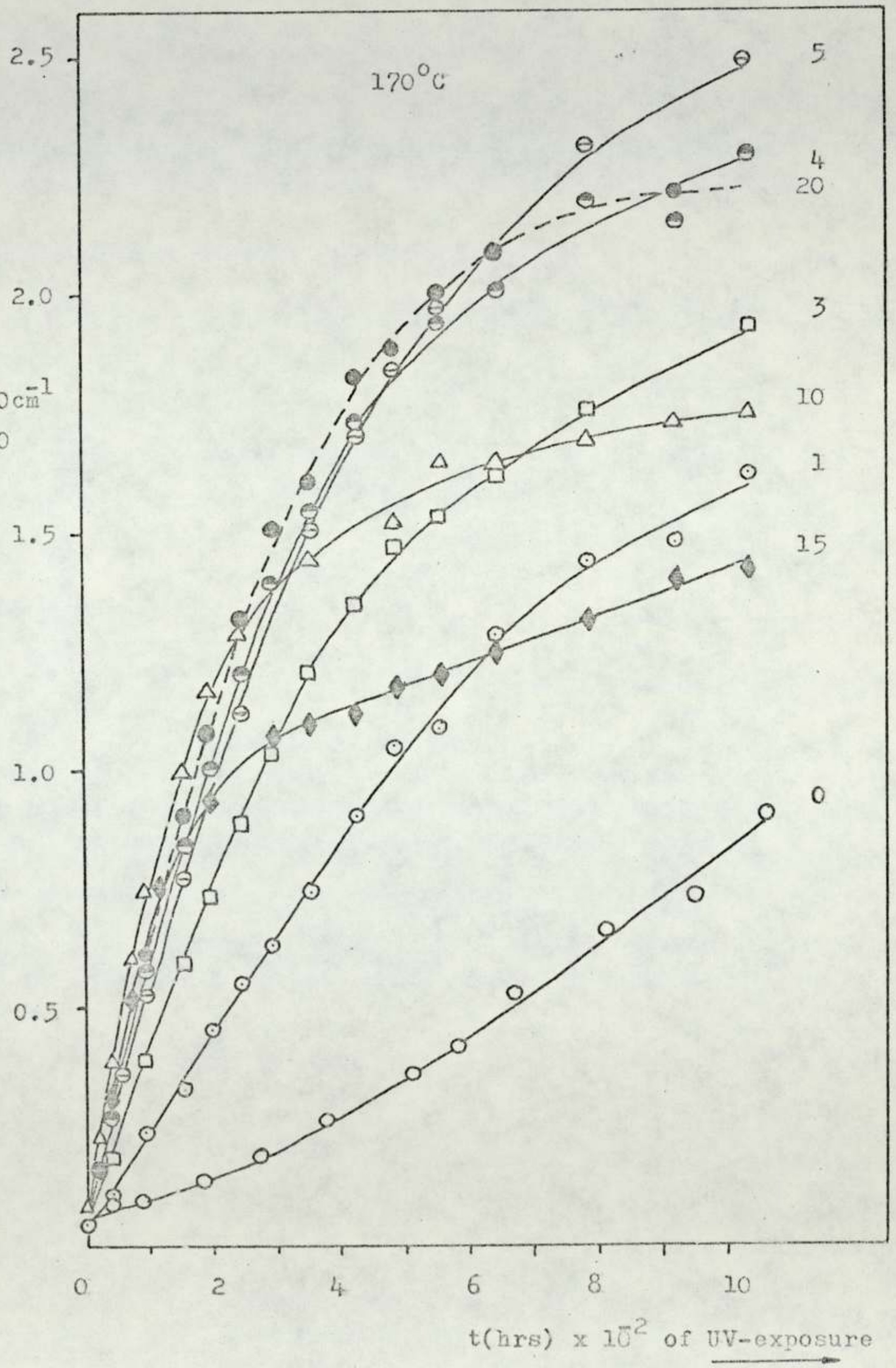


Fig. 6-6

Comparision of the carbonyl absorption at 1720cm^{-1} and hydroxyl absorption at 3450cm^{-1}, formed during UV-exposure of PVC, processed at 210°C without additives.

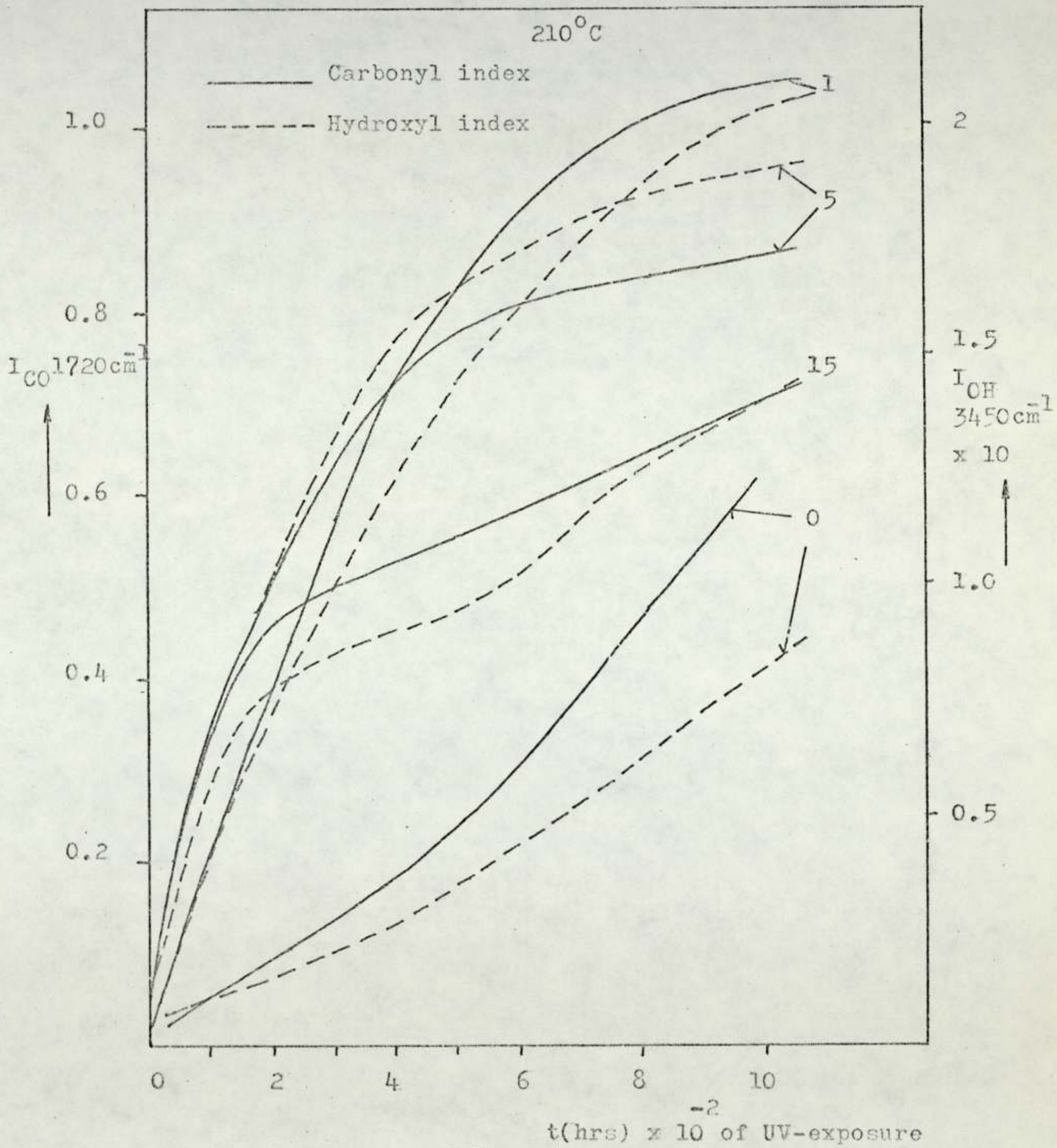


Fig.6-7

Discoloration of PVC during UV-irradiation,
PVC processed at 210°C without additives.

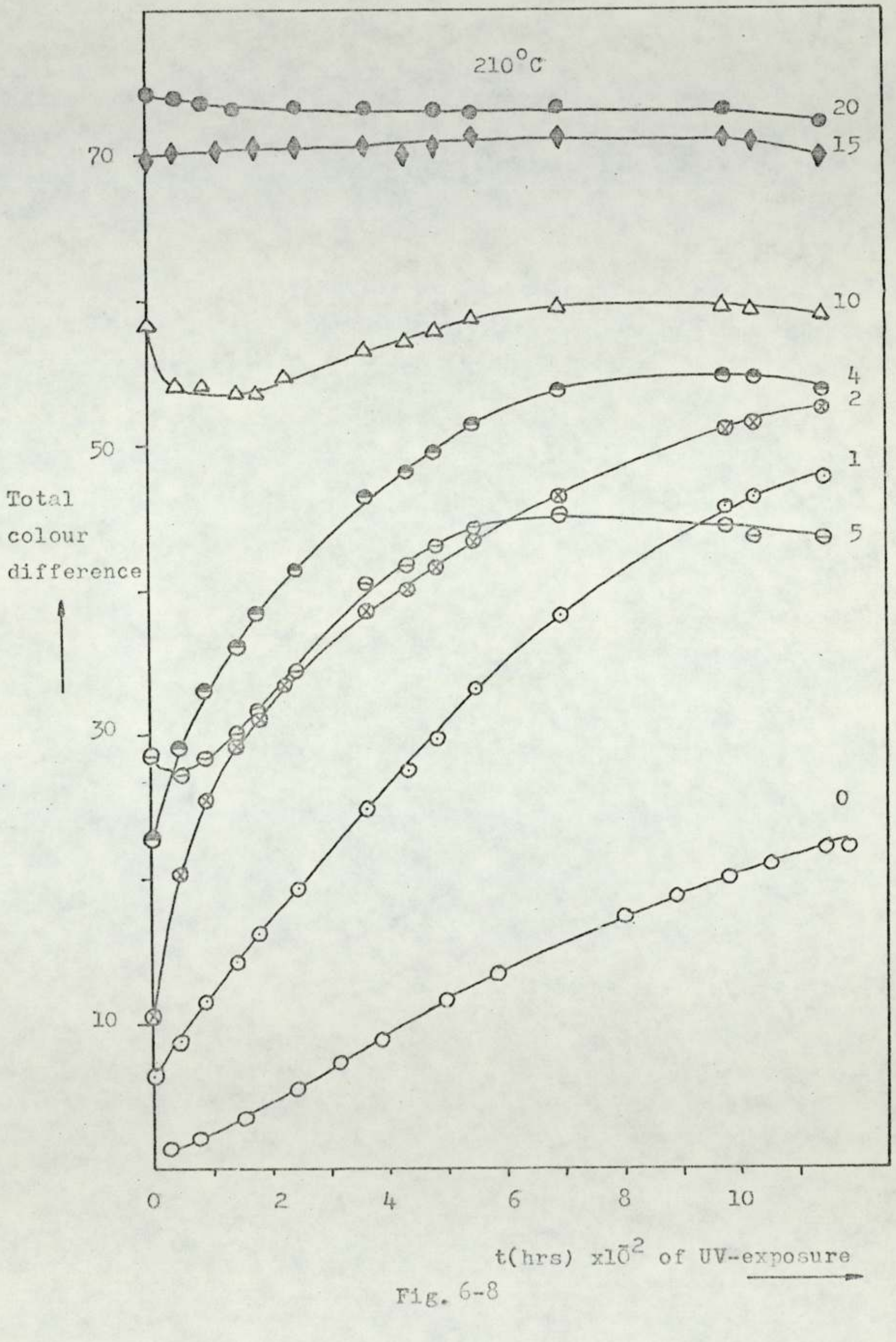


Fig. 6-8

Discoloration of PVC during UV-irradiation, PVC processed at 170°C without additives.

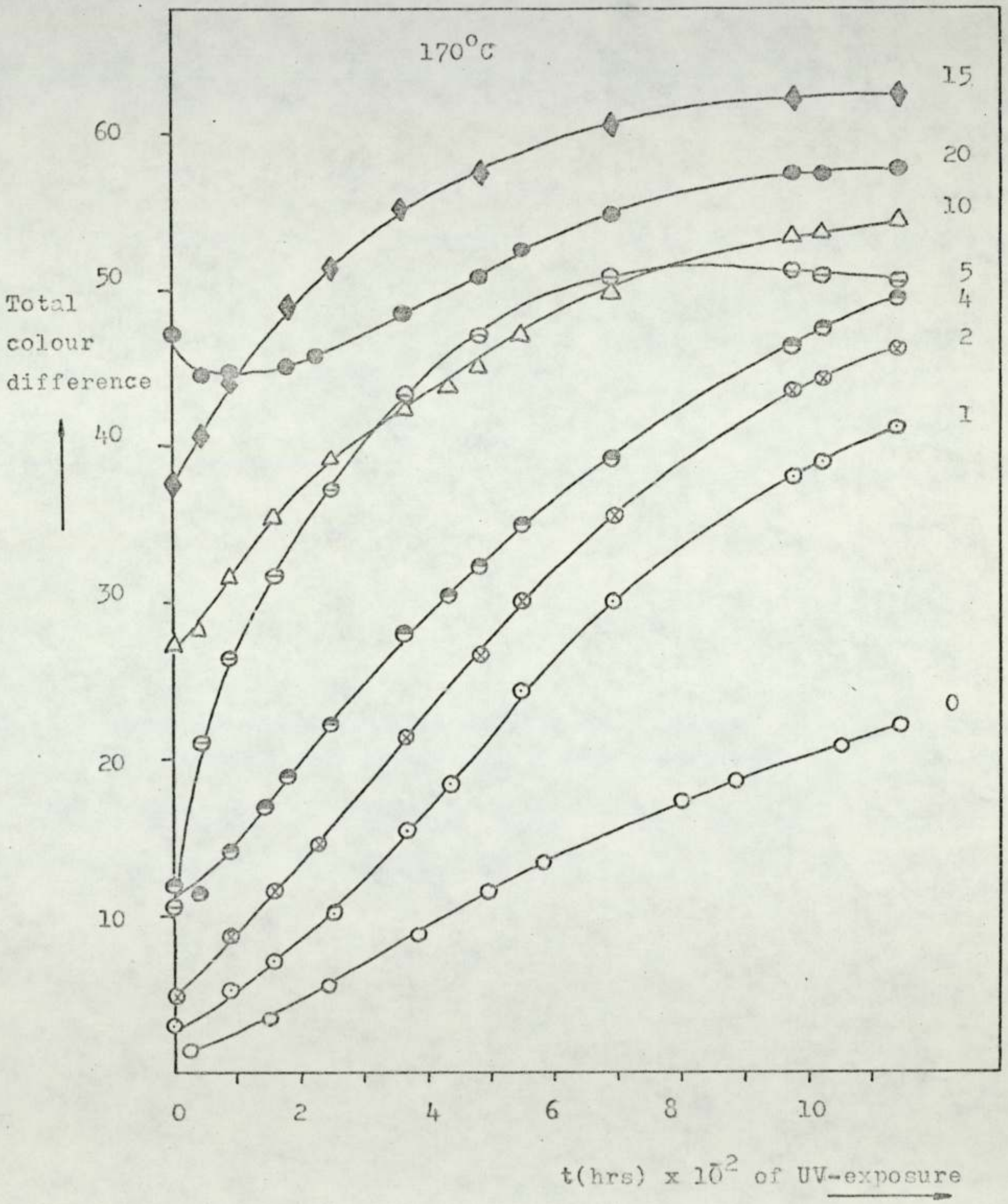


Fig. 6-9

Total colour difference of photooxidized PVC related to carbonyl index for PVC processed at 210°C without additives for different processing times.

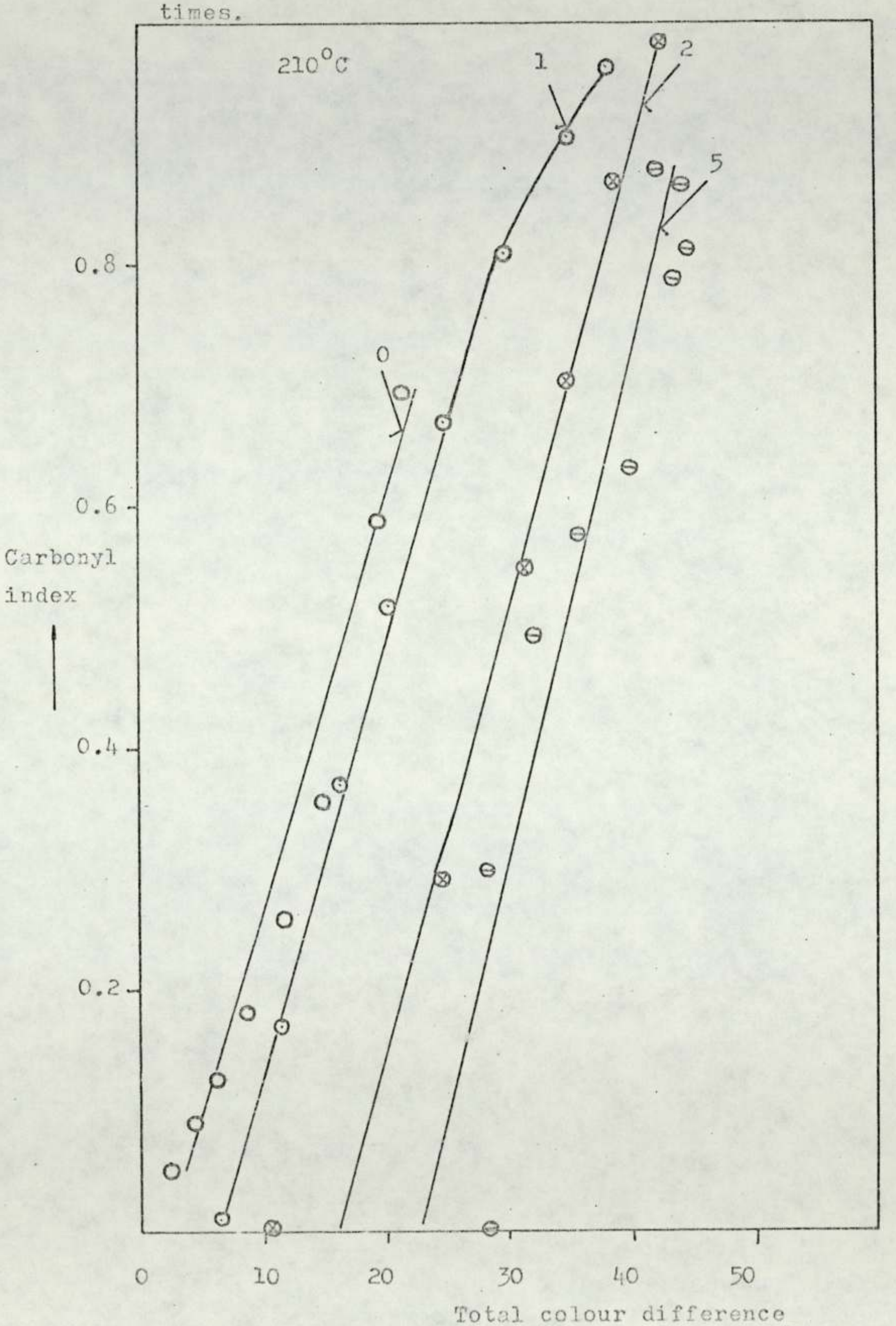


Fig.6-10

Total colour difference of photooxidized PVC related to carbonyl index for PVC processed at 170°C without additives for different processing times.

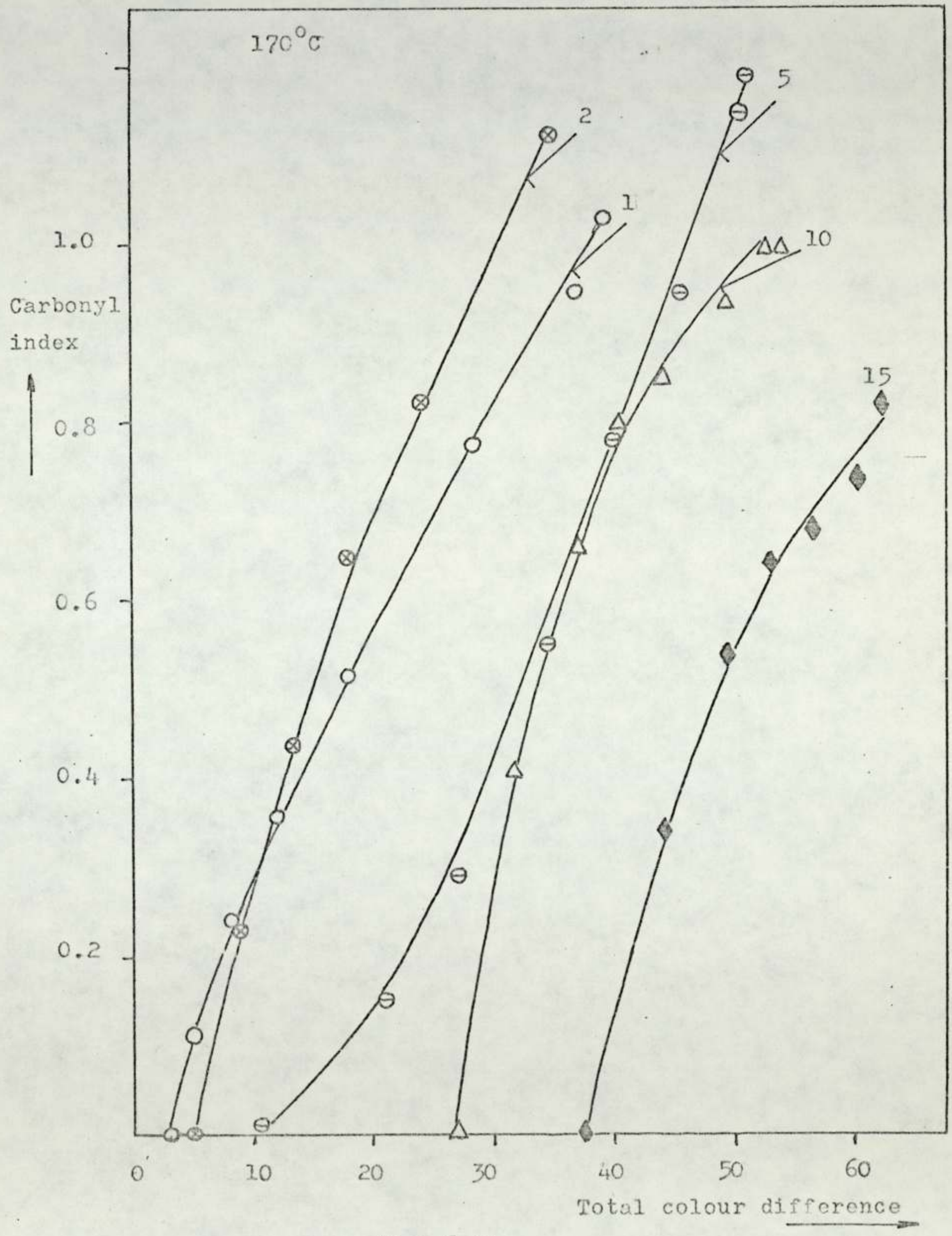


Fig. 6-11

Relationship between the permeability constant P and the gel content in PVC, processed without additives. (Permeability of air at room temperature)

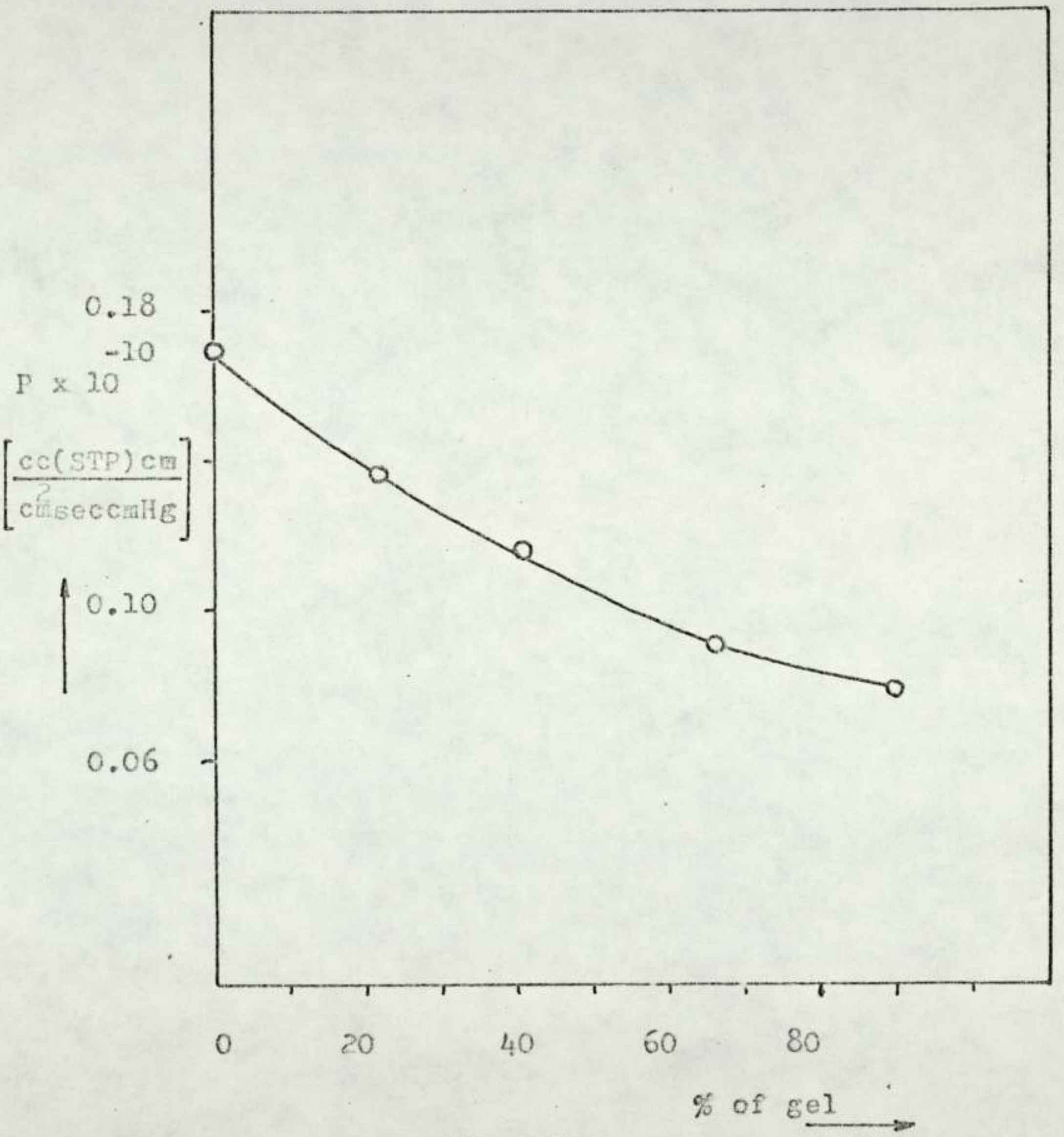


Fig.6-11a

Carbonyl absorption (centred at 1720cm^{-1}) and hydroxyl absorption formation during UV-irradiation of PVC, processed for 3min at 210°C without additives. (Gel phase).

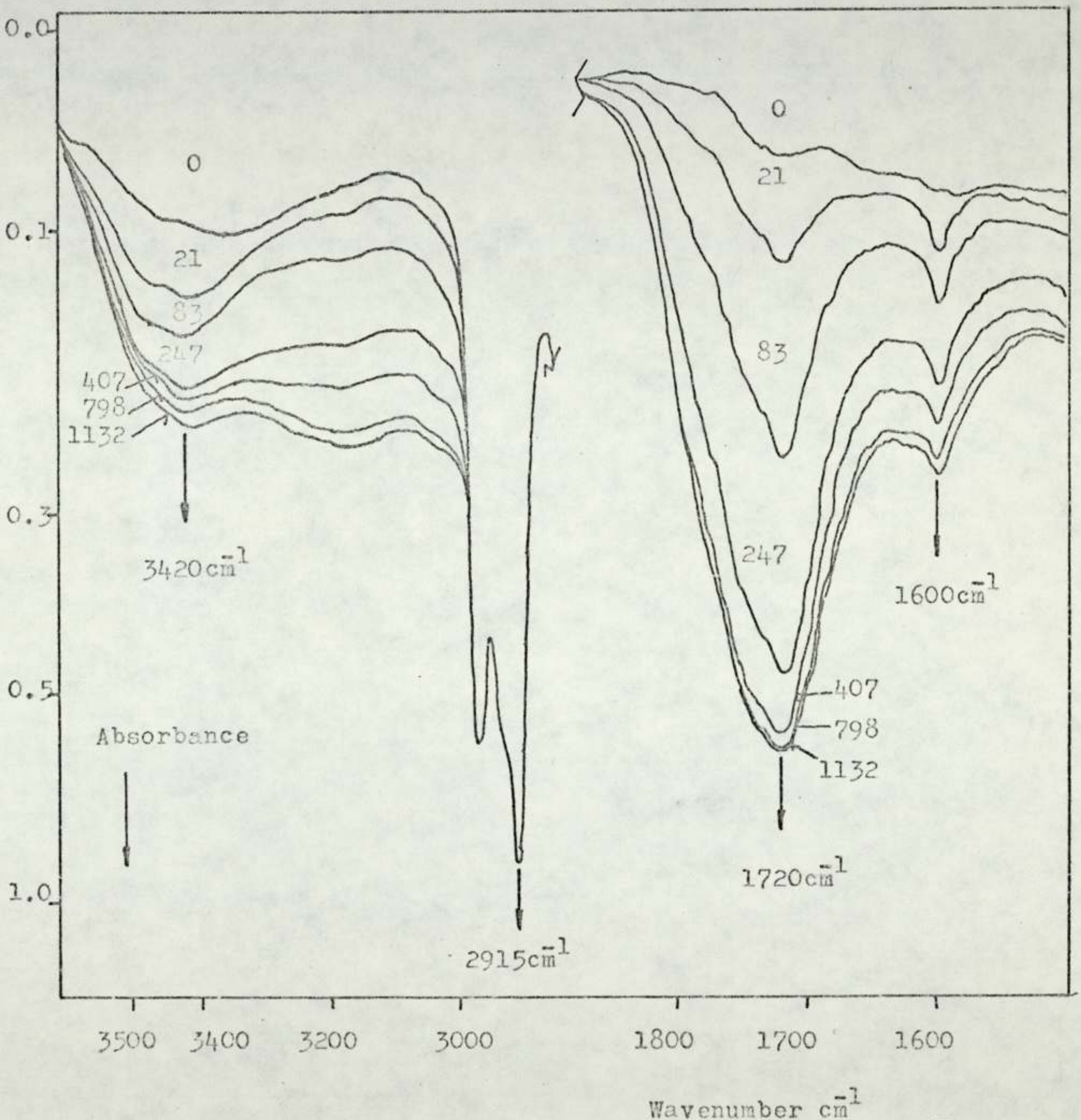


Fig. 6-12

Carbonyl index I_{CO}1715-20cm^{-1} vs UV-exposure time of PVC processed in torque rheometer for different processing times, no additives used (gel phase)

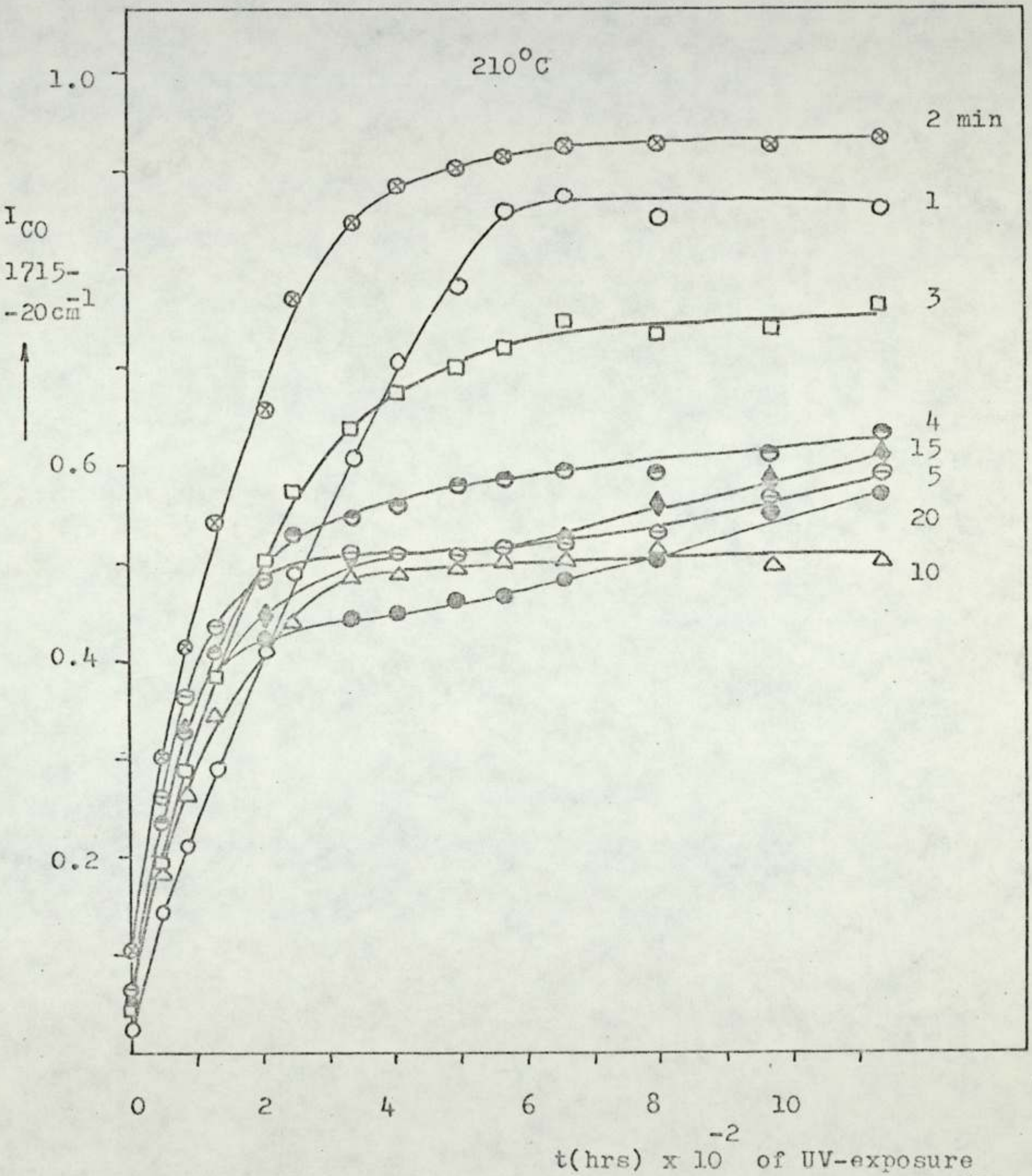


Fig. 6-13

Hydroxyl index $I_{3420-50cm^{-1}}$ vs UV-exposure time of PVC processed in torque rheometer for different processing times, no additives used (gel phase)

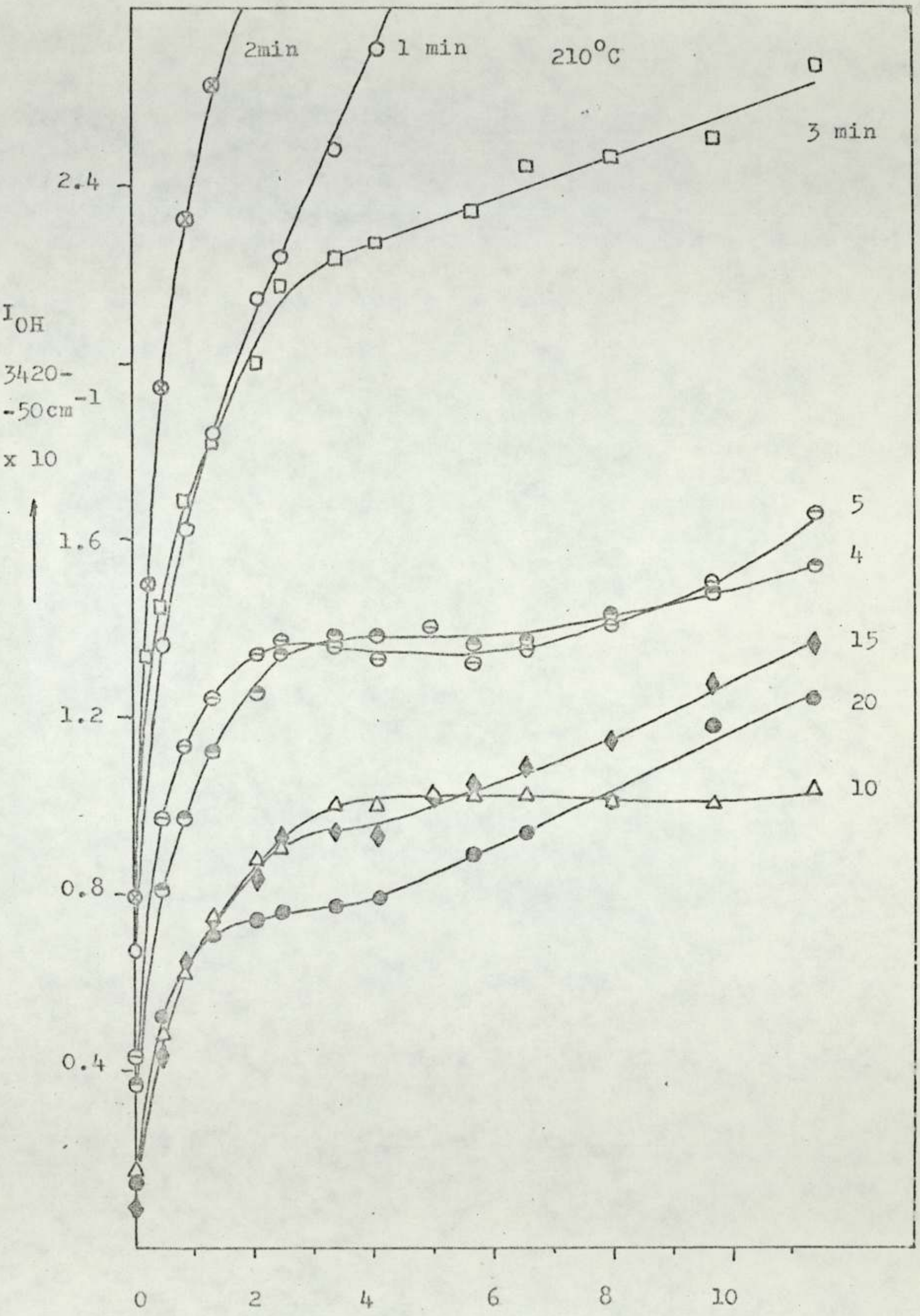


Fig. 6-14

Index $I_{1600cm^{-1}}$ (unsaturation) vs UV-irradiation time of PVC, processed at 210°C without additives. (Gel phase).

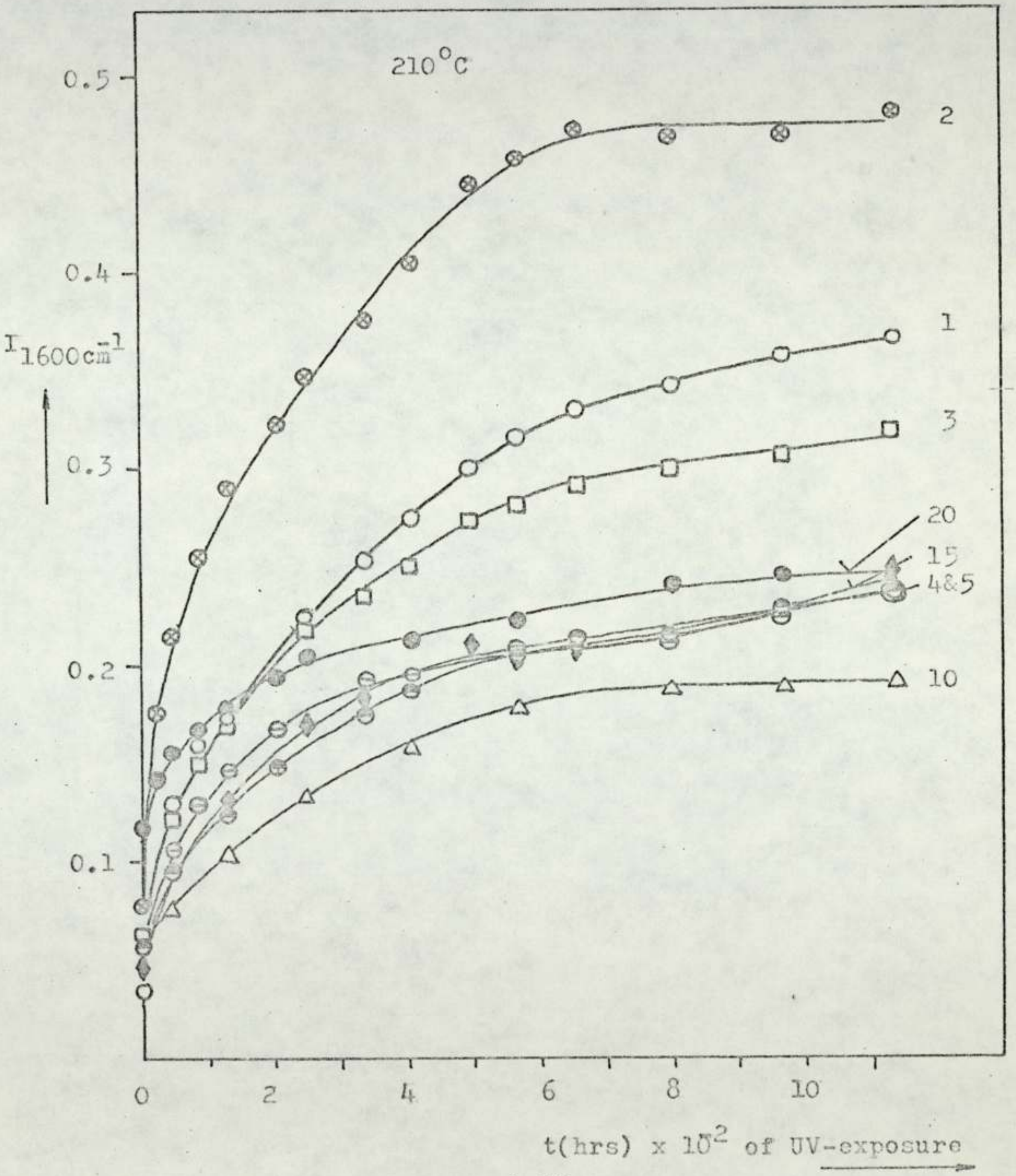


Fig. 6-15

Carbonyl Index I_{CO} 1720 cm^{-1} of the initial stage of photooxidation vs processing time, PVC processed at 210°C without additives.
(Gel phase)

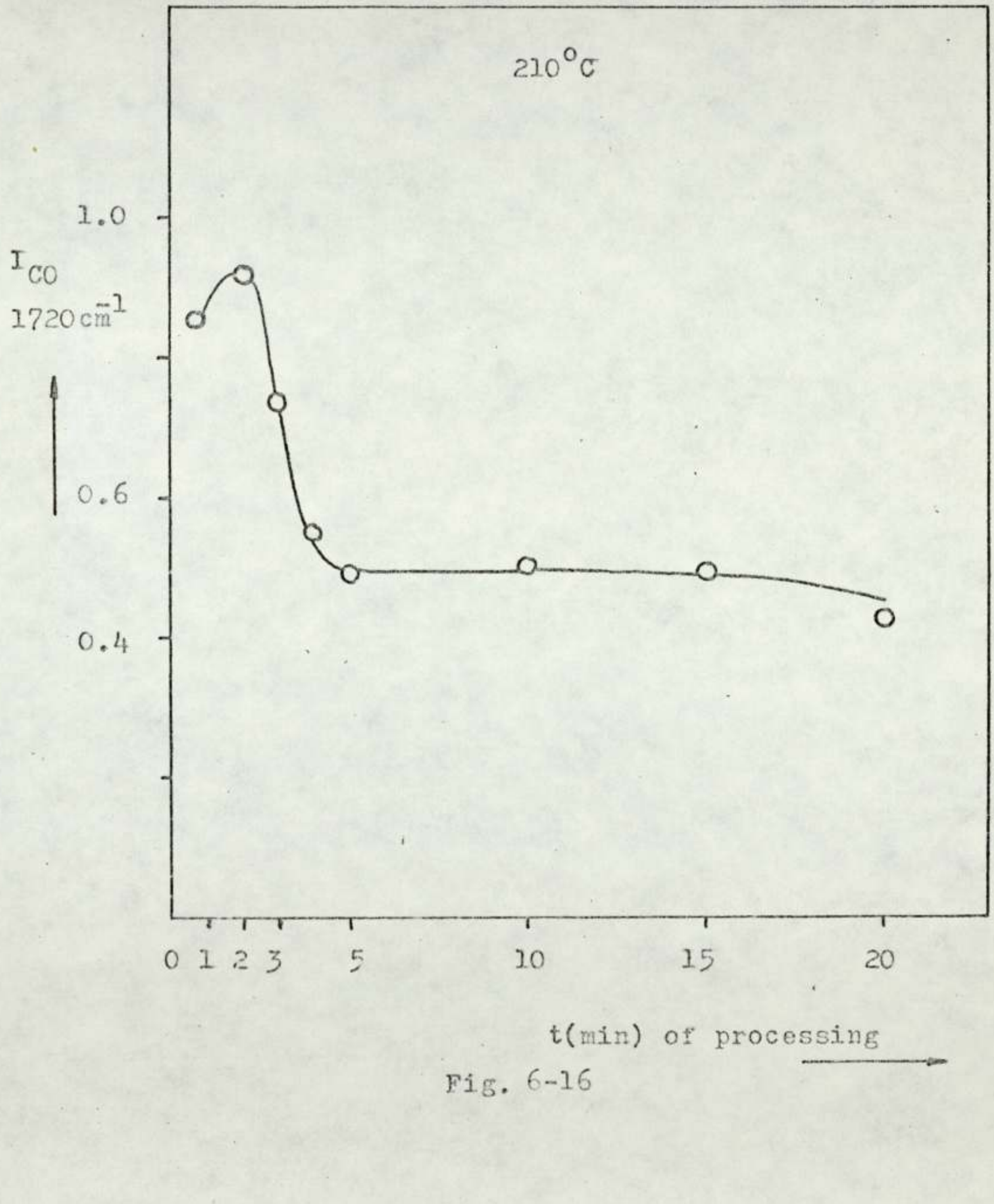


Fig. 6-16

Carbonyl index I_{CO} 1715cm^{-1}-1720cm^{-1} vs UV-exposure time of PVC processed at 170°C without additives.
(Gel phase)

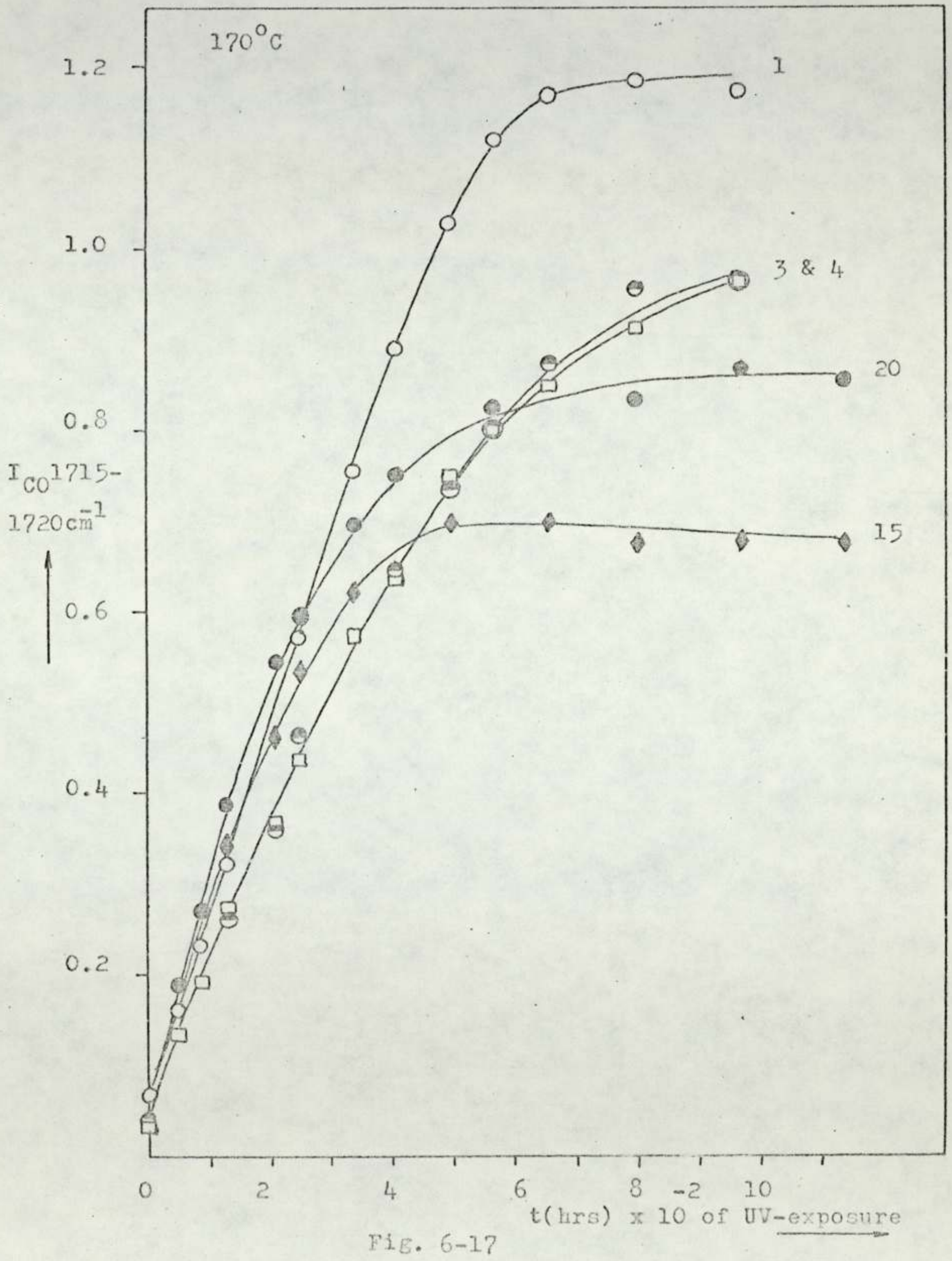


Fig. 6-17

Hydroxyl index I_{OH} $3420cm^{-1}$-$3450cm^{-1}$ vs UV-irradiation time of PVC, processed at 170°C without additives. (Gel phase)

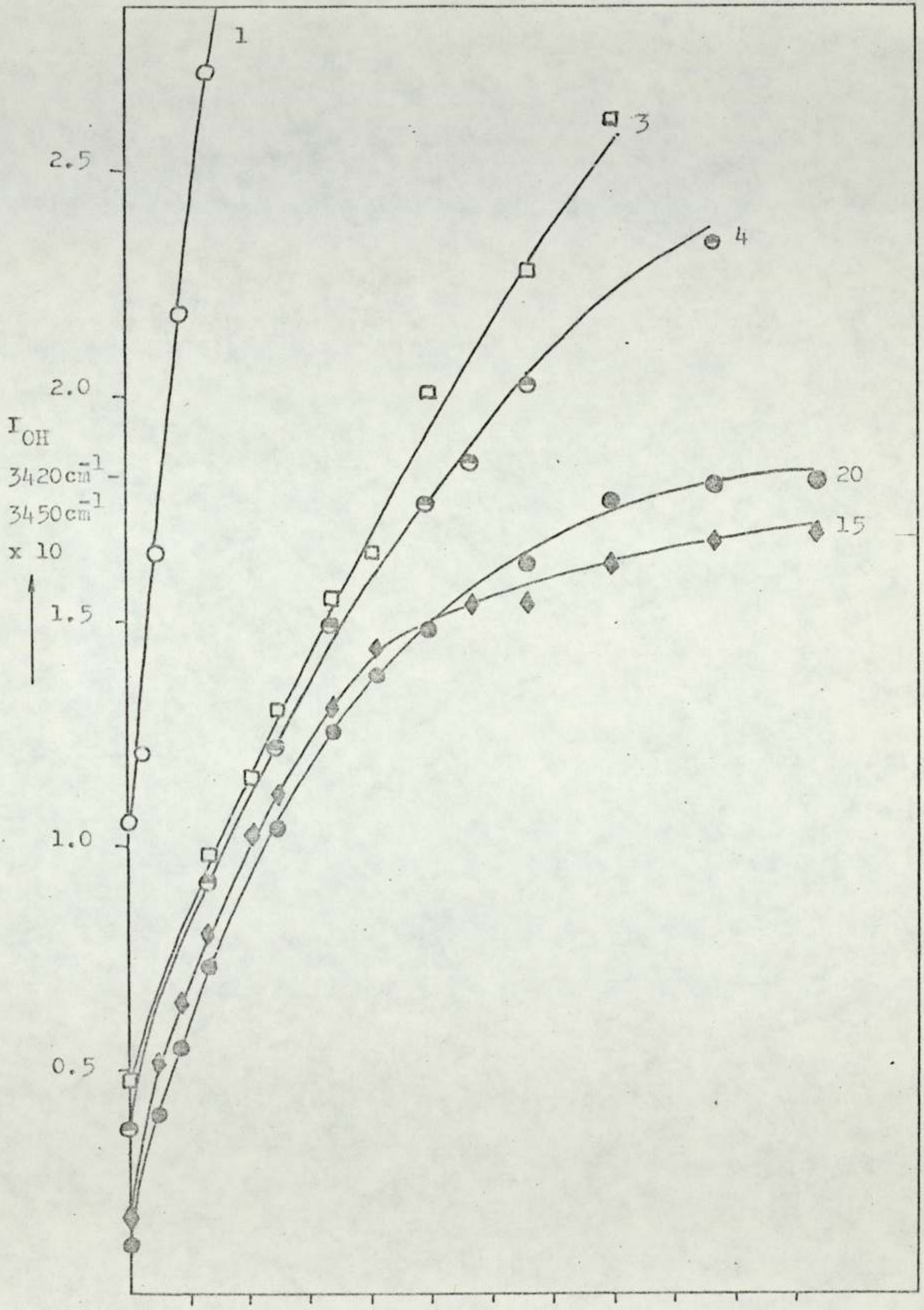


Fig. 6-18

Index $I_{1600 cm^{-1}}$ (unsaturation) vs UV-irradiation time of PVC, processed at 170°C without additives. (Gel phase)

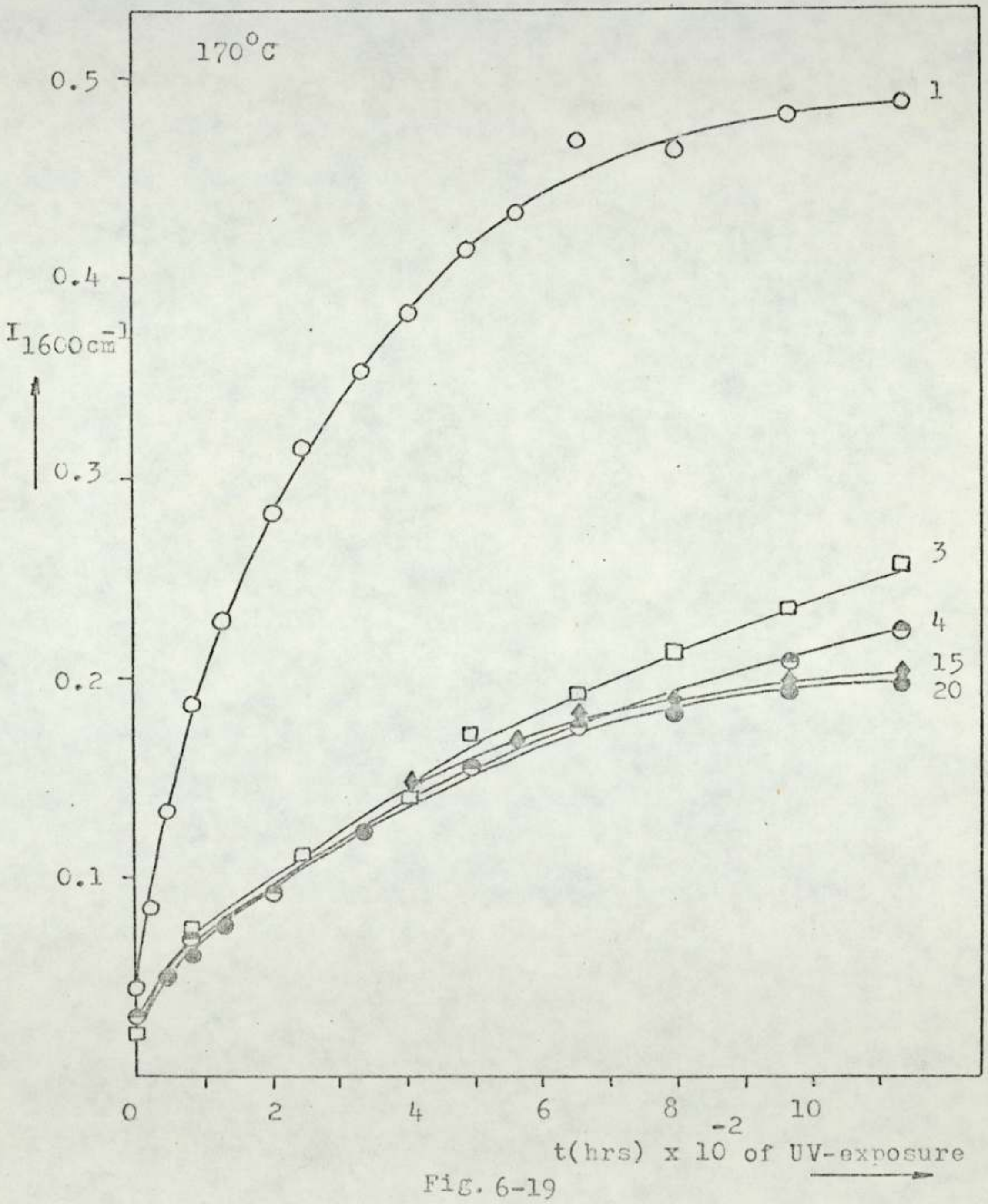


Fig. 6-19

Carbonyl index formation during UV-irradiation of PVC with different concentrations of soluble phase (in CH_2Cl_2) of processed PVC for 15min at 210°C

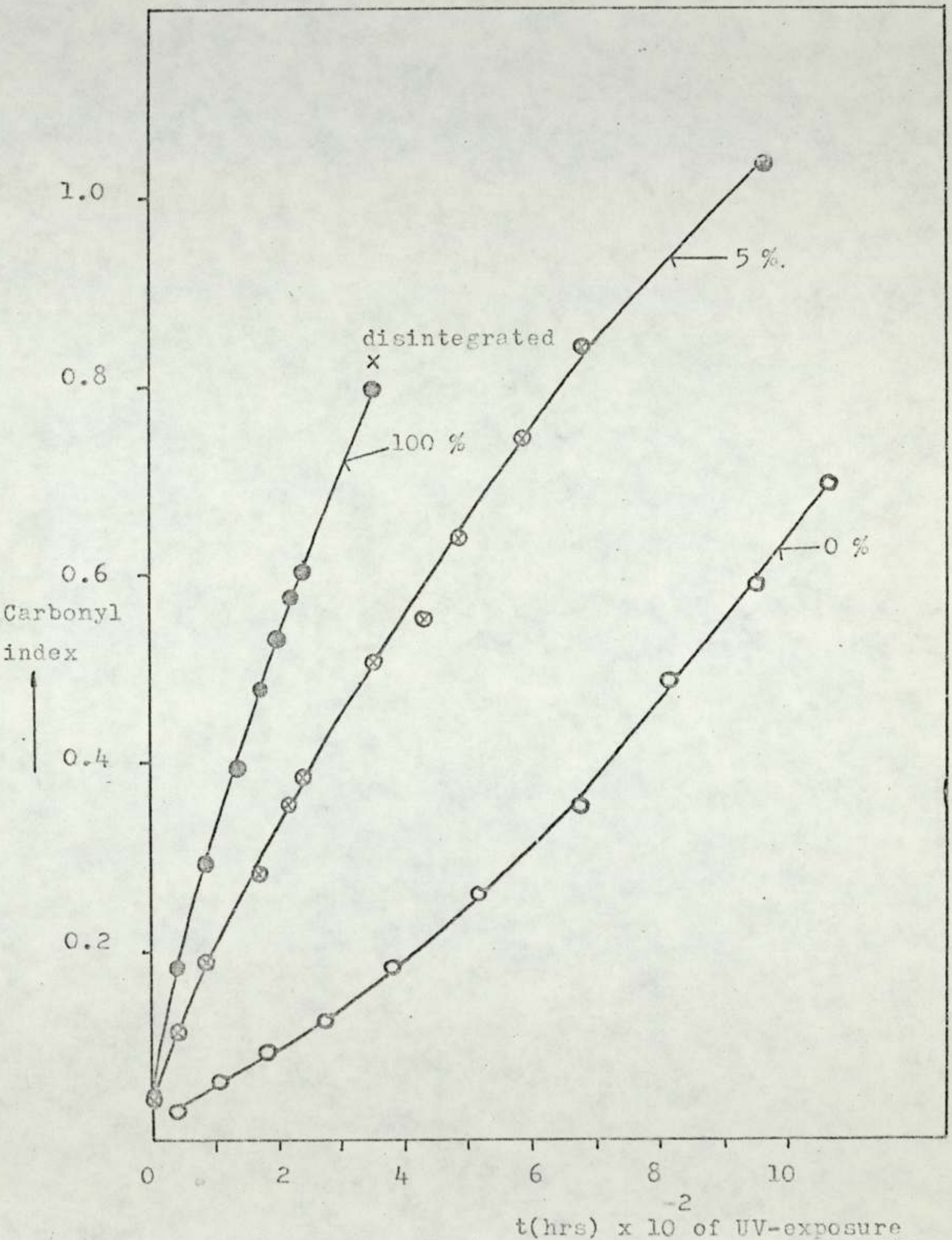


Fig.6-20

Carbonyl index formation during UV-irradiation of PVC with different concentration of soluble (in CH_2Cl_2) phase of processed PVC for 20min at 210°C

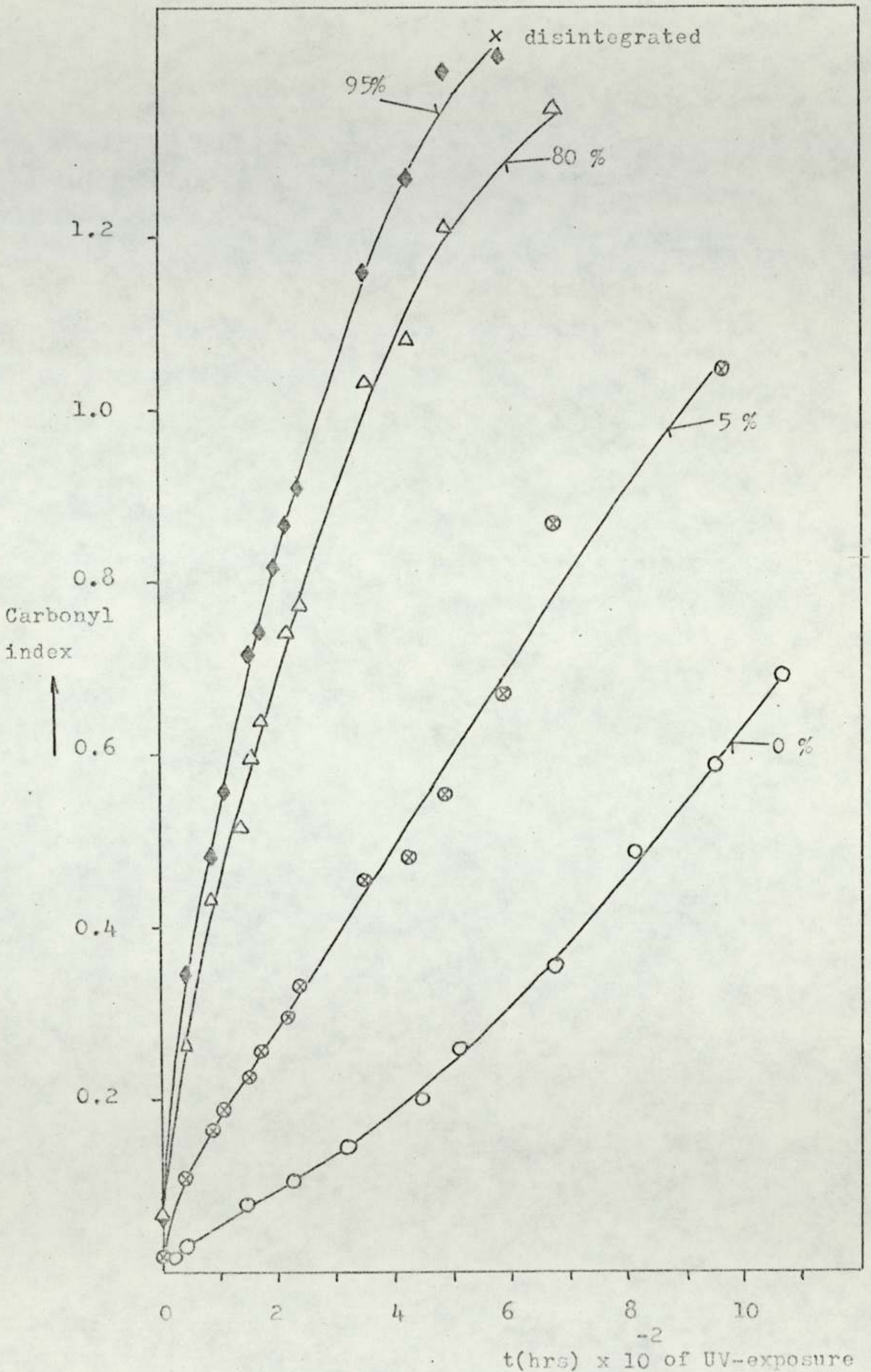


Fig. 6-21

Comparision of carbonyl band (1710 cm^{-1}-1720 cm^{-1}) formation in total sample, gel phase and soluble phase during UV-irradiation of PVC, processed for 15min at 210°C without additives.

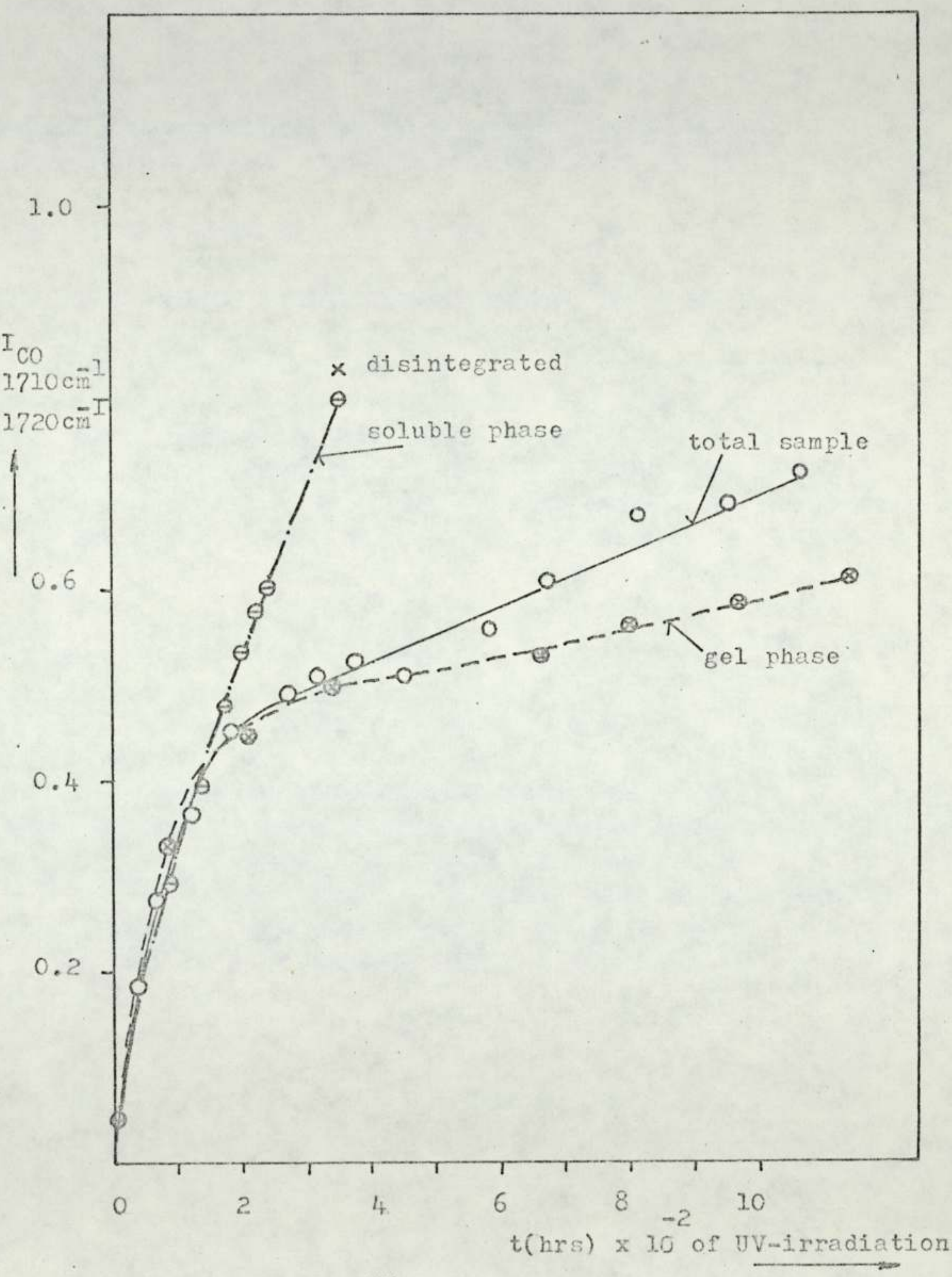


Fig. 6-22

CHAPTER 7. Photodegradation of PVC processed with Irgastab T290, Ca-stearate and Wax E.

Photodegradation of PVC was carried out with the polymer processed with Irgastab T290, Ca-stearate and Wax E for various times. The additives used during processing were added separately and also the processing was carried out with these additives added at the same time. The polymer used for the photodegradation study was in the form of ~~the polymer~~ films and the thickness of the films and the method of preparation was described earlier in the section 6-1.2., chapter 6. The irradiation apparatus and the radiation source used was described earlier in the section 6-1.1. and 6-1.1.1. The experimental methods used were IR-spectroscopy and the colour measurement. These were described in the section 6-1.3. of the chapter 6.

7-1. Photodegradation of PVC processed with Irgastab T290 only.

7-1.1. IR-spectroscopy results.

IR-spectra of processed polymer were obtained before exposure and after various times of irradiation. An example of IR-spectra of a sample processed for 5min at 170°C and irradiated up to ~1200 hrs is shown in Fig. 7-1. At least three absorption peaks developed in the carbonyl region of the spectra, centred at 1785 cm^{-1}, 1745 cm^{-1} and 1715-20 cm^{-1}. The growth of the 1715 cm^{-1}- 20 cm^{-1} peak was fastest and the peaks at 1785 cm^{-1} and 1745 cm^{-1} became the shoulders of the main carbonyl peak during the course of exposure. Furthermore, a peak centred at 1650 cm^{-1}- 55cm^{-1} appeared. The position of this peak (-C=C- stretching mode)[13] suggests formation of unconjugated unsaturation during irradiation. The double peak centred at 1605 cm^{-1} and 1570 cm^{-1}, which was present in the samples processed up to 20min at 170°C and 5-8min at 210°C before irradiation, disappeared during the irradiation. This peak was assigned (see section 4-1.1.3., chapter 4) to the carboxylate anion stretching mode of dibutyltin maleate. In the hydroxyl region of the spectra two broad peaks developed centred at 3200 cm^{-1} and 3450 cm^{-1}. These absorptions were shown to be formed also in the unstabilized polymer and were discussed in the section 6-2.1., chapter 6. 3200 cm^{-1} peak has been previously suggested[11] to be an acidic hydroxyl and 3450 cm^{-1} peak of H-bonded alcoholic hydroxyl (see chapter 6, section 6-2.1., 6-5).

The plot of carboxylate index I_{COO} is shown in Fig.7-2 for 170°C. The index decreased (samples 2-20min) during the irradiation and disappeared after 200-300hrs. This result may suggest that the carboxylate moiety reacted with the sites in the polymer during photodegradation or with HCl evolved during the exposure. It should be noted that the carboxylate peak also disappeared during processing with simultaneous formation of an ester (see e.g. Figs. 4-3a,b,4-5, 6, chapter 4). The carboxylate index of samples processed at 210°C is shown in Fig.7-2a. The index also decreased (samples 2 and 5min) within 200-300hrs of exposure. The index $I_{1650\ cm^{-1}-55cm^{-1}}$ is illustrated in Figs.7-3 and 7-3a for 170°C and 210°C, respectively. At 170°C the index started to increase after ~ 300 hrs (samples 2-20min) and at 210°C after ~ 200 and ~ 350hrs (5min and 2min, respectively). These results suggest that there is an induction period of ~ 200 - 350 hrs (depending on the initial carboxylate concentration) of unsaturation formation.

The plots of carbonyl indices for 170°C and 210°C are shown in Fig.7-4 and 7-5 and of hydroxyl indices in Figs.7-4a and 7-5a, respectively. The carbonyl indices of 170°C (Fig. 7-4, curves 2-20min) and of 210°C (Fig. 7-5, curves 2,5min) increased very slowly within the initial 200-300hrs but with further irradiation the rate considerably increased. The hydroxyl indices (Fig.7-4a, curves 2-20min and Fig. 7-5a, curves 2,5min) initially also increased at a slow rate but after about 200-300hrs the rate increased. It would appear that there was an induction period of ~ 200-300hrs for carbonyl and hydroxyl absorptions formation. This result is in good agreement with the induction period of unsaturation formation and with the decrease of the carboxylate peak, as discussed earlier. The existence of the induction period demonstrates that the thermal stabilizer dibutyltin maleate, which remained in the polymer after processing, is also UV-stabilizer by preventing formation of the unsaturation and significant formation of carbonyl and hydroxyl absorptions.

The carbonyl and hydroxyl indices of samples processed for longer time at 170°C (Figs. 7-4, 7-4a, curves 25,30min) increased immediately from the beginning of exposure at high rate. Similarly, an initial high-rate of formation of carbonyl, hydroxyl and unsaturation indices of 210°C samples (Figs. 7-5, 7-5a, 7-3a, curves 10-25min) was observed. It should be noted that these samples did not contain unreacted dibutyltin maleate because they were processed beyond the induction period (see chapter 4, Figs. 4-1,2,8). With further irradiation, however, the rate of carbonyl, hydroxyl and unsaturation considerably decreased and also the extent of photo-oxidation was smaller for samples processed for longer time. It should be noted that these samples contained increasing amount of the gel before irradiation (see Fig.4-1) and also they were progressively more discoloured (see Fig. 4-2) as a result of the thermal treatment during processing. It appears, that the photo-oxidation proceeded in two distinct stages viz initial fast stage followed by the second lower-rate stage. It is interesting to note that similar kinetic behaviour was observed with the samples processed without additives as it was shown in the previous chapter.

7-1.2. Colour change

Discolouration of the polymer processed at 170°C is illustrated in Fig. 7-6 and at 210°C in Fig. 7-7, respectively. The total colour difference of the samples processed at 170°C for 2-20min remained constant up to 300-400hrs of exposure (Fig. 7-6). With further irradiation the polymer became discoloured and the total colour difference increased. It appears that there was an induction period of 300-400 hrs of colour formation for the 2-20min samples processed at 170°C. An induction period of 300-

400hrs was also observed for 2min and 5min samples processed at 210°C (see Fig. 7-7).

The induction period was not observed for longer-time processed samples (Fig. 7-6, curves 25,30min and Fig.7-7, curves 8, 10-25min) and the polymer was discoloured immediately from the beginning of irradiation. On prolonged exposure the initial higher rate of discolouration decreased. It should be noted that similar kinetic behaviour was observed for the photo-oxidation as expressed by the carbonyl and hydroxyl indices and also for the unsaturation.

7-2. Photodegradation of PVC processed with Ca-stearate only.

7-2.1. IR-spectroscopy results.

IR-spectra of irradiated polymer contained broad carbonyl absorption peak centred at 1710 cm^{-1}-20 cm^{-1}. This main carbonyl peak contained two distinct shoulders, centred at 1745 cm^{-1} and 1785 cm^{-1}. Furthermore, an absorption peak centred at 1625 cm^{-1}-30 cm^{-1} was observed. The formation of the 1625 cm^{-1} peak has been previously shown[11] to be formed when the polymer containing Ca-stearate was UV-degraded. It is known[13] that the -C=C- stretching mode of unconjugated olefins shows an absorption at 1640 cm^{-1} - 1660 cm^{-1} and conjugated olefin an absorption at 1600 cm^{-1}. The nature of the band at 1625 cm^{-1}-1630 cm^{-1} is not yet clear but it may be due to conjugated or isolated double bonds, respectively.

In the hydroxyl region of the spectra a broad absorption developed with two distinct shoulders at 3200 cm^{-1} and

3450 cm^{-1}. These absorptions were observed previously (see Fig. 6-2 and 7-1 and the section 7-1.1.).

Before irradiation, the IR-spectra of the samples processed for 2min and 5min at 170°C and 2min at 210°C contained a double absorption peak centred at 1570 cm^{-1} and 1535 cm^{-1} (see Fig. 4-16, 17, chapter 4). These absorptions were attributed to the carboxylate of Ca-stearate (see section 4-2.1.2.). Both absorptions upon irradiation disappeared within the first 48-100 hrs (170°C processed samples) and 48 hrs (210°C processed samples).

The plots of carbonyl and hydroxyl indices vs UV-exposure time of 170°C processed samples are shown in Fig.7-8 and 7-9, respectively. The indices of 2min and 5min samples increased within the first 100hrs and then continued to increase linearly on prolonged exposure. It appears that there is an initial slow rate of hydroxyl and carbonyl formation during the first 100 hrs. The indices of longer-time processed samples increased immediately from the beginning of exposure at higher rate than 2 and 5min samples. However, after at about 600 hrs the rate considerably decreased.

The plots of carbonyl and hydroxyl indices of the 210°C processed samples are shown in Fig. 7-10 and 7-11, respectively. The indices increased immediately from the beginning of exposure for all the samples examined. The initial rate of photo-oxidation of longer-time processed samples was higher (see Fig.7-10,11, curves 10,15 and 22) than the 2 and 5min samples, but the rate considerably decreased after about 200-300 hrs of exposure.

Comparison of carbonyl and hydroxyl indices of the samples processed for 20min at 170°C and 22min at 210°C is shown in Fig. 7-12. It can be seen that the extent of the initial fast-rate stage of photo-oxidation is higher for 170°C sample and also the duration is longer (600hrs compared with 200-300 hrs). It can also be seen that the hydroxyl absorption peak was formed simultaneously with the carbonyl absorption. It should be noted that the 210°C sample contained 89% of gel before irradiation and the 170°C sample only 25.7%. Also the total colour difference data of the 210°C sample before irradiation was 71.1 whereas of the 170°C sample was 39.5.

The plot of the index of the absorption peak at 1625 cm^{-1}-1630 cm^{-1} vs UV-exposure time is shown in Fig.7-13 for 170°C samples and for 210°C samples in Fig. 7-14, respectively. The index of 2 and 5min samples (Fig. 7-13) increased rapidly after 100 hrs and of the 10 -30 min samples the rate considerably decreased after the initial higher rate. In Fig.7-14 only the index of 2 and 5min samples is shown because the absorption peak of 10-22min samples, initially observed at 1625 cm^{-1} -1630 cm^{-1}, has broadened towards the 1600 cm^{-1} region. The index of 2min sample rapidly increased after 48hrs and of the 5min sample the index increased initially but the rate decreased on prolonged exposure.

7-2.2. Colour change

Discolouration of PVC processed at 170°C and 210°C is illustrated in Fig. 7-15 and 7-16, respectively. The total colour difference of 2 and 5 min samples (Fig. 7-15) exhibited a short induction period of 100 - 200 hrs and on prolonged exposure the discolouration considerably increased. Discolouration of the longer-time processed sample increased immediately at a higher rate, but the rate decreased at longer time of exposure. Furthermore, a decrease of discolouration was observed of 20min and 30min/170°C samples within the initial 100hrs of exposure. This initial decrease was also observed with 2-10 min/210°C samples (Fig.7-16). This initial drop may be the result of 'bleaching' of the polymer, a phenomenon observed previously [98,31,102,103] and associated with the oxidation of the polyenes present in the polymer. The total colour difference then continued to increase but again the rate decreased at longer time (Fig.7-16, curves 5,10). The colour of 15 and 22min/210°C samples, however, showed only an insignificant decrease during the whole exposure period. Similar results were observed for the polymer processed without additives (see Fig. 6-8, curves 15,20, chapter 6). The discolouration of these samples before the irradiation was relatively high (the polymer was brown-black). It may be that the high initial discolouration fulfilled the role of a light-screening agent and prevented significant photo-oxidation of the interior of the film. It is likely, however, that the crosslinked structure decreased the rate of diffusion of oxygen through the polymer film (as it was shown in chapter 6) and therefore photo-oxidation was retarded.

7-3. Photodegradation of PVC processed with Wax E only

7-3.1. IR-spectroscopy results

IR-spectra of irradiated polymer contained similar absorption peaks observed in the spectra of irradiated unstabilized polymer (see e.g. Fig. 6-2) viz a predominant carbonyl absorption centred at 1720 cm^{-1}, a broad hydroxyl absorption with two distinct shoulders at 3200 cm^{-1} and 3450 cm^{-1}. Also a significant broadening of the main carbonyl peak in the region of 1600 cm^{-1}-1700 cm^{-1} was observed. The plots of carbonyl and hydroxyl indices vs UV-exposure time of 170°C processed samples are shown in Figs. 7-17 and 7-18, respectively. The indices rapidly increased from the beginning of irradiation but significantly decreased after about 400 hrs.

The plots of carbonyl and hydroxyl indices of 210°C processed samples are shown in Figs. 7-19 and 7-20, respectively. Here again the rapid initial increase was followed by a slower rate of photo-oxidation for longer-time processed samples (curves 5-22 min); the retardation of photo-oxidation appeared after about 200 hrs of exposure. Furthermore, the extent of photo-oxidation of higher temperature processed samples was smaller. This is illustrated in Fig.7-21, where the carbonyl and hydroxyl index is plotted against the exposure time for the 15 min samples of both processing temperatures. It should be noticed that the gel content before irradiation of 15min/210°C sample was 74% and of 15min/170°C sample was 22.9% and also the total colour difference was 72.2 and 21.5, respectively.

7-3.2. Colour change

Discolouration of the polymer processed at 170°C and at 210°C is illustrated in Figs.7-22 and 7-23, respectively. The total colour difference increased rapidly (Fig.7-22) and on prolonged exposure the rate decreased. For 20min and 30min samples a decrease within the first 50-100hrs was observed. This result may suggest that the 'bleaching' of the polymer occurred as was discussed in the previous section 7-2.2. The total colour difference of 2-10min samples (Fig. 7-23) also increased initially at the high rate but the rate later decreased. It is interesting to note that the discolouration appeared to follow the same kinetics as photo-oxidation as measured by carbonyl and hydroxyl formation viz a fast initial rate followed by a second stage slower reaction. Discolouration of 15 and 22min/210°C samples (Fig.7-23) was high before the exposure and during the exposure only an insignificant decrease of discolouration was observed.

7-4. Photodegradation of PVC processed with Irgastab T290, Ca-stearate and Wax E.

7-4.1. IR-spectroscopy results.

The absorption peaks which developed during exposure were centred at 1710 cm^{-1}-20 cm^{-1}, 1735 cm^{-1}- 45 cm^{-1} and 1785 cm^{-1}. The growth of the 1710 cm^{-1}-1720 cm^{-1} peak was fastest, thus it became predominant during the course of exposure. In the hydroxyl region of the spectra a broad peak with two distinct shoulders developed, centred at 3200 cm^{-1} and 3450 cm^{-1}. Furthermore, a distinct absorption peak at 1655 cm^{-1} was also observed. These spectral changes were identical to the changes observed with the polymer processed with Irgastab T290 (see e.g. Fig.7-1) and described in the section 7-1.1. In the spectra of samples, processed within the thermal induction period, a broad peak centred at 1570 cm^{-1} was present and this peak progressively disappeared during the exposure. This broad peak contained distinct shoulders centred at 1605 cm^{-1} and 1535 cm^{-1}-1540 cm^{-1} and were attributed (see section 4-4.1.3.) to the carboxylate anion of dibutyltin maleate (absorptions at 1605 cm^{-1} and 1575 cm^{-1}) and Ca-stearate (absorptions at 1572 cm^{-1} and 1535 cm^{-1}).

The plot of the carboxylate index vs exposure time is shown in Fig. 7-24 for 2-20min/170°C samples. The index decreased linearly and the peak disappeared after 300-375hrs. The 1655 cm^{-1} absorption index is shown in Fig.7-25. It can be seen that for the same samples the latter absorption was not detected up to 400 hrs, but after this time the index rapidly increased. It is clear that the index increased only when all the carboxylate has reacted.

The carbonyl and hydroxyl indices of 170°C samples are shown in Figs. 7-26 and 7-27, respectively. The hydroxyl index exhibited an induction period of about 300hrs for 2-20min samples. This is in good agreement with the decrease of the carboxylate index within this time and also with the formation of the absorption at 1655 cm^{-1} (due to C=C stretching mode) which was observed after this induction period. The induction period of carbonyl formation was not, however, clearly seen. This may be explained by the contribution of the acidic carbonyl of stearic acid, which might have been formed by the reaction of Ca-stearate with HCl.

The plot of the carboxylate index of 210°C samples is shown in Fig. 7-28 and of the 1655 cm^{-1} peak index in Fig. 7-29. The carboxylate index of 2 and 5min samples decreased and the absorption peak disappeared after 370 hrs and 250 hrs, respectively. The peak at 1655 cm^{-1} appeared at about 400 hrs and the index rapidly increased with further irradiation. The plots of carbonyl and hydroxyl indices are shown in Figs. 7-30 and 7-31, respectively. Here again the hydroxyl index of 2 and 5min samples exhibited an induction period of 350 hrs and 200hrs, respectively. The induction period of carbonyl formation was again less pronounced as for the carbonyl index of 170°C samples mentioned above.

The rate of photo-oxidation of the samples processed at both temperatures beyond the induction period (samples 25, 35min/170°C and 10-22min/210°C), was initially higher but the rate significantly decreased at longer exposure times. The similar kinetic behaviour was observed for the formation of the absorption peak at 1655 cm^{-1} (see Figs. 7-25, 7-29).

7-4.2. Colour change

Discolouration of the polymer processed at 170°C and 210°C is shown in Figs. 7-32 and 7-33, respectively. An induction period of ~300 hrs for 2-20min/170°C and 2 and 5 min/210°C samples was observed. This induction period is in good agreement with the observed induction period of photo-oxidation coupled with the disappearance of carboxylate absorption at 1570 cm^{-1}. The samples processed beyond the induction period were discoloured immediately from the beginning of exposure and the rate decreased at longer time of irradiation.

7-5. Discussion

It was shown in the section 7-1.1. and 7-1.2. that the samples processed with Irgastab T290 up to 20min at 170°C and 5-8min at 210°C exhibited an induction period in carbonyl and hydroxyl formation and also an induction period in colour formation. The duration of the induction period of photo-oxidation (the carbonyl and hydroxyl absorptions formation) was 200 - 300 hrs. During this induction period the carboxylate peak (see Fig. 7-2, 2a) decreased and disappeared at the end of the induction period and the absorption at 1655 cm^{-1}, due to the unsaturation, appeared. It is clear that the stabilizer which remained in the polymer after processing acted as UV-stabilizer. The disappearance of the carboxylate absorption was also observed during the thermal treatment (see chapter 4, Fig. 4-5). This may suggest that during UV-degradation, the carboxylate moiety of the stabilizer reacted with the sites in the polymer (for example with allylic chlorine) and prevented the formation of unsaturation. It is also possible that the stabilizer reacted with HCl evolved during irradiation. The fact that the stabilizer prevented formation of unsaturation is demonstrated by the existence of the induction period of formation of 1655 cm^{-1} absorption peak (see Fig.7-3,3a) and also by the induction period to colour formation (see Fig. 7-6 and 7-7). It has been previously shown[11] that during UV-exposure the carboxylate absorption (centred at 1580 cm^{-1}) disappeared and also the formation of the peak at 1655 cm^{-1} has been demonstrated[11]. The formation of allylic hydroperoxide has been also previously suggested[11]. Because of the reaction of the stabilizer with the reactive sites in the polymer (probably allylic), the formation of allylic hydroperoxide was prevented. Consequently the formation of carbonyl and hydroxyl absorptions was minimized (see Figs. 7-4, 5 and 7-4a, 5a) and the induction period of photo-oxidation was observed. These results demonstrate that during UV-ageing of PVC the presence of an agent which reacts with evolved HCl and also with reactive sites (e.g. allylic) in the polymer, prevents formation of polyenes and consequently prevents significant photo-oxidation of the polymer. It has been previously pointed out[104] that UV-screening agents are not effective enough in stabilizing PVC against light unless an efficient thermal stabilizer is also employed.

After the induction period the carbonyl and hydroxyl indices (see Figs. 7-4, 5 and 7-4a, 5a) and also the unsaturation rapidly increased (see Figs. 7-3, 3a). The unsaturation, carbonyl and hydroxyl indices of the samples processed for longer time increased immediately from the beginning of exposure. They were also discoloured immediately from the start of exposure (see Fig. 7-6 and 7-7). However, on prolonged exposure the rate of photo-oxidation decreased (see e.g. Figs. 7-5,5a) and also the extent of photo-oxidation of longer time processed samples was smaller. It appears that the photo-oxidation proceeded in two stages viz initial fast-rate stage followed by the second slower-rate stage. The similar behaviour was observed during UV-degradation of PVC processed without additives (see chapter 6) where it was shown that the retardation of photo-oxidation was predominantly the result of slower diffusion of oxygen through the crosslinked structure. It should be pointed out that the gel content before irradiation (see Fig.4-1, chapter 4) in the samples was progressively increased up to 68.2% and therefore it is likely that the observed retardation of photo-oxidation is due to the slower oxygen diffusion as mentioned above.

The hydroxyl and carbonyl indices of polymer processed for 2min and 5min at 170°C with Ca-stearate increased at a slower rate within the first 100 hrs of exposure (see Figs. 7-8,9) and also a small induction period of colour formation was observed (see Fig. 7-15). During this period the carboxylate double peak at 1570 cm^{-1} and 1535 cm^{-1}-1540 cm^{-1} disappeared. Furthermore, absorption peak at 1625cm^{-1}-1630cm^{-1} which is probably due to unsaturation (see Fig.7-13, curves 2,5) appeared after 100 hrs of exposure. It is therefore clear that Ca-stearate which remained in the polymer after processing reacted with the polymer during UV-degradation and and acted as an UV-stabilizer. The photodegradation of the samples processed for longer time proceeded again in two stages viz initial fast photo-oxidation followed by the slower-rate second stage (see Figs. 7-8, 9, curves 10-30 and Figs.7-10, 11, curves 10-22).

Similar kinetic behaviour, as expected, was observed for the polymer processed with Wax E (see Figs. 7-17, 18, 19, 20). Furthermore, comparison of carbonyl and hydroxyl indices (Figs. 7-12 and 7-21) suggests that the polymeric ketone and polymeric alcohol were formed simultaneously as a result of photolysis of intermediate hydroperoxide. Also the extent of photo-oxidation of samples processed at higher temperature was smaller and this result again demonstrates the role of the crosslinking on the retardation of photo-oxidation as it was discussed earlier in this section and in the section 6-5 of chapter 6.

The results of photo-degradation study with the polymer processed with all additives together appear to be similar to the results obtained with the polymer processed with Irgastab T290 only. The induction period of hydroxyl absorption was observed (see Figs. 7-27 and 7-31). The carboxylate peak at 1570 cm^{-1} decreased during the induction period (see Figs.7-24,28) and the induction period of unsaturation was also observed (see Figs. 7-25, 29) together with the induction period of colour formation (Figs. 7-32, 33). The induction period of carbonyl absorption (Figs. 7-26, 30) was, however, not pronounced probably because of the formation of carbonyl peak of stearic acid formed by the reaction of Ca-stearate with evolved HCl.

The photo-oxidation of samples processed beyond the induction period proceeded, as expected, in two stages viz initial fast stage followed by the slow second stage (see example Figs. 7-30, 31, curves 10-22). This result is similar to the results obtained with the polymer processed without additives and with longer time processed samples discussed earlier in this section.

IR-spectra of UV-irradiated PVC, processed in torque rheometer for 5min at 170°C with Irgastab T290

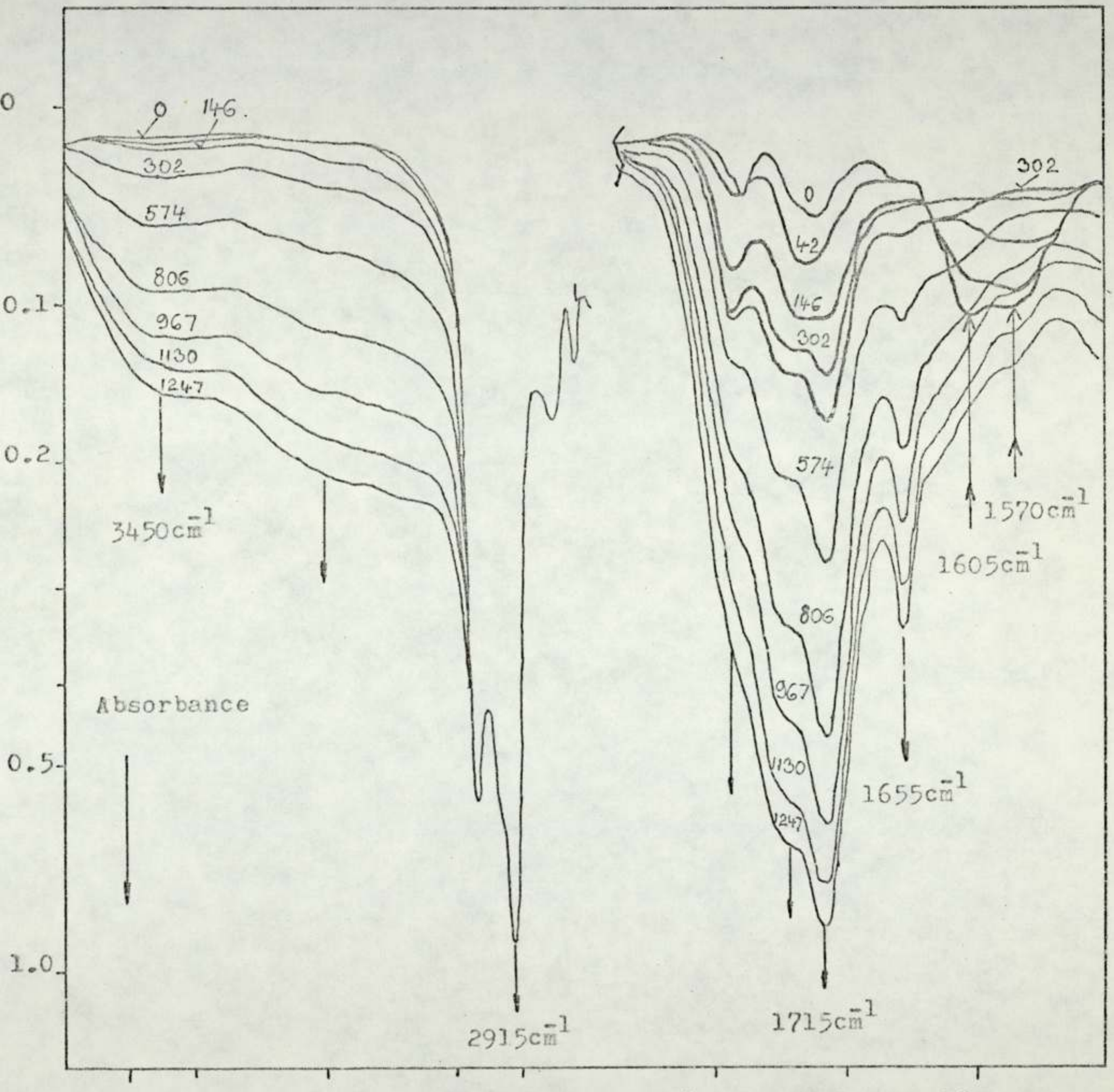


Fig. 7-1

Carboxylate index vs UV-exposure time, PVC processed with Irgastab T290 at 210°C

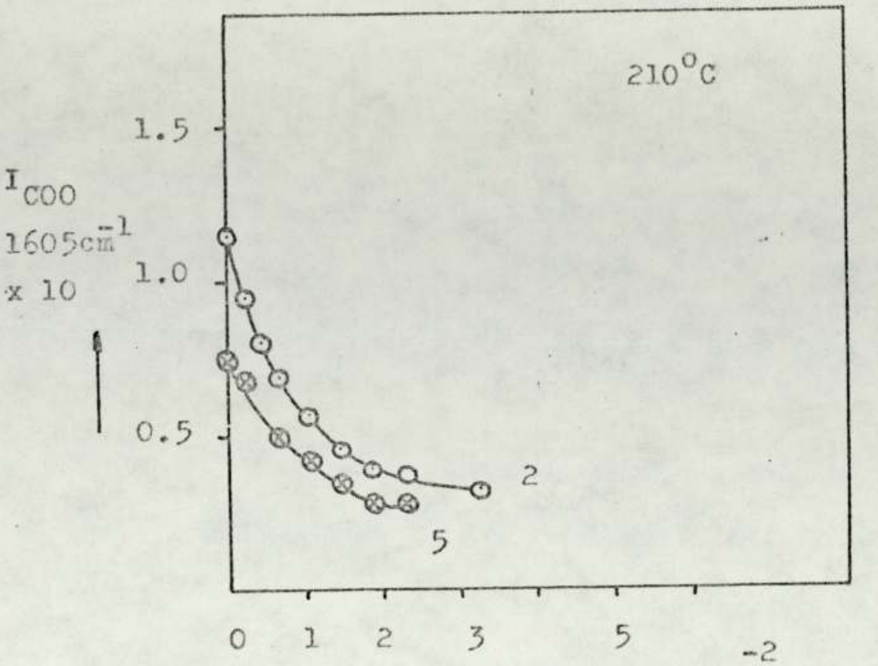


Fig.7-2a

Index $I_{1650-55cm^{-1}}$ vs UV-exposure time, PVC with Irgastab T290

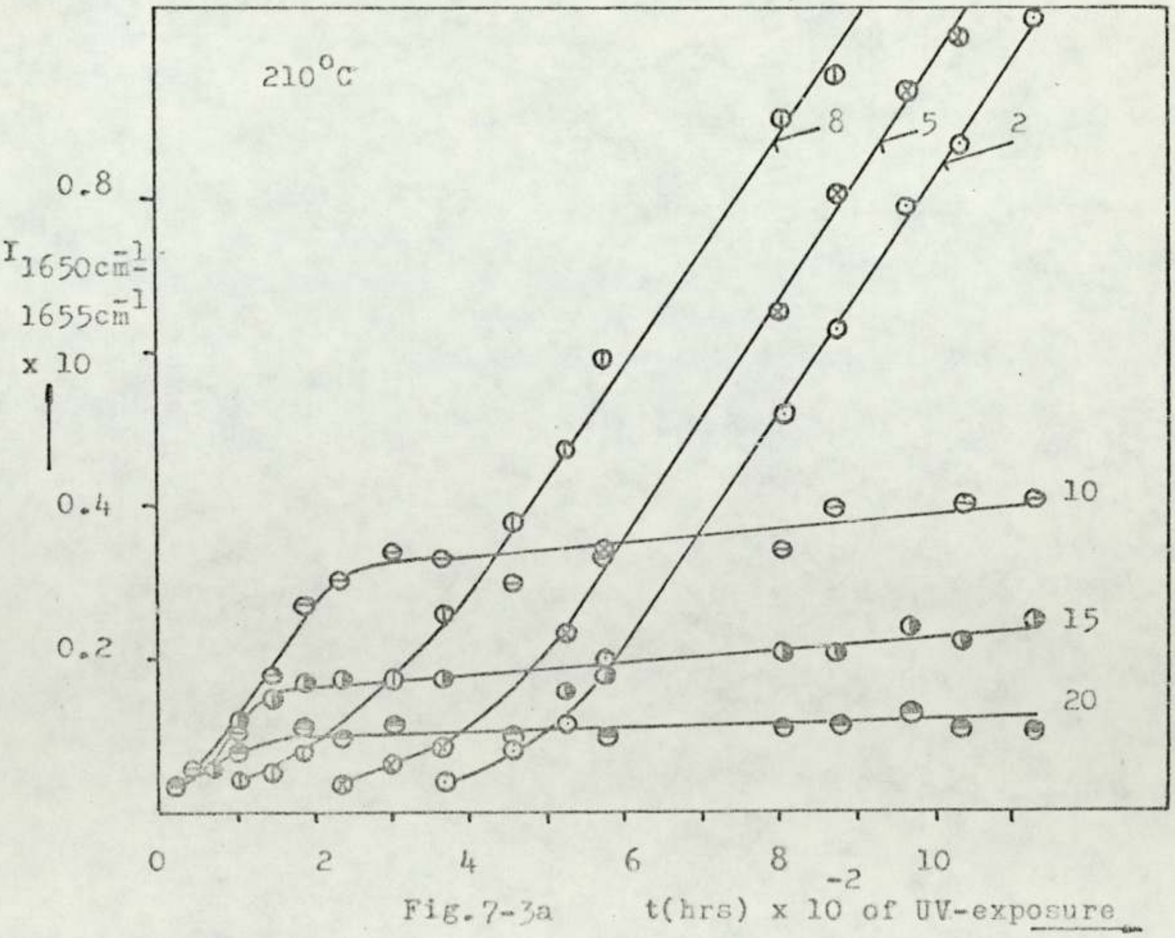


Fig.7-3a

Carboxylate index vs UV-exposure time

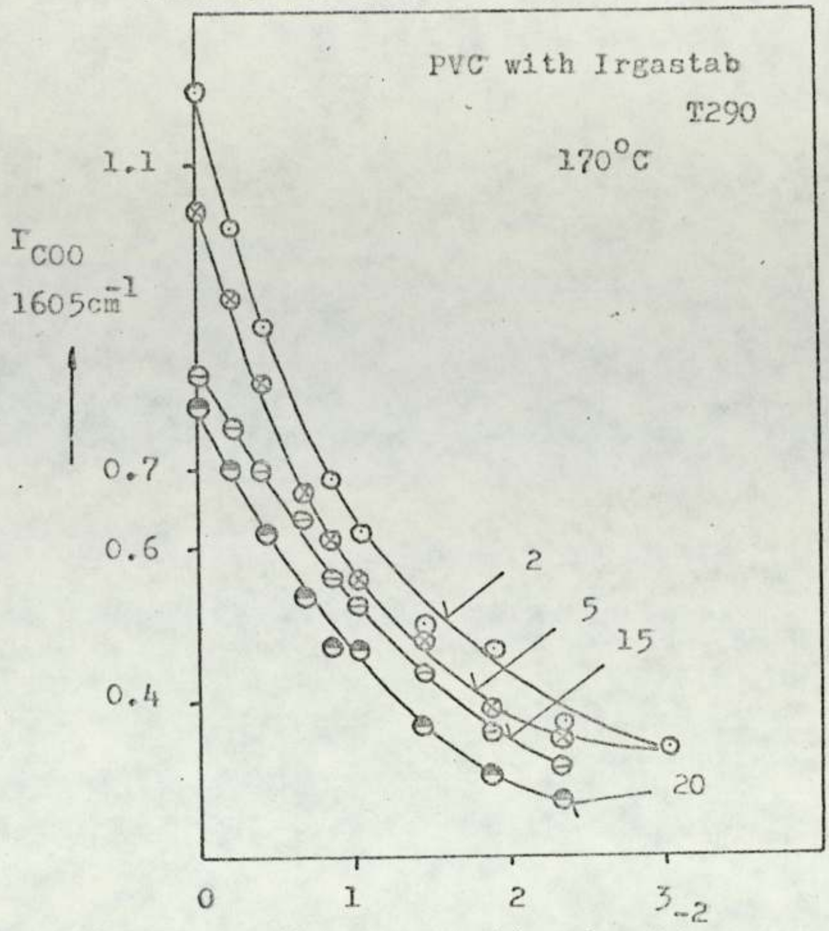


Fig. 7-2 t(hrs) x 10^{-2}

Carbonyl index vs UV-exposure time,PVC with Irgastab T290,170°C

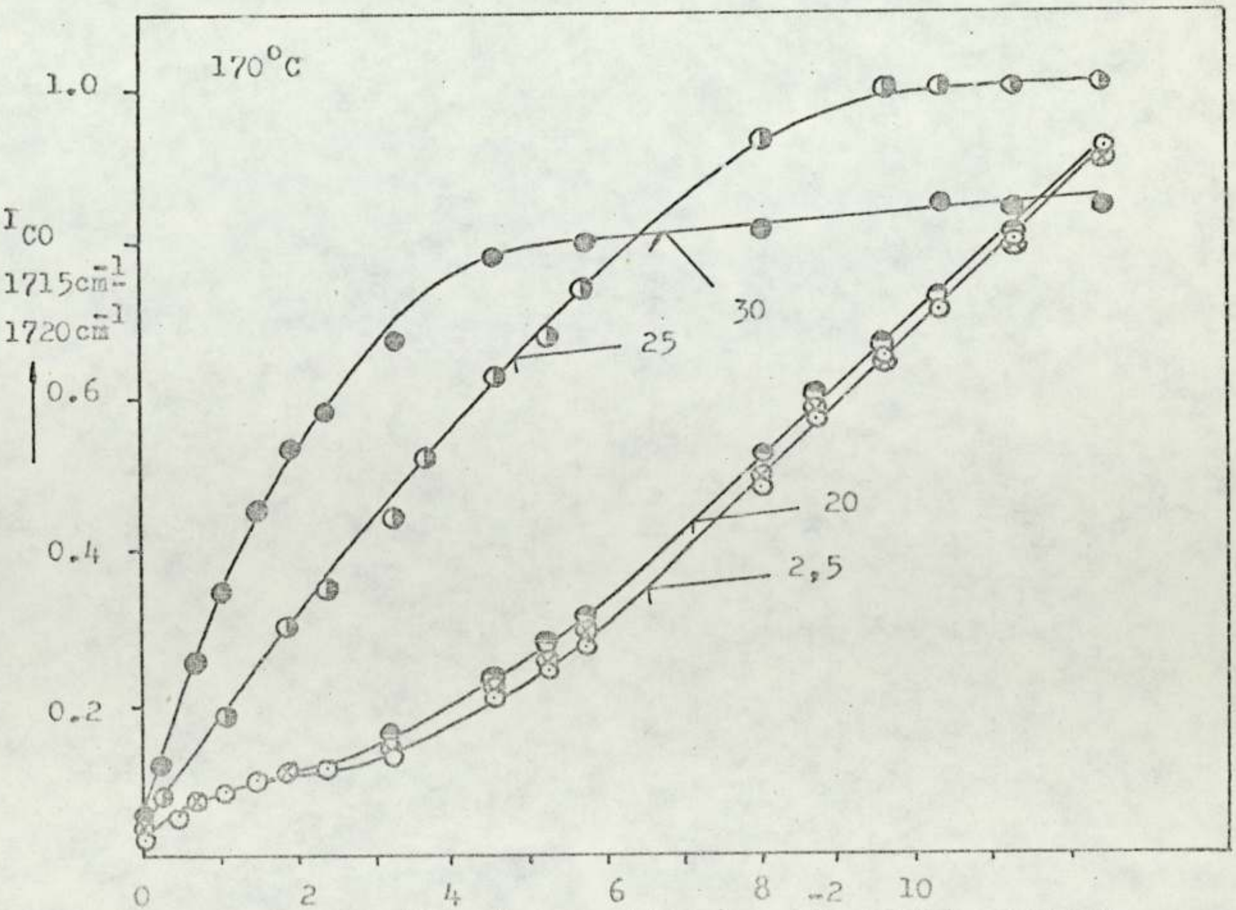


Fig. 7-4 t(hrs) x 10^{-2} of UV-exposure

Hydroxyl index vs UV-exposure time,PVC with Irgastab T290,170°C

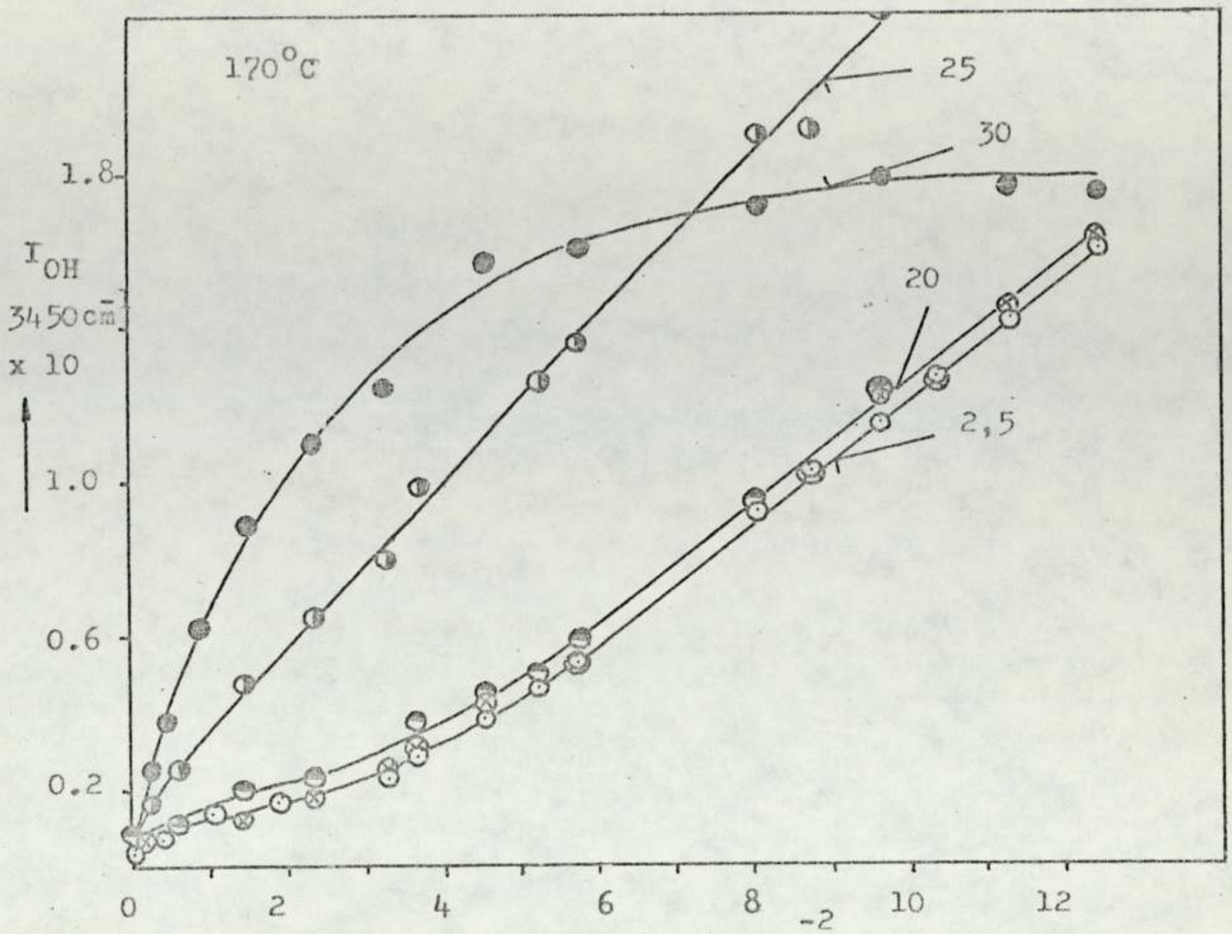


Fig.7-4a

Index $I1650cm^{-1}-55cm^{-1}$ vs UV-exposure time,PVC with Irgastab T20

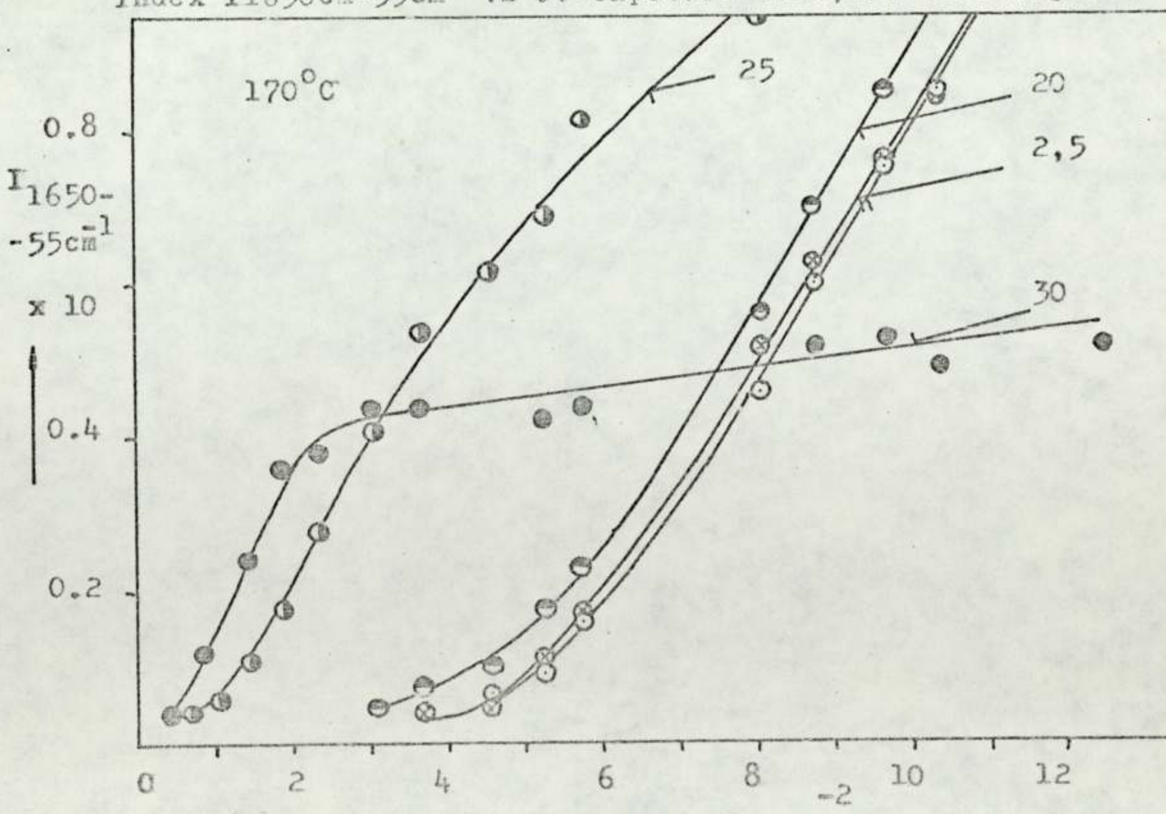


Fig. 7-3

Carbonyl index vs UV-exposure time,PVC with Irgastab T290

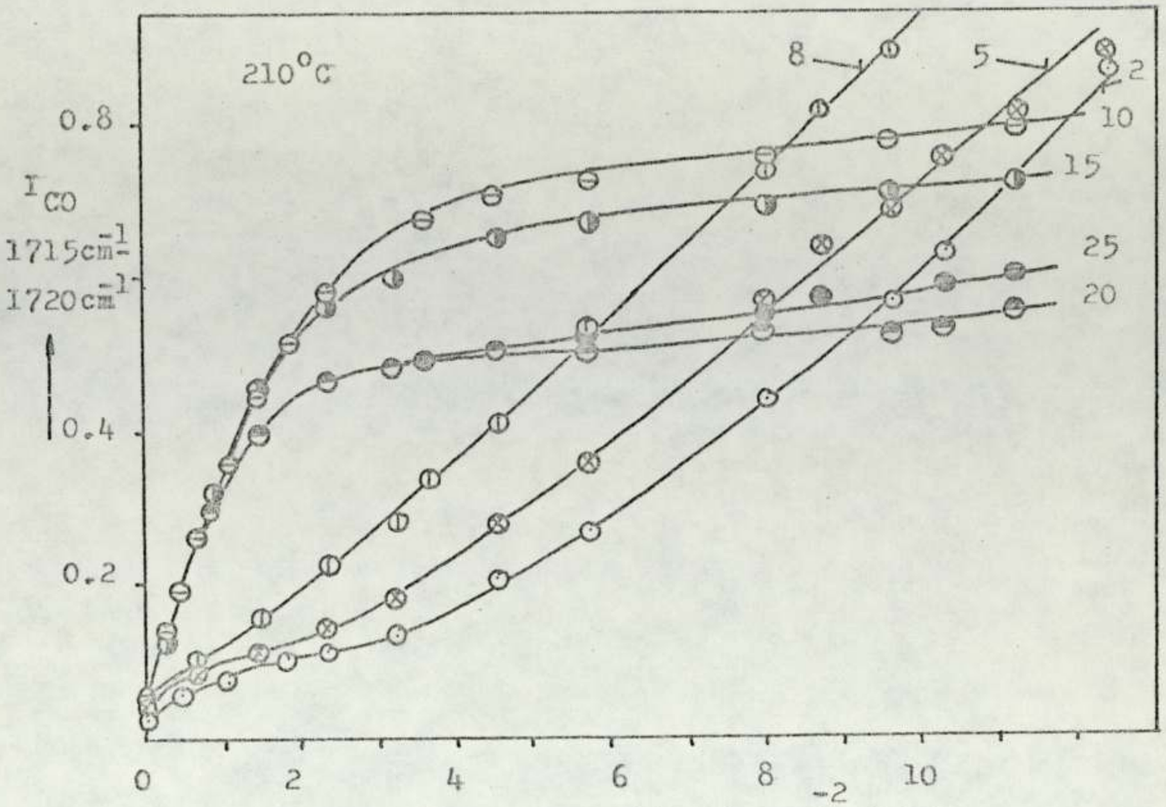


Fig. 7-5 t(hrs) x 10^{-2} of UV-exposure

Hydroxyl index vs UV-exposure time,PVC with Irgastab T290

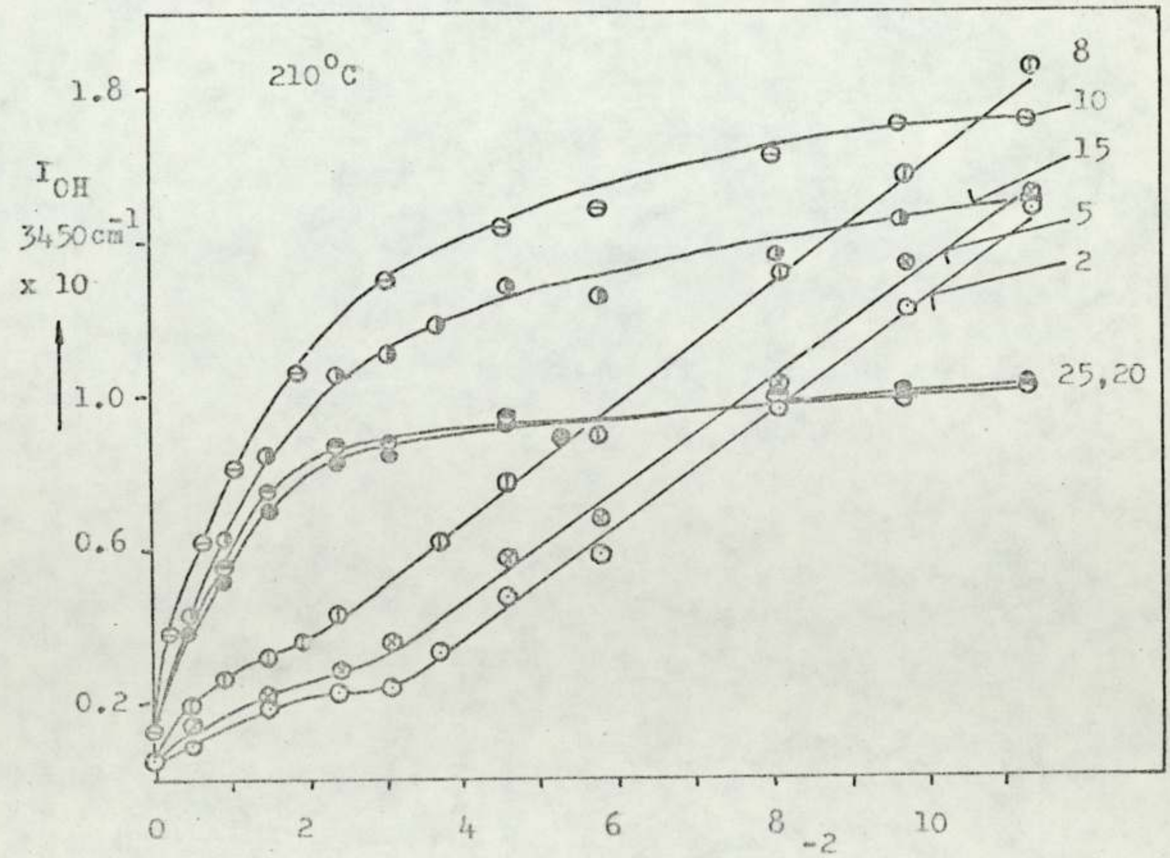


Fig. 7-5a t(hrs) x 10^{-2} of UV-exposure

Discoloration of PVC during UV-irradiation.

PVC processed with Irgastab T290 at 170°C

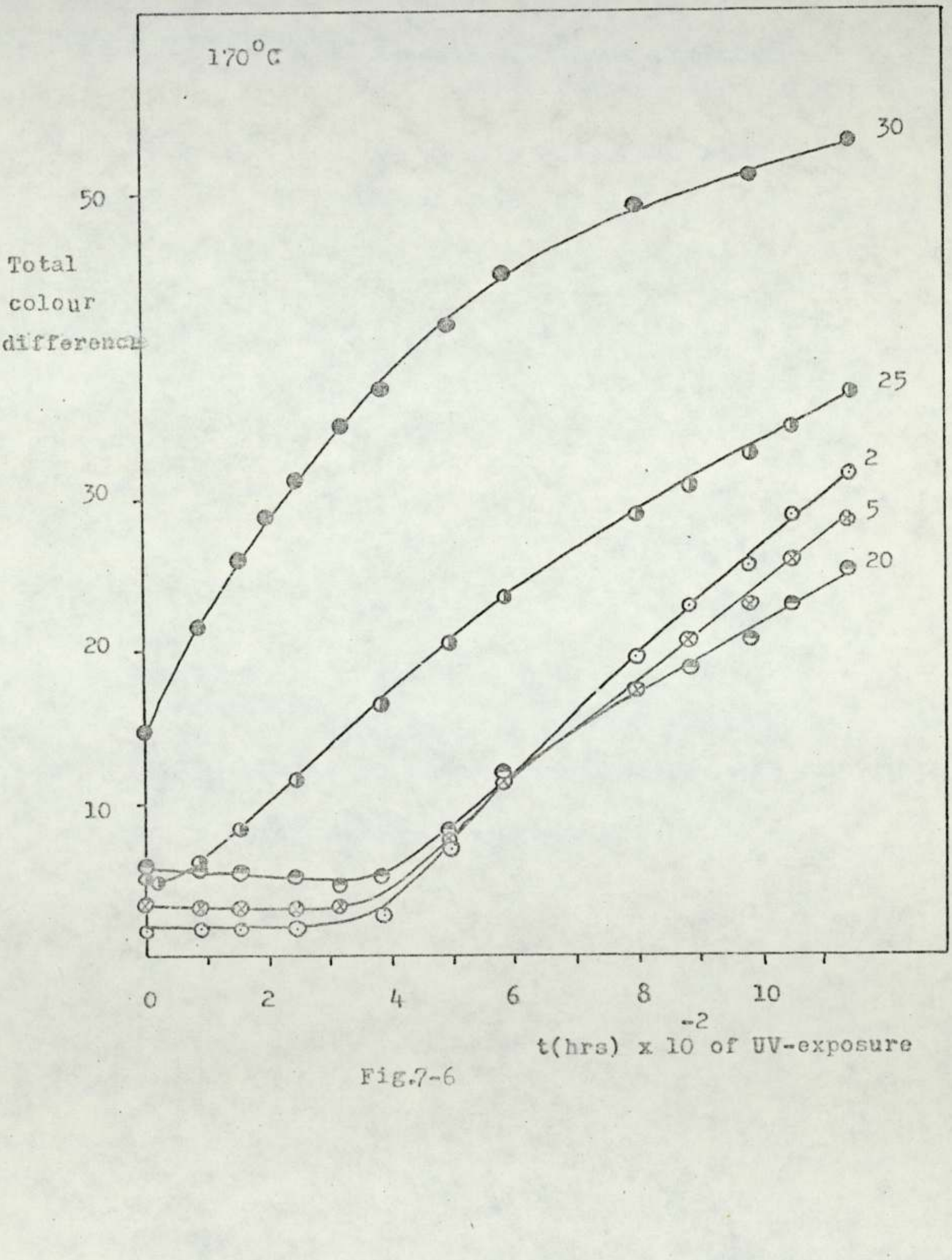


Fig.7-6

Discoloration of PVC during UV-exposure. PVC processed with Irgastab T290 at 210°C.

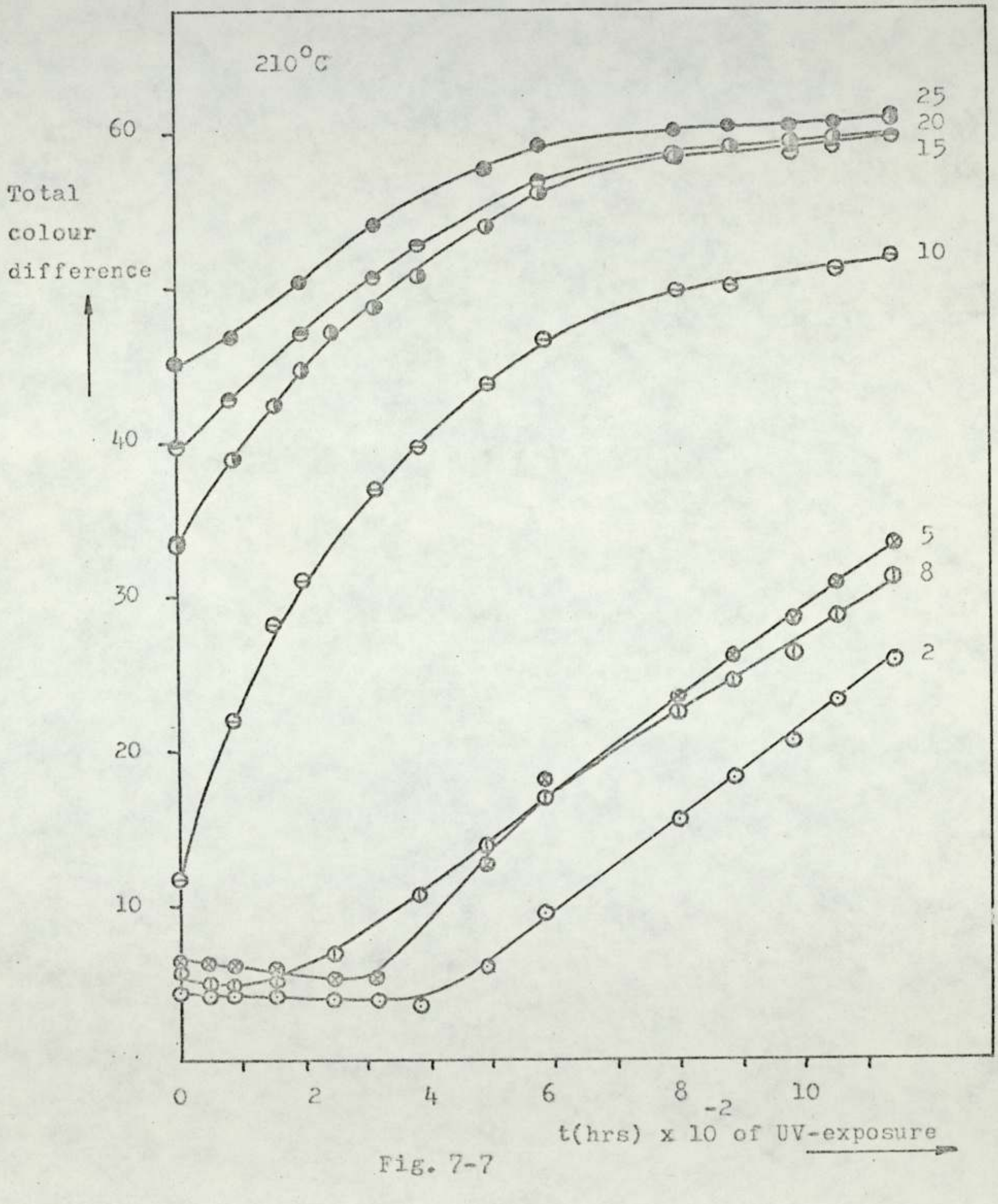


Fig. 7-7

Carbonyl index vs UV-exposure time,PVC with Ca-stearate

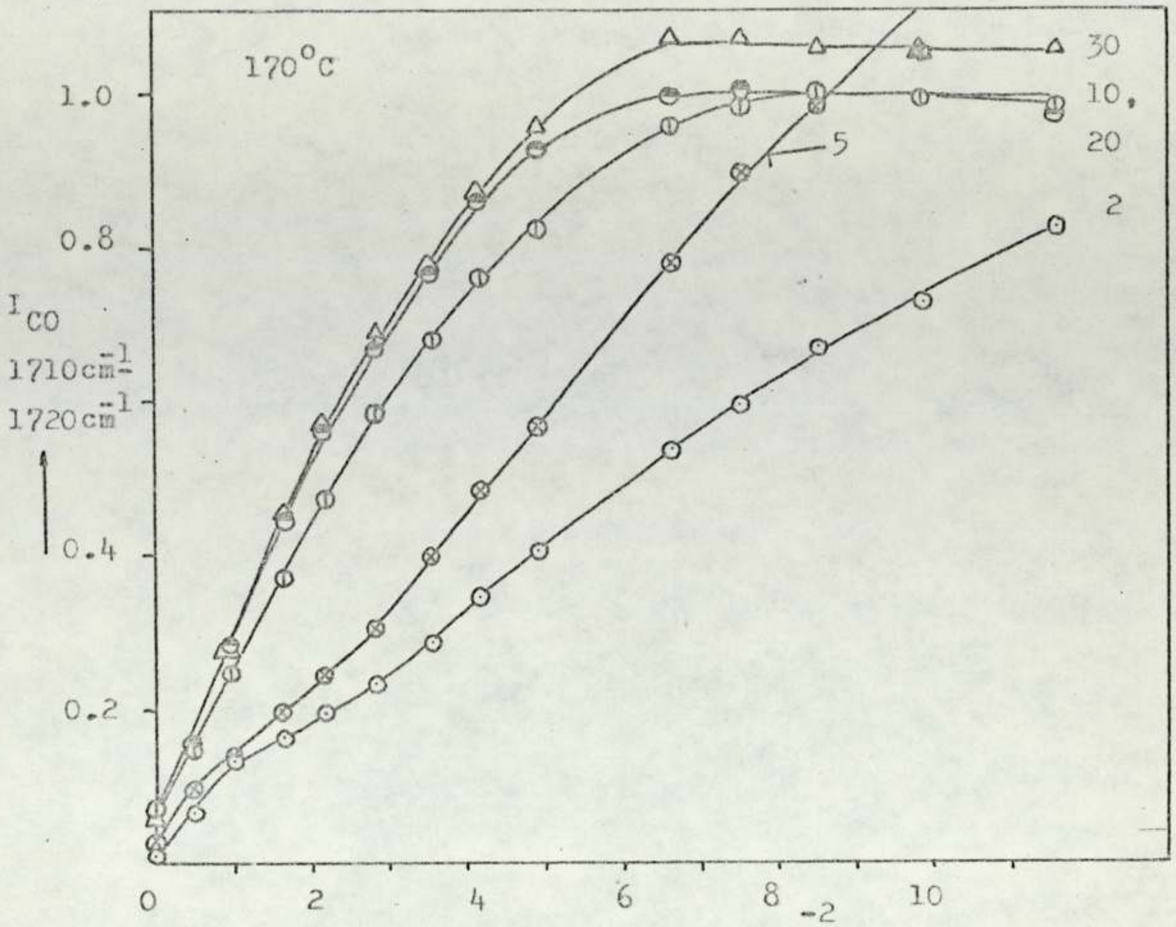


Fig.7-8

Hydroxyl index vs UV-exposure time,PVC with Ca-stearate

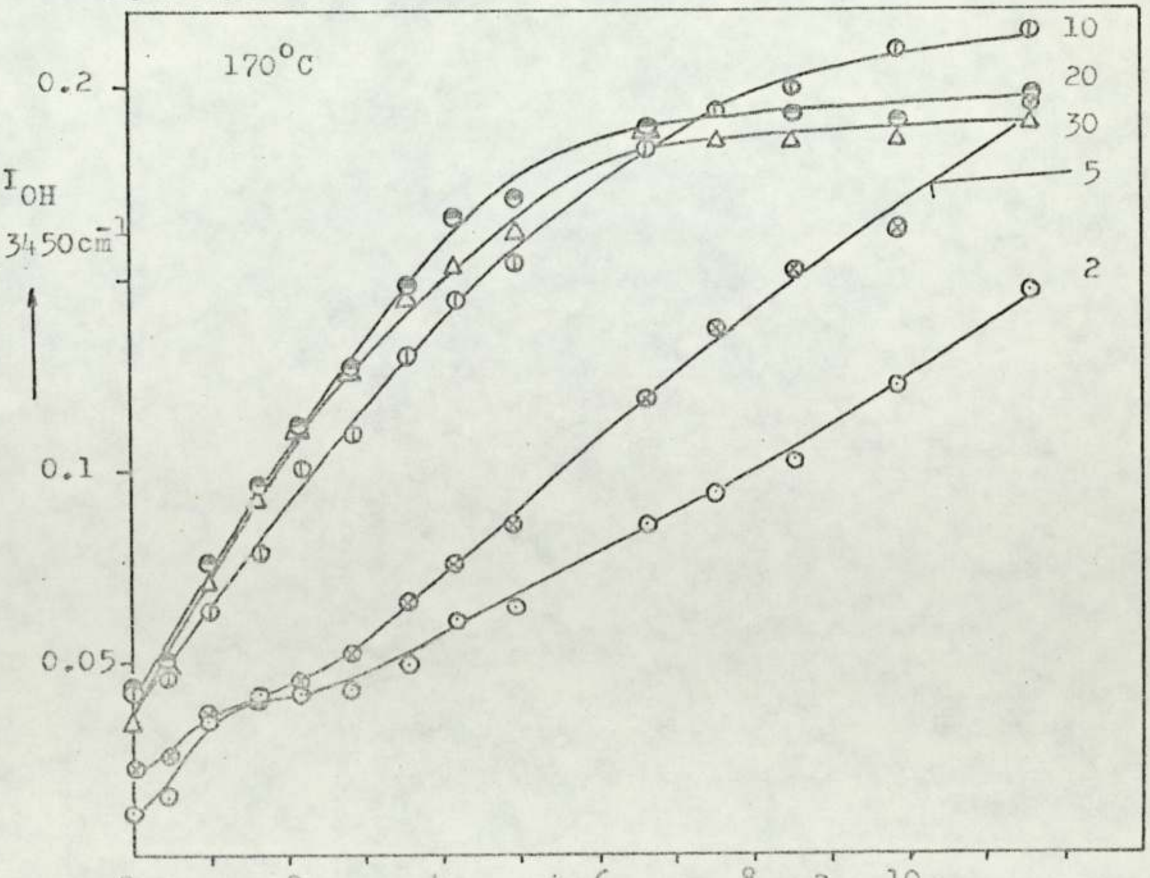


Fig.7-9

Carbonyl index vs UV-exposure time, PVC with Ca-stearate, 210°C

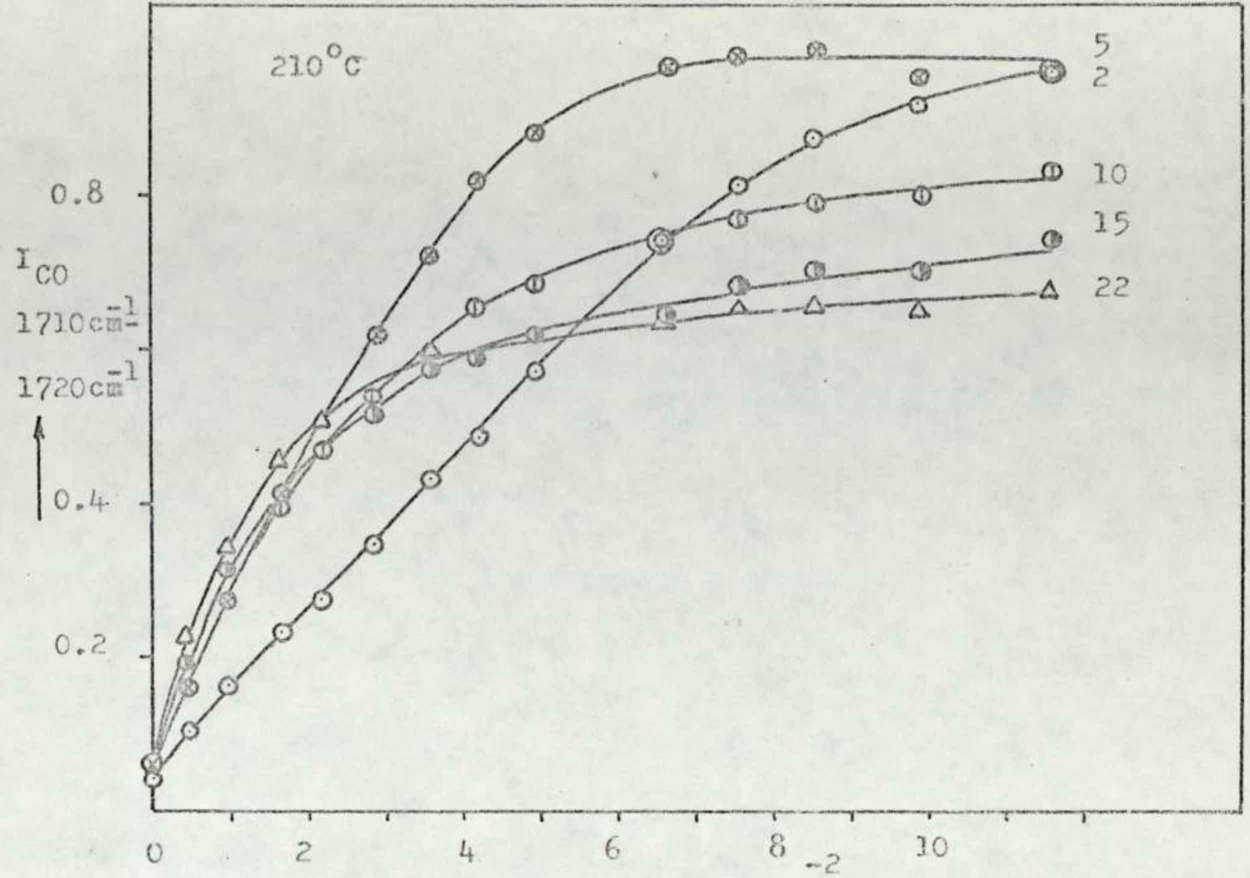


Fig.7-10 t(hrs) x 10^{-2} of UV-exposure

Hydroxyl index vs UV-exposure time, PVC with Ca-stearate, 210°C

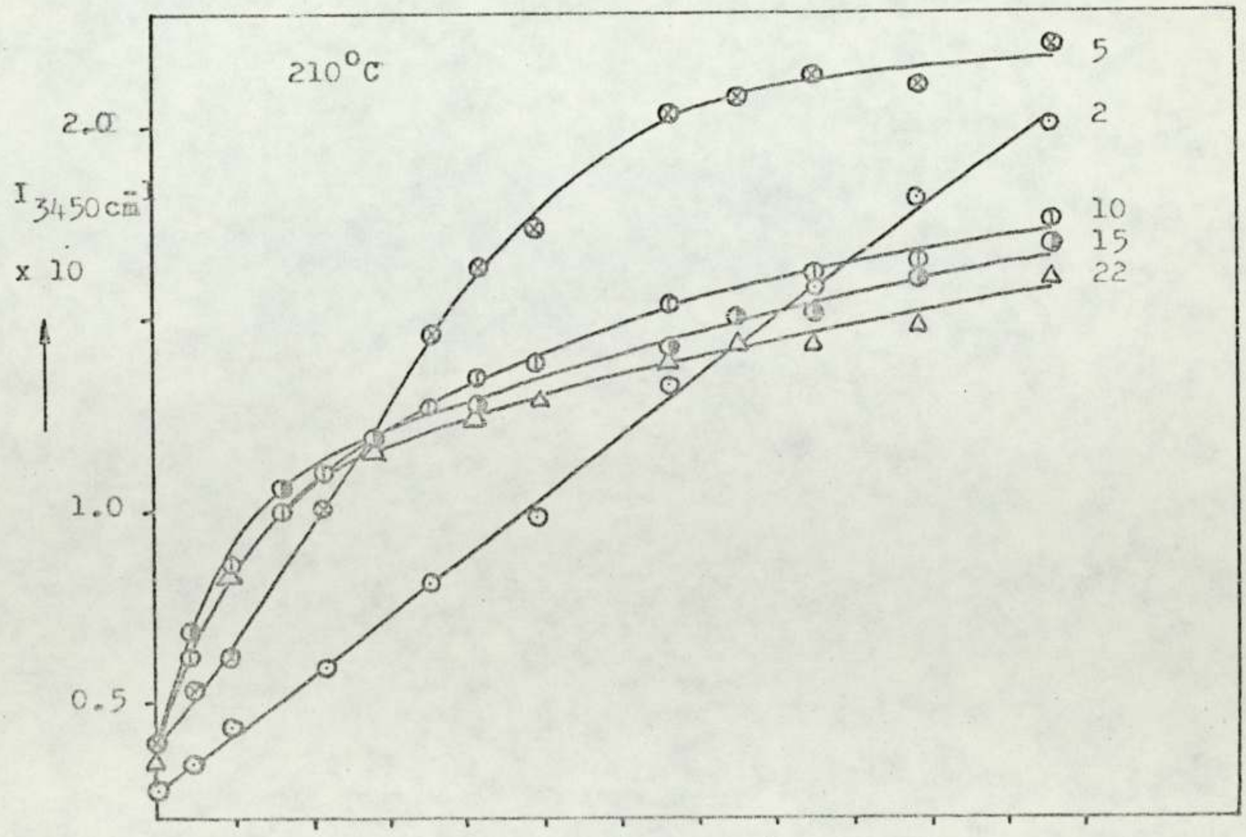


Fig. 7-11 t(hrs) x 10^{-2} of UV-exposure

Comparison of carbonyl and hydroxyl absorption peaks (I_{CO} 1710 cm^{-1}-20 cm^{-1} and I_{OH} 3450 cm^{-1}) formed during UV-exposure. PVC processed with Ca-stearate at 170°C and 210°C.

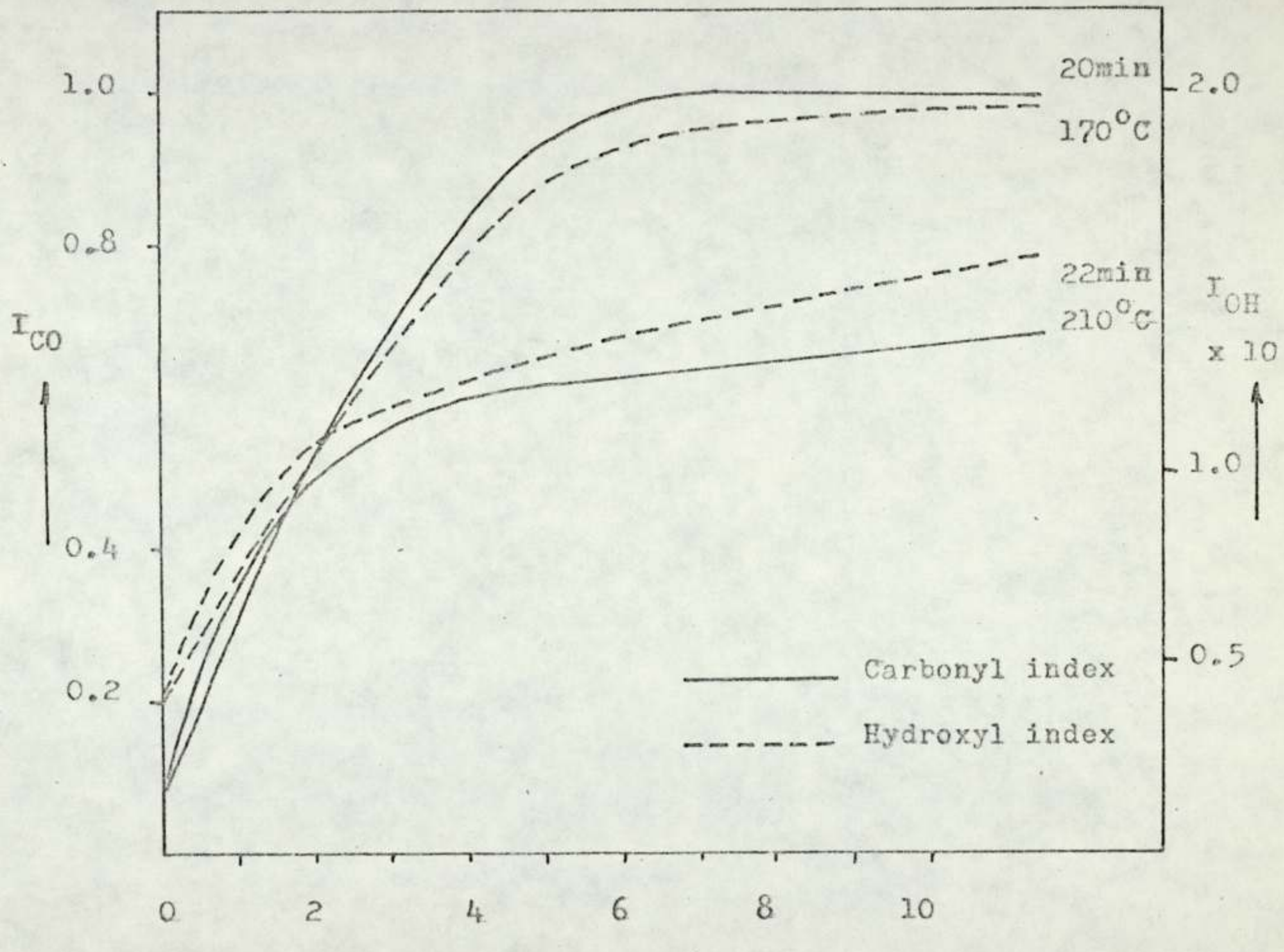


Fig.7-12 t(hrs) x 10^{-2} of UV-exposure

Index $I_{1625cm^{-1}-30cm^{-1}}$ vs UV-exposure time,PVC with Ca-stearate

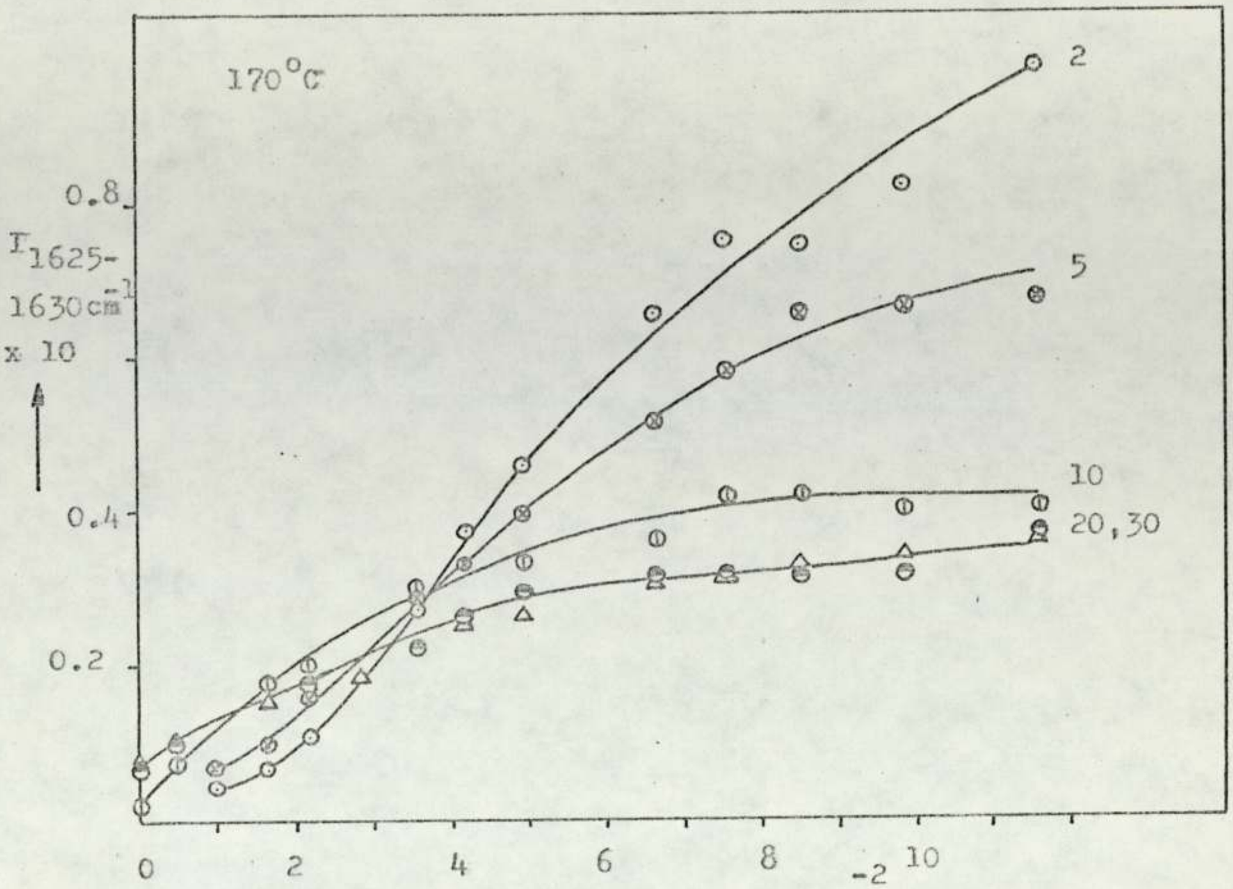


Fig. 7-13 t(hrs) x 10^{-2} of UV-exposure

Index $I_{1625cm^{-1}-30cm^{-1}}$ vs UV-exposure time,PVC with Ca-stearate

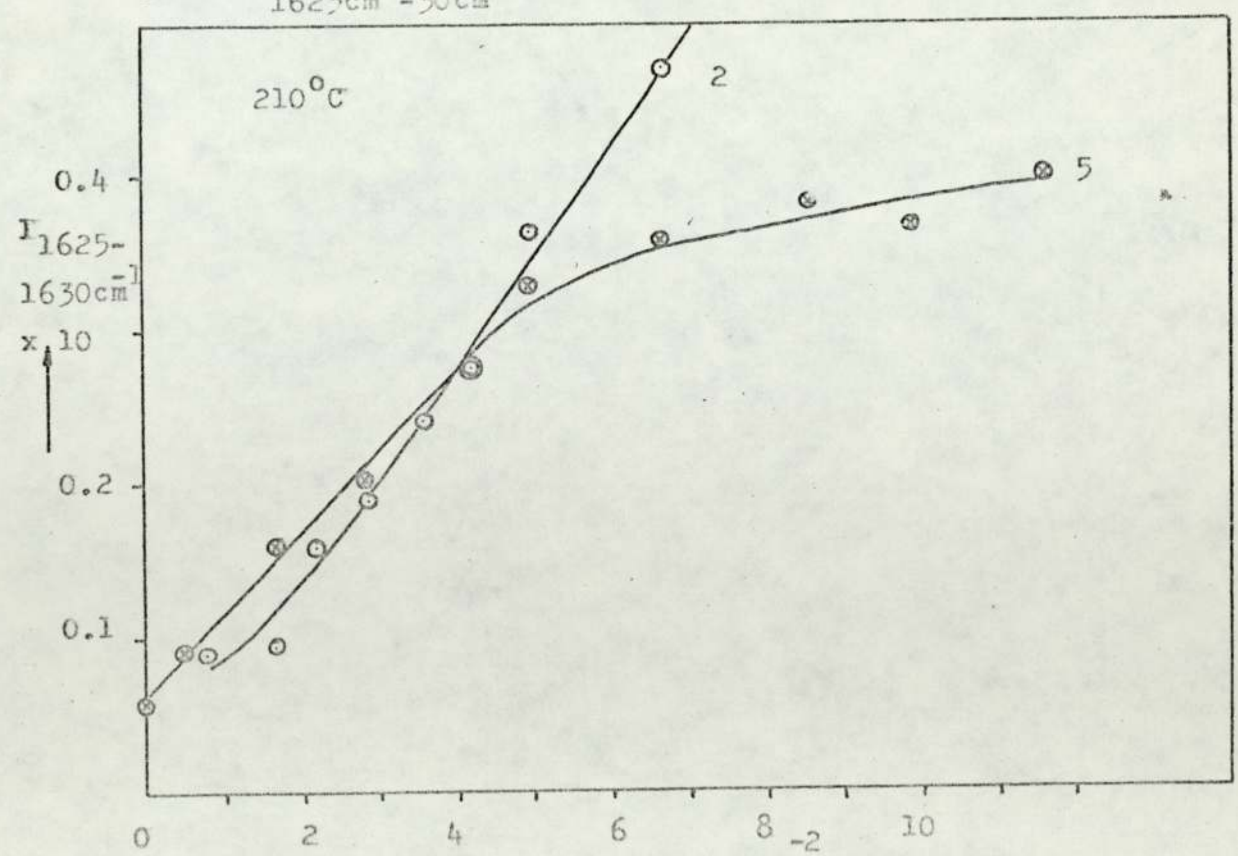


Fig.7-14 t(hrs) x 10^{-2} of UV-exposure

Discoloration of PVC during UV-exposure.PVC processed with Ca-stearate at 170°C.

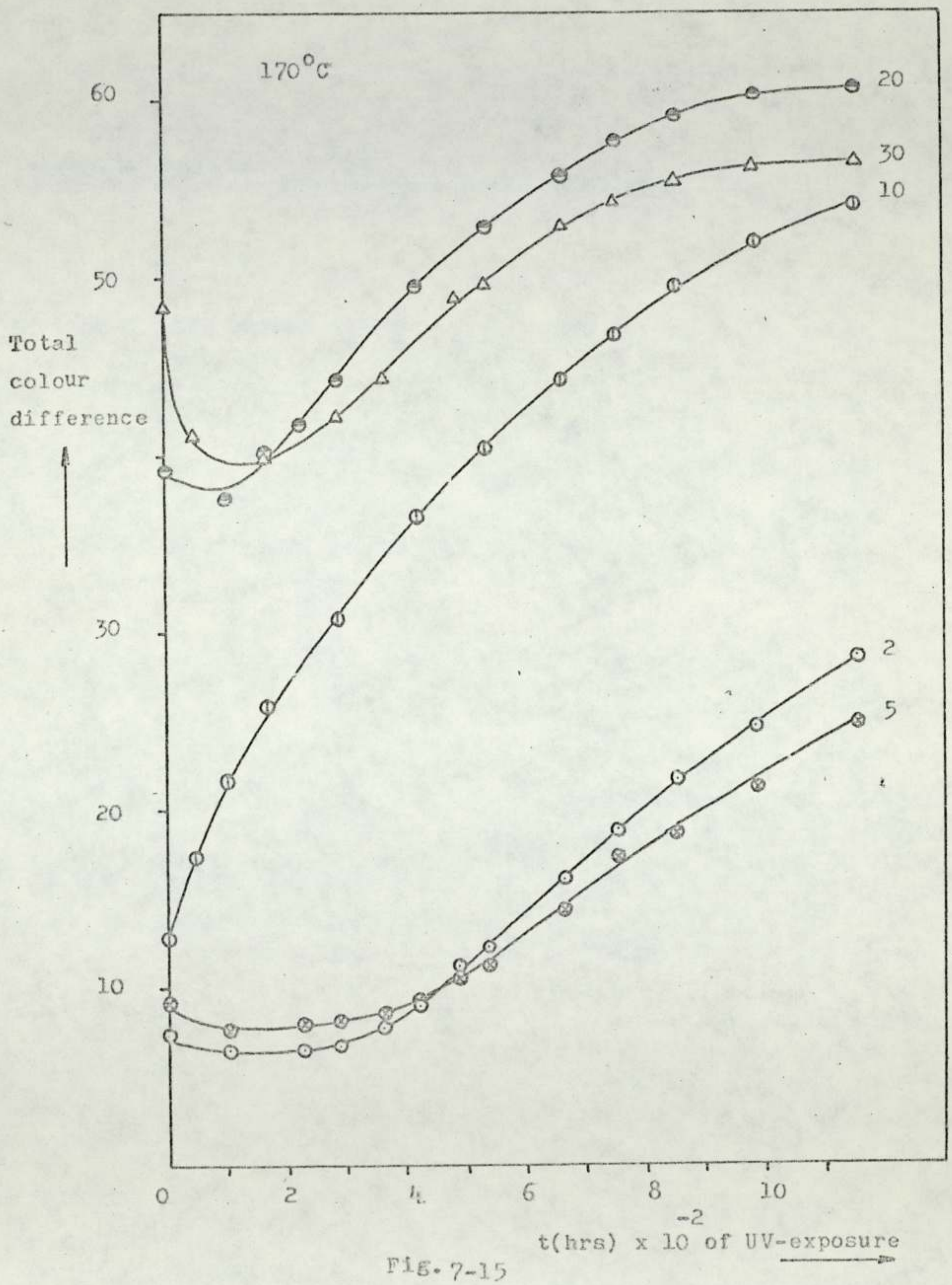


Fig. 7-15

Discoloration of PVC during UV-irradiation. PVC processed with Ca-stearate at 210°C.

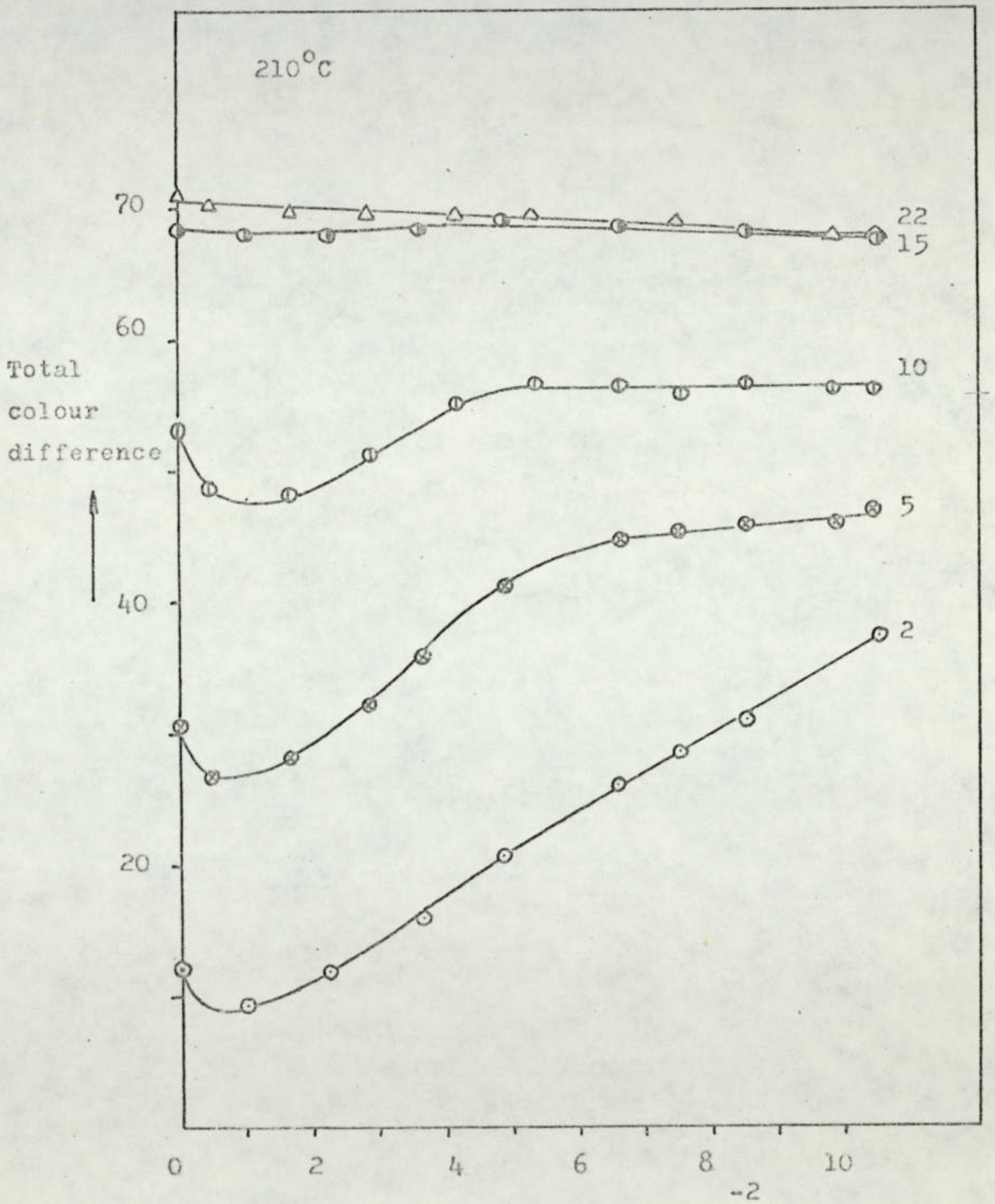


Fig. 7-16 t(hrs) x 10^{-2} of UV-exposure

Carbonyl index vs UV-exposure time, PVC with Wax E, 170°C

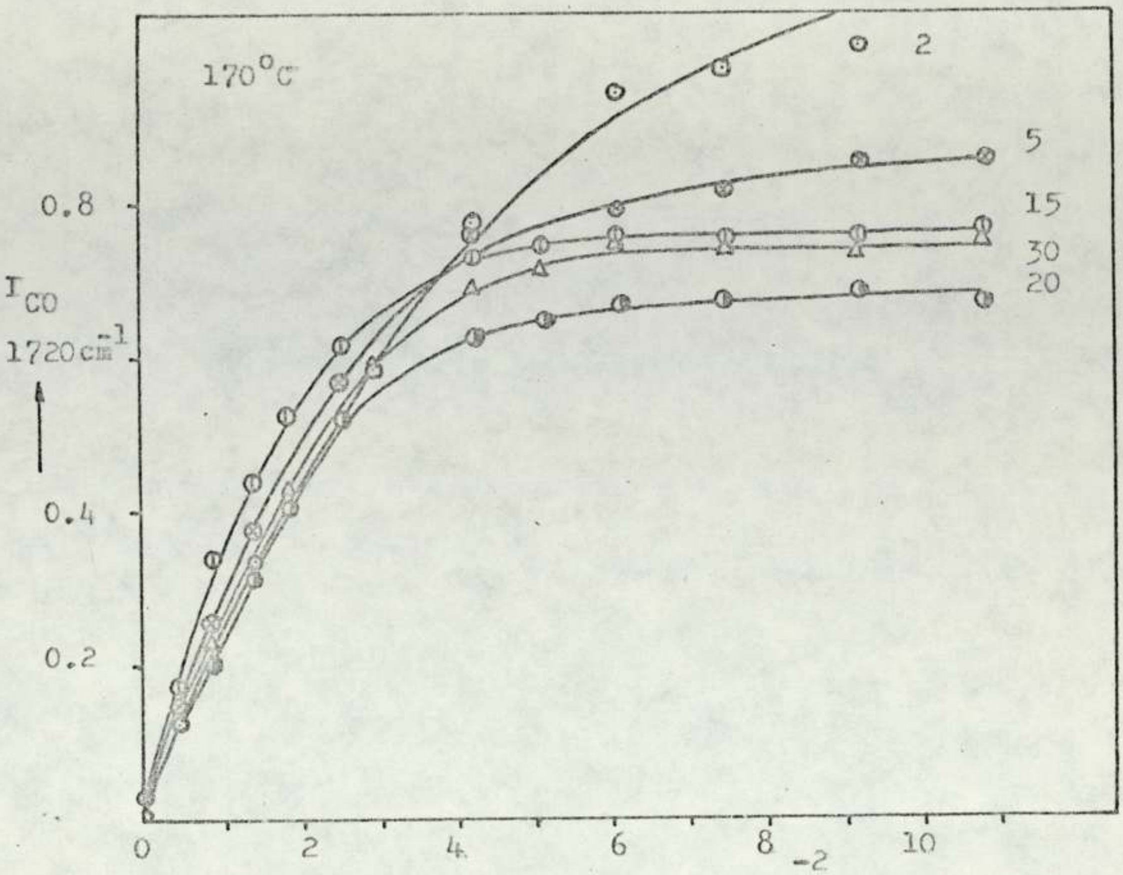


Fig. 7-17 t(hrs) x 10^{-2} of UV-exposure

Hydroxyl index vs UV-exposure time, PVC with Wax E, 170°C

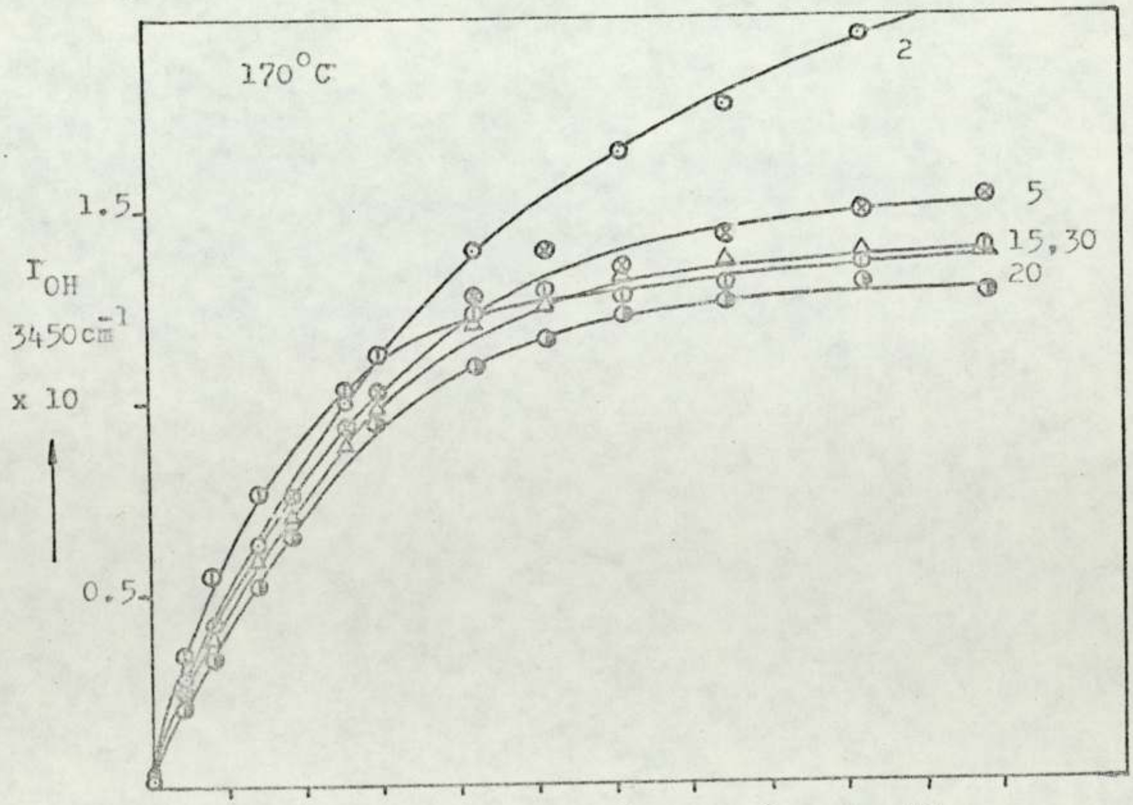


Fig. 7-18 t(hrs) x 10^{-2} of UV-exposure

Carbonyl index vs UV-exposure time, PVC with Wax E, 210°C

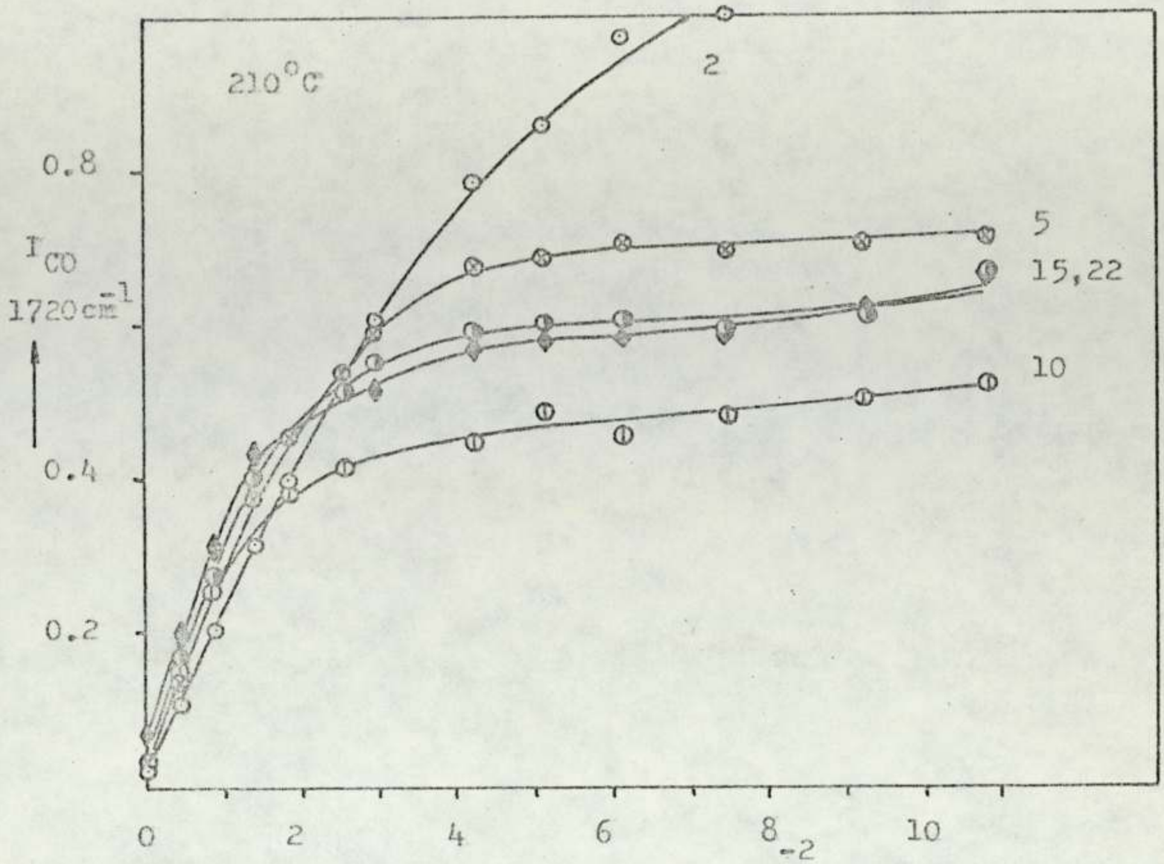


Fig.7-19 t(hrs) x 10^{-2} of UV-exposure

Hydroxyl index vs UV-exposure time, PVC with Wax E, 210°C

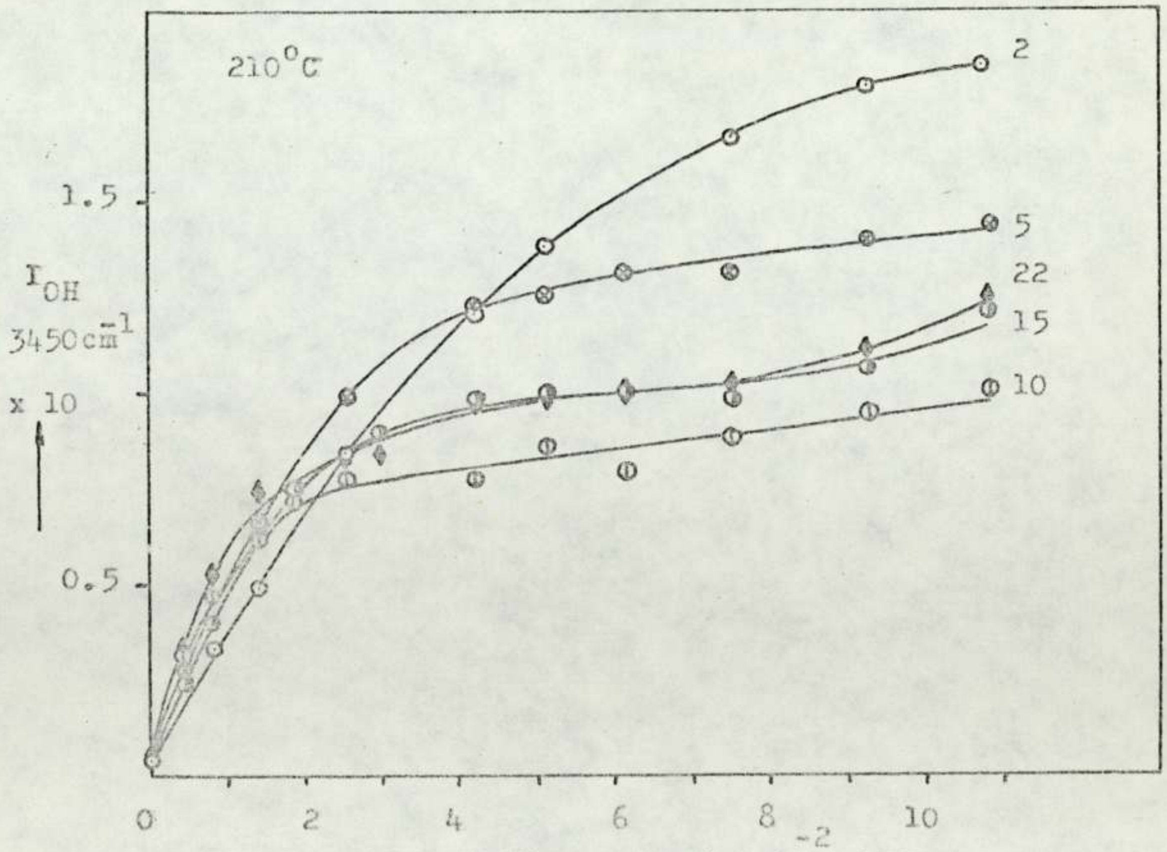


Fig.7-20 t(hrs) x 10^{-2} of UV-exposure

Comparison of carbonyl and hydroxyl absorption peaks (expressed as indexes I_{CO} 1720 cm^{-1} and I_{OH} 3450 cm^{-1}) formed during UV-exposure. PVC processed with Wax E for 15min at 170°C and 210°C.

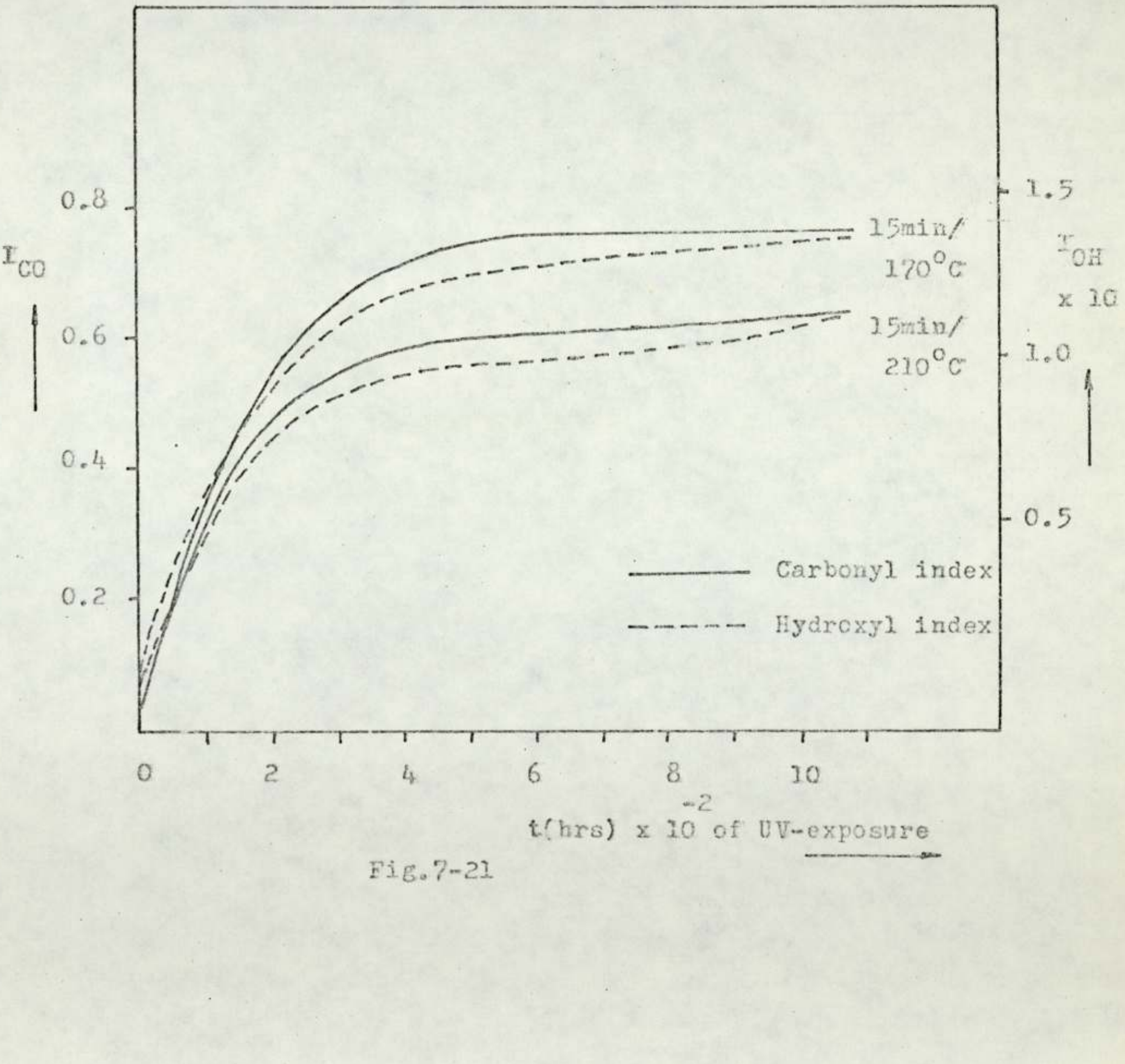


Fig.7-21

Discoloration of PVC during UV-exposure. PVC processed with Wax E at 170°C.

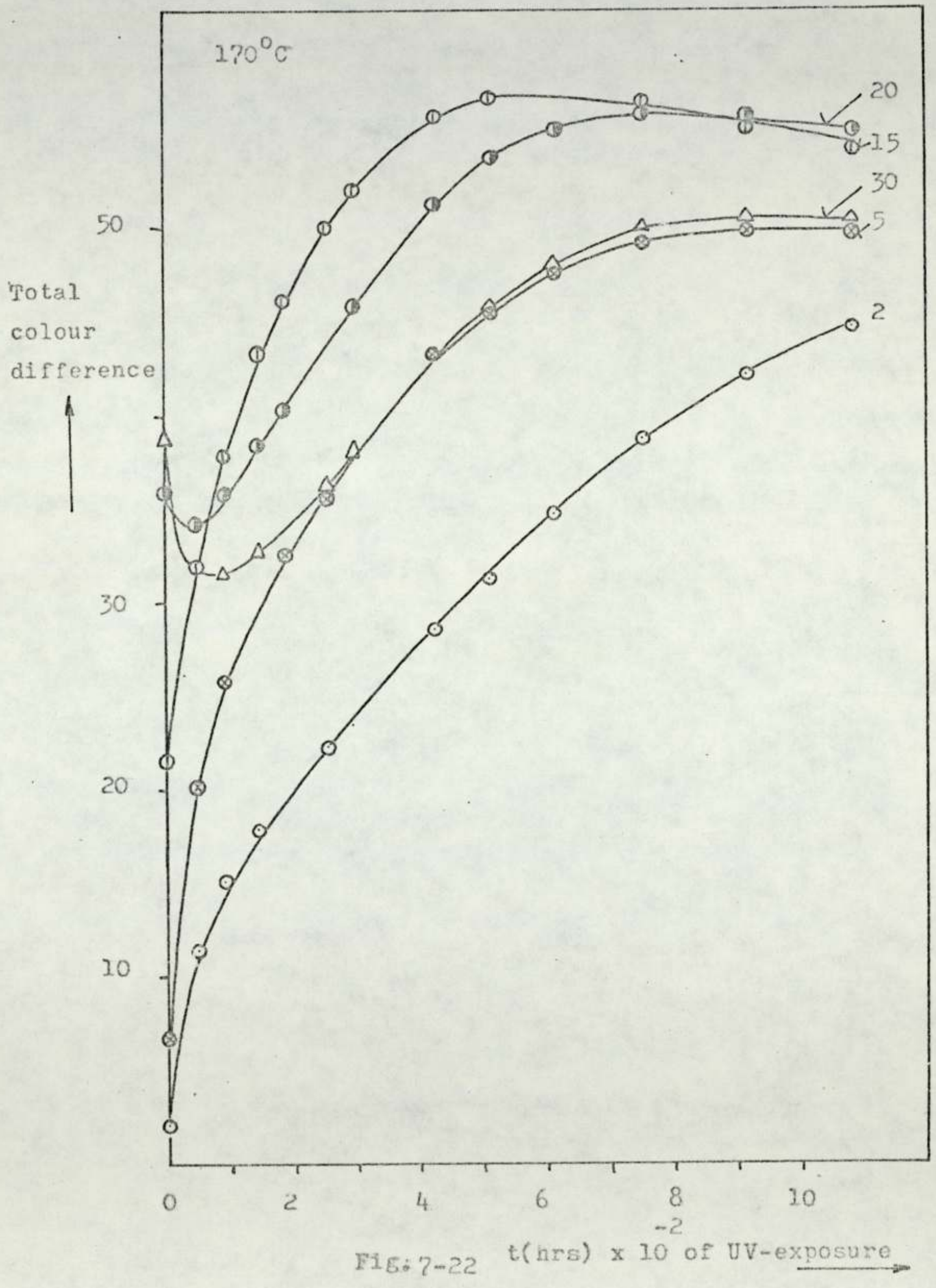


Fig. 7-22

Discoloration of PVC during UV-exposure. PVC processed with Wax E at 210°C.

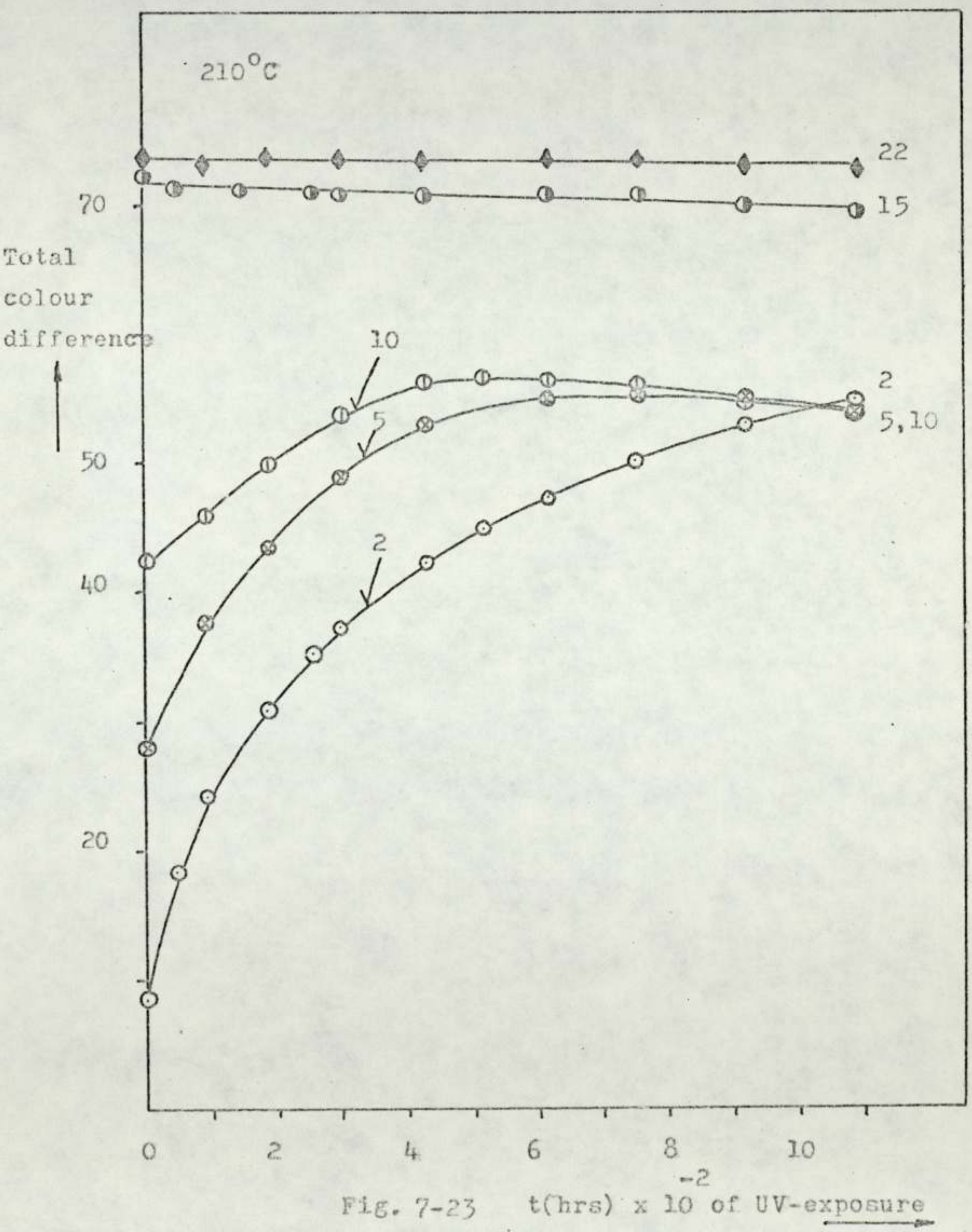


Fig. 7-23 t(hrs) x 10^{-2} of UV-exposure

Carboxylate index vs UV-exposure time, 170°C

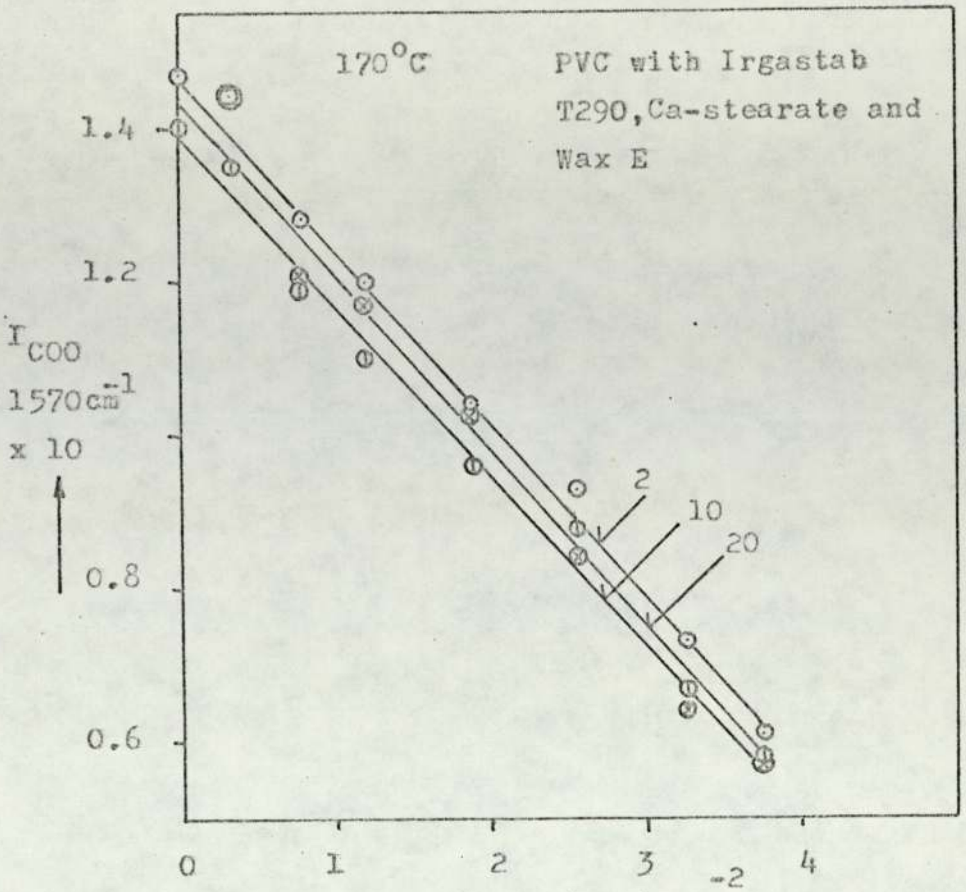


Fig.7-24 t(hrs) x 10^{-2}

$I_{1650 cm^{-1}-55 cm^{-1}}$ index vs UV-exposure time, PVC with all additives

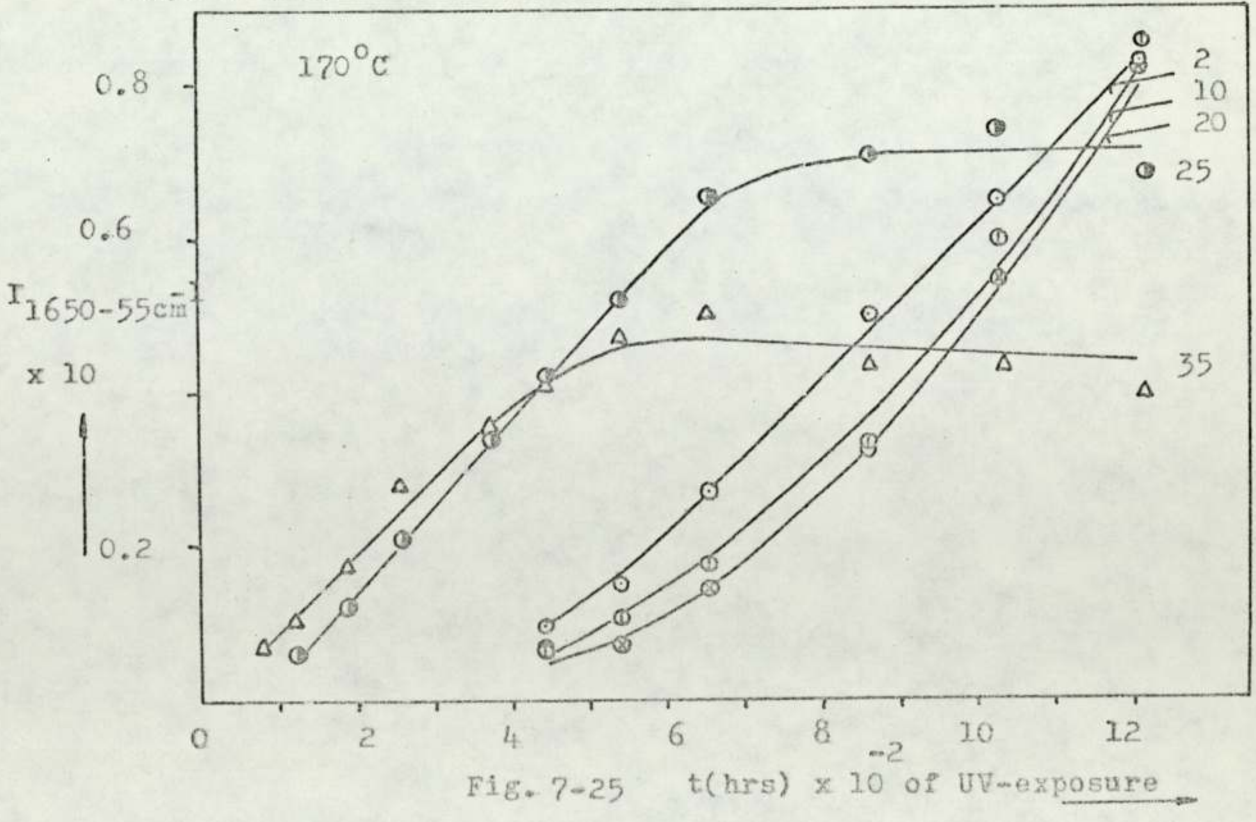


Fig. 7-25 t(hrs) x 10^{-2} of UV-exposure

Carbonyl index vs UV-exposure time, PVC with all additives, 170°C

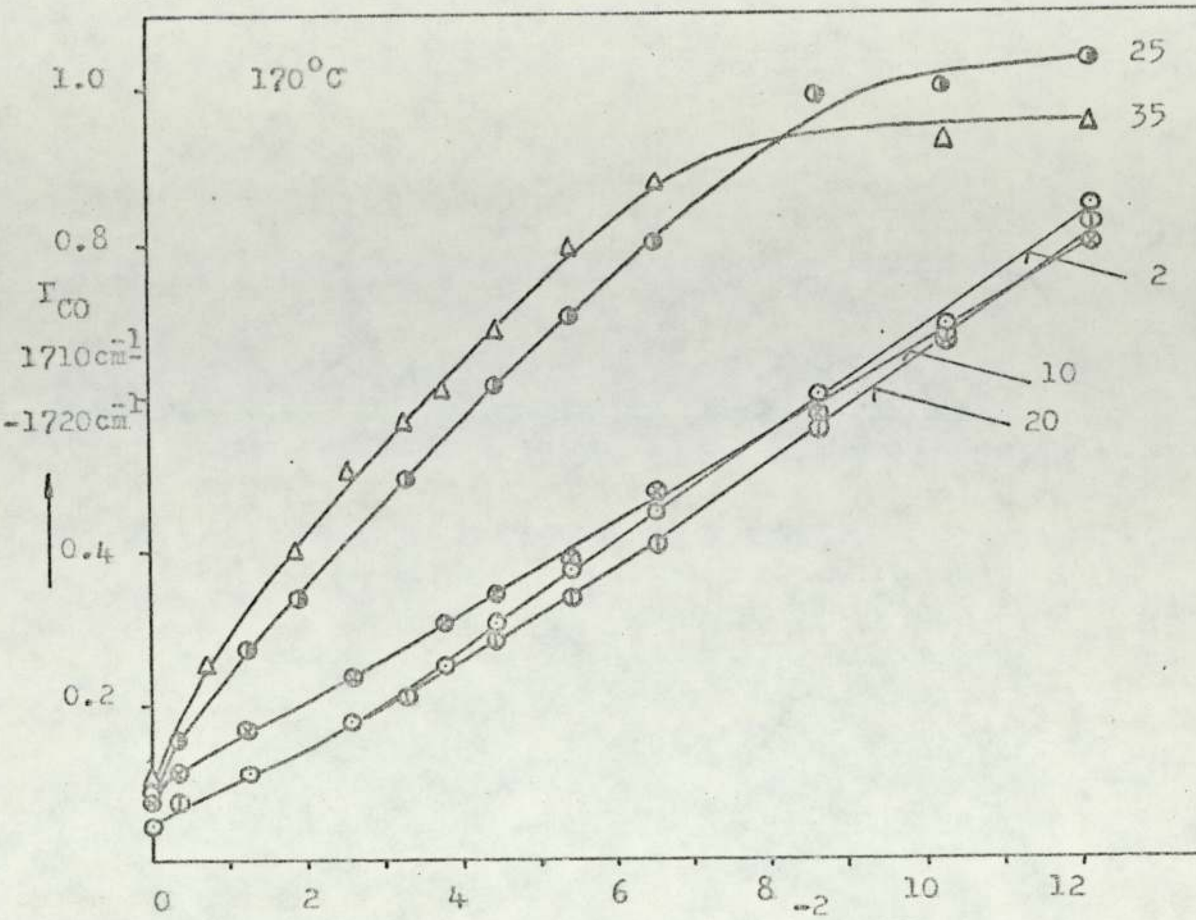


Fig. 7-26

Hydroxyl index vs UV-exposure time, PVC with all additives, 170°C

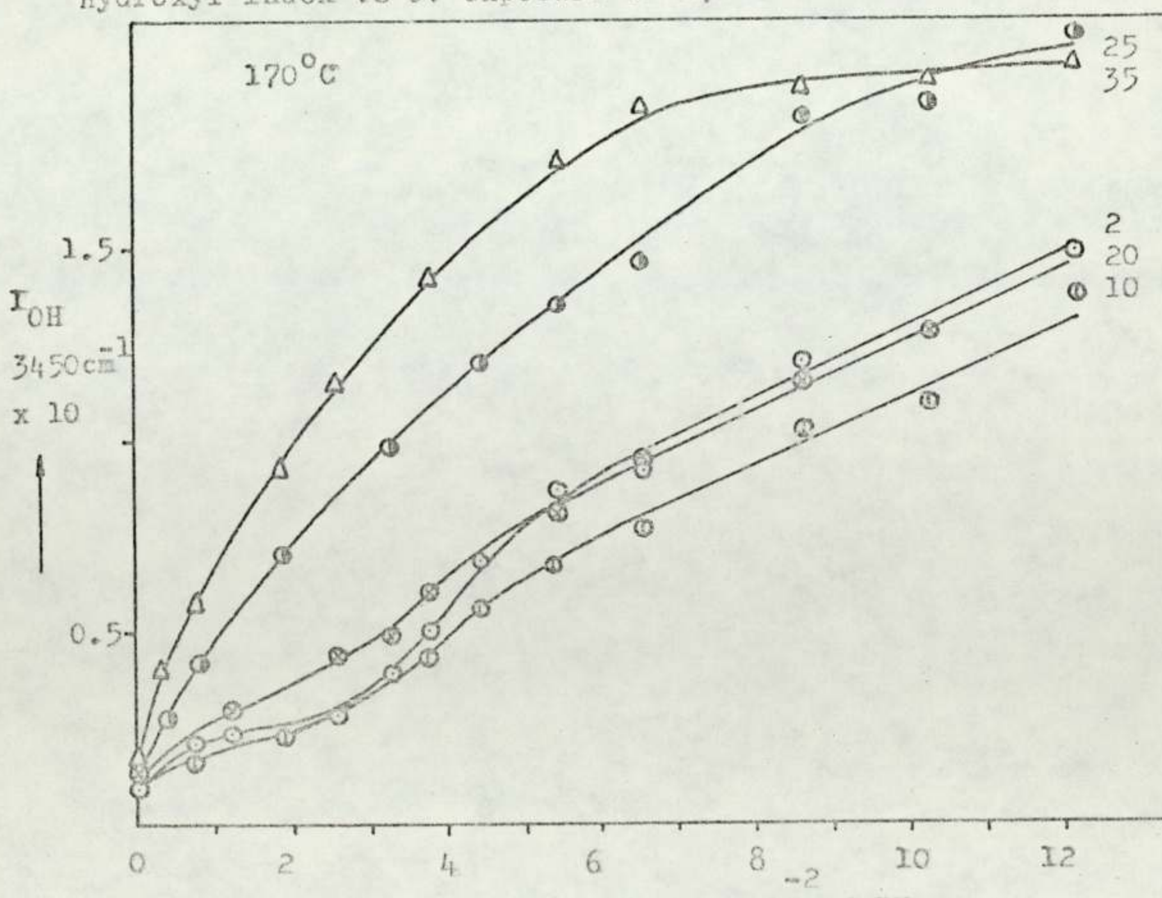


Fig.7-27

Carboxylate index vs UV-exposure time

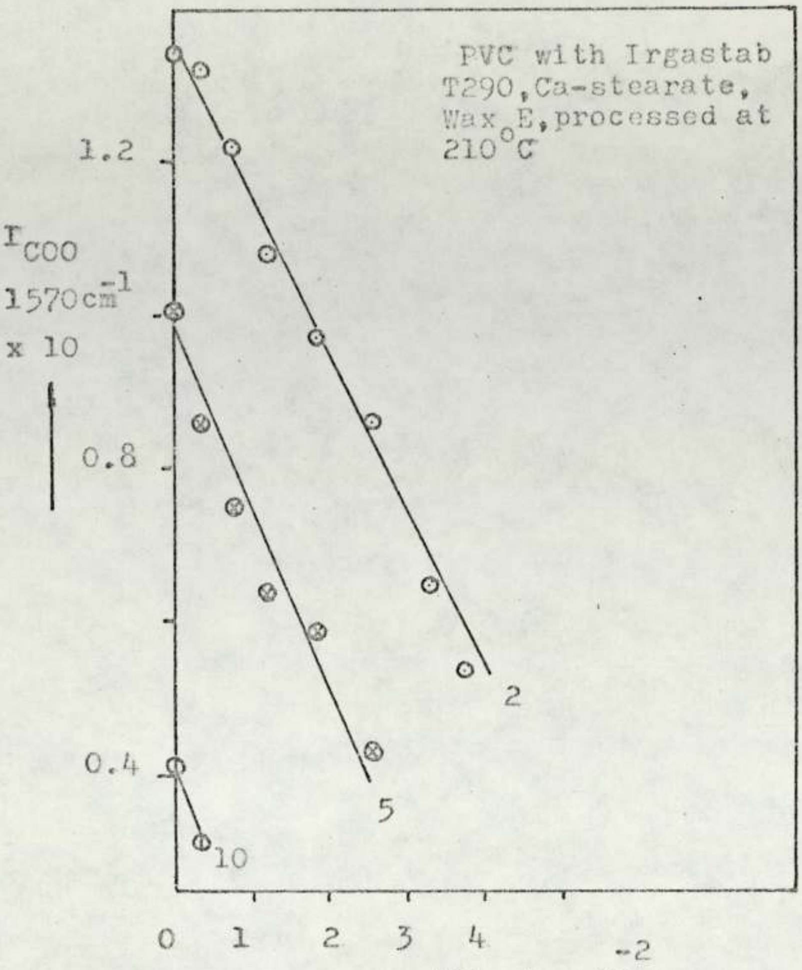


Fig. 7-28

$I_{1650\,cm^{-1}-55\,cm^{-1}}$ index vs UV-exposure time, PVC with all additives

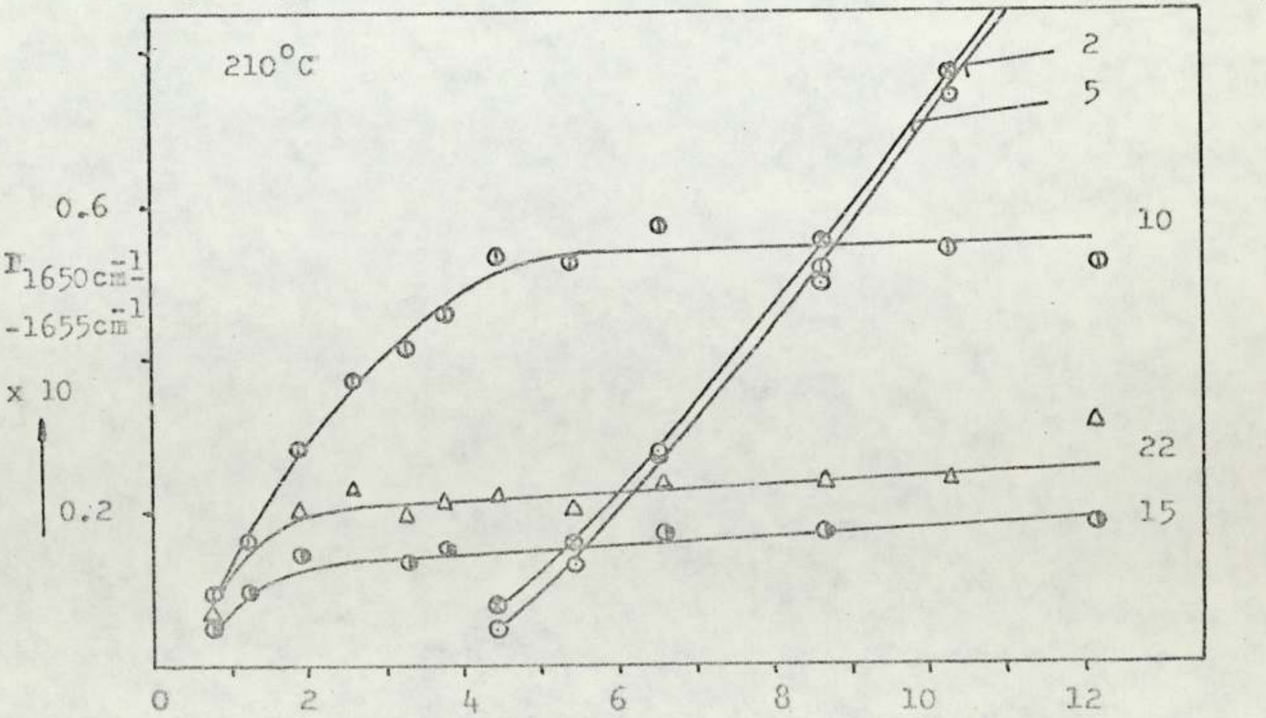


Fig. 7-29

Carbonyl index vs UV-exposure time, PVC with all additives, 210°C

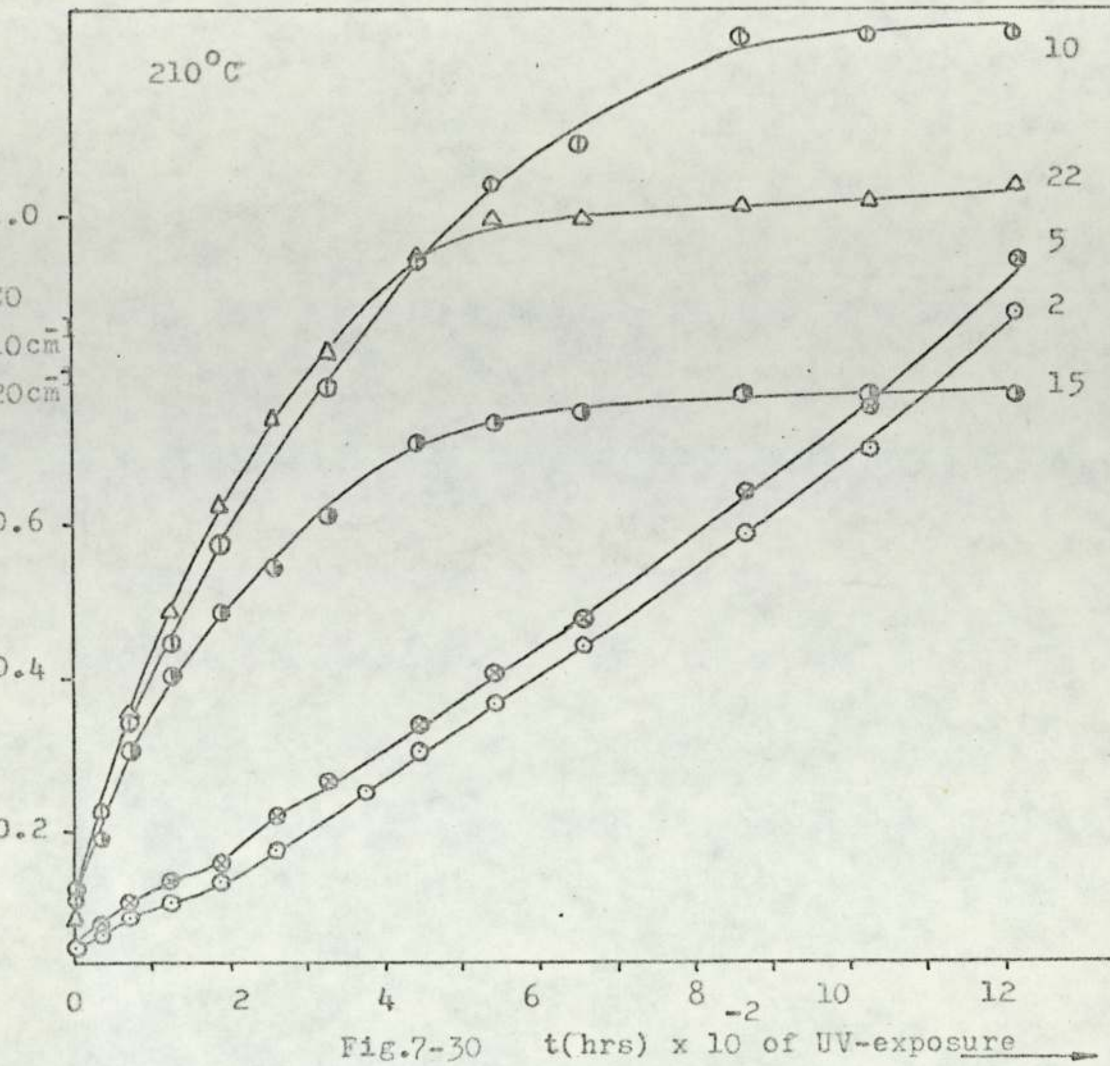


Fig.7-30 t(hrs) x 10^{-2} of UV-exposure

Hydroxyl index vs UV-exposure time, PVC with all additives, 210°C

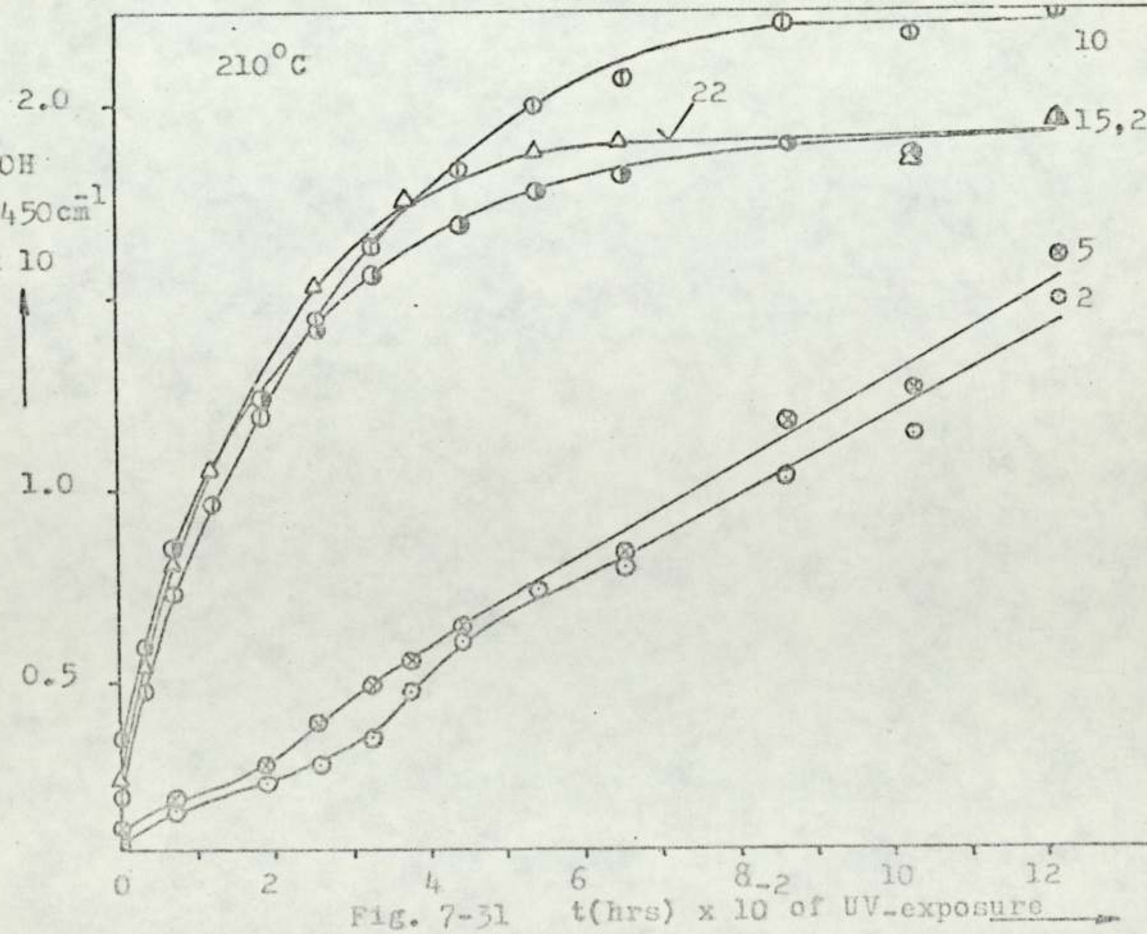


Fig. 7-31 t(hrs) x 10^{-2} of UV-exposure

Discoloration of PVC during UV-exposure.PVC processed with Irgastab T290,Ca-stearate and Wax E at 170°C.

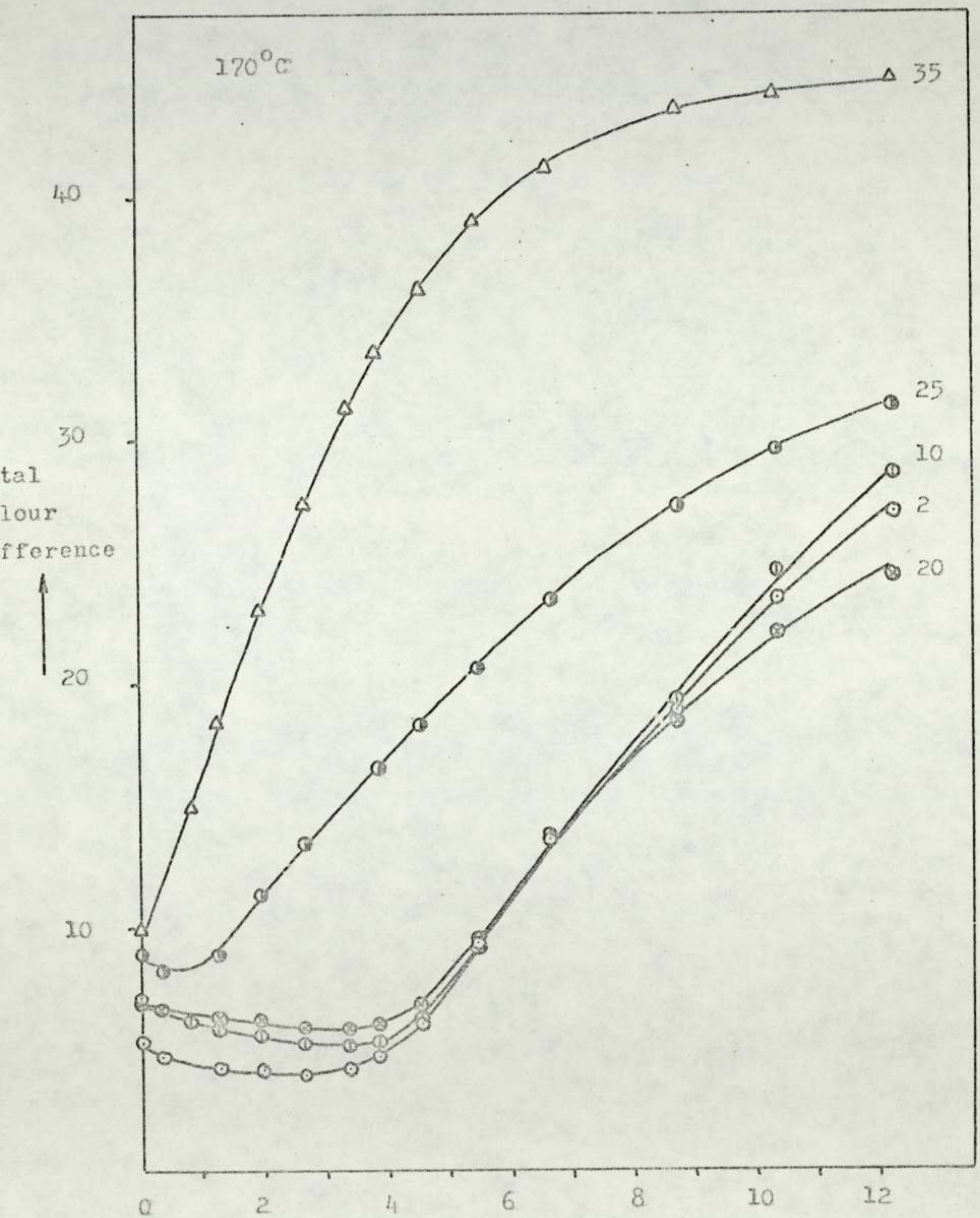


Fig. 7-32 t(hrs) x 10^{-2} of UV-exposure

Discoloration of PVC during UV-exposure. PVC processed with Irgastab T290, Ca-stearate and Wax E at 210°C.

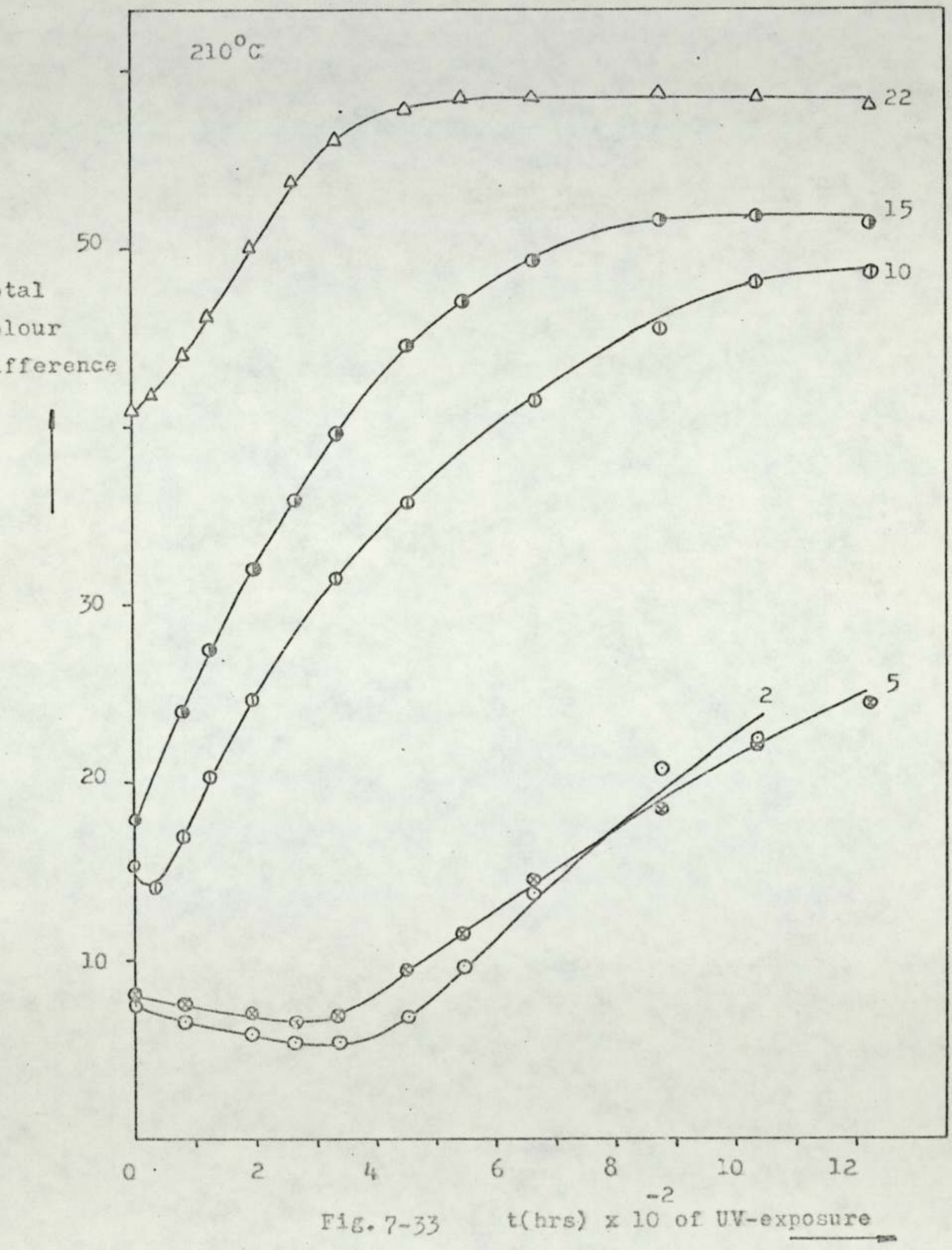


Fig. 7-33 t(hrs) x 10^{-2} of UV-exposure

CHAPTER 8 Conclusions

The degradation of PVC processed in torque rheometer without additives was found to be influenced by several factors viz thermal energy, mechanical work (shear stresses or torque) and also by the presence of oxygen. It was demonstrated that peroxide was formed in the initial stage of processing. The torque at lower temperature in the initial stage of processing was higher than the torque at higher temperature and the contribution of the pure mechanical process to the overall thermomechanical degradation was considered to be important. The presence of external lubricant Wax E decreased the torque during the fusion and immediately after the fusion and the consequence of this was to reduce the severity of the mechanochemical reaction at 170°C compared with that at 210°C. In accord with this the rate of discolouration of PVC during processing at 170°C was substantially lower than in the polymer processed without lubricant.

The rapid initial dehydrochlorination was attributed to the catalytic action of intermediate free radicals ($R;ROO;RO;OH^{\bullet}$) present in the initial stage of processing. The peroxide formed in the initial stage of processing rapidly disappeared. Since the initial unsaturation at lower temperature was higher than at higher processing temperature, the initial concentration of evolved HCl was also higher and the rapid destruction of peroxide was attributed to the occurrence of hydrogen chloride-induced decomposition of the peroxide.

In the second stage of processing the torque and the gel content at higher temperature rapidly increased. At lower temperature this increase occurred at longer processing time.

The increase of the torque and the gel content was considered to be due to a crosslinking reaction. The presence of this crosslinking was shown to have increased the Tg considerably especially for the polymer with high gel content. Also the molecular weight distribution results especially of lower temperature processed samples demonstrated the occurrence of the crosslinking reaction.

The peroxide content rapidly increased during the second stage especially at higher temperature and infrared spectroscopy showed the presence of carbonyl absorptions. Although the exact mechanism of the crosslinking reaction is not yet clear, the occurrence of oxidation suggested the participation of alkoxy, hydroxyl and alkylperoxy radicals in formation of ether and/or carbon-carbon crosslinks and of peroxy-crosslinks.

Molecular weight distribution results have demonstrated the occurrence of a competitive chain scission reaction. This reaction was also shown by the increase in the UV-absorbance of the soluble phase. It was shown that the extent of the chain scission was higher at higher processing temperature and and the maximum in loss tangent ($\tan \delta_{min}$) was interpreted by the presence of lower molecular weight species formed by the chain scission. Spectroscopic results showed the presence of carbonyl and conjugated carbonyl and this demonstrated that the chain scission was of oxidative character. The formation of carbonyl and conjugated carbonyl was considered to be a result of the rearrangement of the intermediate alkoxy radicals. The thermal breakdown of peroxy-crosslinks with subsequent rearrangement of resulting alkoxy radicals was considered to be important in the formation of lower molecular weight species.

Dehydrochlorination at lower temperature proceeded at a constant rate but at higher temperature this reaction had an autoaccelerated character. Because of the existence of competitive crosslinking and especially oxidative chain scission, which was associated with kinetic chain branching, the concentration of macro-radicals $R^\bullet$ has increased. The presence of free intermediate radical species together with thermal energy increased the rate of dehydrochlorination and the accelerated evolution of HCl resulted.

When PVC was processed with thermal stabilizer Irgastab T290 (dibutyltin maleate) an induction period was demonstrated. This induction period was shown by the measurement of torque, the gel formation, colour formation and unsaturation (measured chemically and also by UV-spectroscopy). Infrared spectroscopy results also correlated with the results of the experimental techniques mentioned above. It was found that esterification occurred between the maleate moiety of the stabilizer and the labile chlorine atoms (probably allylic). The ester formation during the induction period corresponded well with the decrease of the carboxylate absorption of the stabilizer. The formation of anhydride and dibutyltinchloride was observed and these species were considered to be a result of the reaction between the stabilizer and hydrogen chloride. The discolouration of the polymer during the induction period and therefore formation of conjugated unsaturation was minimized by the Diels-Alder reaction between the stabilizer's maleate moiety and the conjugated unsaturation. The peroxide was not formed during the induction period. This was accounted for by the absence of reactive allylic sites in the polymer. A deactivation of peroxide by a hindered phenol which might have been present in Irgastab T290 in a small concentration was also considered.

A small induction period in gel formation and colour formation was observed when PVC was processed with Ca-stearate at lower temperature. Discolouration of the polymer during this induction period was, however, higher than the discolouration observed when the polymer was processed with dibutyltin maleate. Infra-red spectroscopy indicated that an esterification took place within the induction period and this was also demonstrated by the disappearance of the carboxylate absorption of Ca-stearate. It was also shown that Ca-stearate ~~absorption~~ reacted with evolved hydrogen chloride with formation of stearic acid. The role of Ca-stearate as a lubricant was attributed to the formation of stearic acid.

When the additives (Irgastab T290, Ca-stearate and Wax E) were added at the same time during processing a similar induction period, measured by the increase of the torque and the gel content, was observed as in the case when Irgastab T290 was used alone. It was shown that Ca-stearate was present after 30min of processing at lower temperature and that stearic acid was formed only towards the end of the induction period. It was suggested that the role of Ca-stearate in the presence of dibutyltin maleate was predominantly of a lubricant. As in the case of dibutyltin maleate, the formation of an ester and anhydride during the induction period was demonstrated.

The degradation of the polymer processed without additives by ultraviolet radiation of wavelength greater than 280nm in the open atmosphere resulted in an extensive photo-oxidation. The photo-oxidation was shown by the formation of carbonyl and hydroxyl absorptions in the infra-red spectra of irradiated polymer films. The infra-red spectroscopy results also suggested a formation of conjugated carbonyl and also unsaturation. The formation of conjugated unsaturation as a result of hydrogen chloride evolution was also shown by the infra-red spectra of irradiated gel phase of processed unstabilized PVC. The photo-oxidation proceeded in two stages viz initial fast-rate stage followed by a second slower-rate stage. The initial fast-rate stage was considered to be due to the presence of unsaturation formed by the hydrogen chloride evolution during processing. Spectroscopic data of UV-degraded gel phase also showed that the initial fast-rate of photo-oxidation and the extent of photo-oxidation was the result of catalytic action of alkoxy and hydroxyl radicals formed by the photolysis of peroxide formed during processing. The results of degradation of the gel phase obtained from the samples processed for a longer time at higher temperature and also air permeability results demonstrated that the retardation of photo-oxidation was due to a slower diffusion rate of oxygen through the cross-linked structure. The polyenes formed by HCl evolution during processing were also considered to act as a possible UV-screening agent. A correlation was found between the infra-red spectroscopy data and the degree of colour formation. It was suggested that the discolouration during photo-oxidation was due to a chromophore (possibly conjugated carbonyl) formed during

UV-degradation. Comparison of carbonyl and hydroxyl absorptions have shown that they were formed simultaneously during the exposure. It was suggested that polymeric ketone and polymeric alcohol were the products of photolysis of intermediate hydroperoxide. The extent of photo-oxidation of samples containing higher concentration of the gel phase before irradiation was smaller. This was again interpreted as being due to a slower diffusion of oxygen through the cross-linked structure.

The UV-degradation of the polymer with dibutyltin maleate (which remained in the polymer after processing) showed an induction period in carbonyl and hydroxyl absorptions formation, in colour formation and also in unsaturation. It was shown that during the induction period the carboxylate moiety of the stabilizer disappeared. The disappearance of the carboxylate of Ca-stearate was also shown. It was suggested that stabilizer reacted with sites in the polymer activated by irradiation (possibly allylic) or with HCl evolved during exposure, or with both as in the case of thermal degradation. It was concluded that the thermal stabilizer dibutyltin maleate which remained in the polymer after processing acted as UV-stabilizer. It was pointed out that an agent which reacts with evolved HCl and with reactive allylic sites in the polymer and therefore prevents formation of unsaturation consequently prevents photo-oxidation.

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Appendix I

Calculation of total colour difference using M.E.E.C.C. Colourmaster, Model V.

The total colour difference was calculated using the following formula:

$$\text{Total colour difference} = \sqrt{\Delta R^2 + \Delta G^2 + \Delta B^2}$$

where: ΔR is the difference between the instrument reading (red filter) of the measured sample and the standard sample (cast unprocessed PVC film).

ΔG is the reading obtained with green filter

ΔB is the reading obtained with blue filter.

An example of the computer programme[113] is enclosed.

```
#LISTING OF :SCS0201.SAVEP(1/B1B0)  PRODUCED ON 16JUL73 AT 13.43.03

#OUTPUT BY LISTFILE IN ':SCS0201.SAVEP' ON 16JUL73 AT 13.43.19

DOCUMENT    :SCS0201.SAVEP(/B1B0)


STARTED :SCS0201,SAVEP,16JUL73  13.30.55 TYPE.BACK
13.30.57+ JOB SAVEP,:SCS0201
13.31.01+ SAVEP
13.31.02+ JT 100
13.31.11+ ER TAHANPROG
13.31.28+ UAALGOL SAVE TAHANPROG
13.31.37+ IF MOP,(TA NONE)ELSE(TA CE,DP,OL,LS)
13.31.39+ TA CE,DP,OL,LS

13/37/42        16/07/73        COMPILED BY XALV MK. 3A
LINE STATEMENT
   0     0      'PROGRAM'(AXXX)
   1     0      'INPUT'0=CR0
   2     0      'INPUT'3=TR0
   3     0      'OUTPUT'0=LP0
   4     0      'OUTPUT'4=LP1
   5     0      'COMPACTDATA'
   6     0      'COMPACT'
   7     0      *****
   0     0      'BEGIN'
   1     1      'REAL'P,G,B,P1,UI,VI,WI,UJ,VJ,WJ,A,BB,L,TOL,BS,AS,LS,E;
   2     1      'INTEGER'I,N;
   3     2      'PROCEDURE'DIFF(G,VJ);'REAL'G,VJ;
   4     5      'BEGIN''REAL'VI; VI:=8;
   5     7      STARTA:VJ:=VI-(4.404'10'-4*VI↑5-2.101'10'-2*VI↑4+2.395'10'-1*VI↑3-2.311'
   6     7      10'-1*VI↑2+1.222*VI-G)/(4.202'10'-3*VI↑4-8.404'10'-2*VI↑3+7.185'10'-1*VI
   7     7      ↑2-4.622'10'-1*VI-1.222);
   8     8      'IF'ABS(ABS(VI)-ABS(VJ))>TOL'THEN'
   9     8      'BEGIN'VI:=VJ;'GOTO'STARTA;
  10    11      'END';
  11    12      'END';
  12    12      PAPERTHROW; NEWLINE(3);
  13    15      WRITETEXT('('('3S')'P'('12S')'G'('12S')'B'('12S')'A
  14    15      '('12S')'BB'('12S')'L'('12S')'E')');   NEWLINE(3);
  15    17      REPEAT: N:=READ;  'IF' N=0 'THEN' 'GOTO' FINISH;
  16    19      'FOR'I:=1'STEP'1'UNTIL'N'DO'
  17    20      'BEGIN'
  18    20      P:=READ;
  19    22      G:=READ;
  20    23      B:=READ;
  21    24      P1:=(4.0*B+2.0*G)/10.0;
  22    25      TOL:='10'-3;
  23    26      DIFF(G,VJ);
  24    27      DIFF(P1,UJ);
  25    28      DIFF(P,WJ);
  26    29      A:=41.66*(UJ-VJ);
  27    30      BB:=16.74*(VJ-WJ);
  28    31      L:=10.00*VJ;
  29    32      NEWLINE(2);SPACE(5);
```

```
   33   40        PRINT(A,3,2);SPACE(4);
   34   42        PRINT(BB,3,2);SPACE(4);
   35   44        PRINT(L,3,2);
   36   45        'IF' I=1 'THEN'
   37   45        'BEGIN' LS:=L; BS:=BB; AS:=A; 'END'
   38   49        'ELSE' 'BEGIN'
   39   49        E:=SQRT((LS-L)↑2+(AS-A)↑2+(BS-BB)↑2);
   40   51        SPACE(4); PRINT(E,3,2);'END'; 'END';  'GOTO' REPEAT;
   41   56        FINISH; 'END';
SEGMENT AXXX          LENGTH   313
NO OF BUCKETS USED     14
COMPILED   #AXXX             EC



CONSOLIDATED BY XPCK 12B

PROGRAM AXXX
COMPACT DATA (15AM)
COMPACT PROGRAM (DBM)
CORE               6720


  LISTDIR LISTING OF DIRECTORY      :SCS0201

  TYPE     NAME        GEN.NO. LANG.    REEL.NO.  SERIAL NO.

FILE     TAHANPRUG           1   ALBN
FILE(T) SAVEP                1   B1BU
FILE(T) SAVEP                1   B5RT
ALLOT        *LPO     N
0.11: MONITOR
ALLOT        *CRO     N
0.11: MONITOR
15.41.43 FREE *CRO ,7 TRANSFERS
15.41.48 FREE *LPO ,21 TRANSFERS
0.12 :HALTED : EE
15.42.00 0.12 DELETED,CLOCKED 0.07
0.12 :DELETED
END OF MACRO
END OF MACRO
MAXIMUM ONLINE BS USED 22 KWORDS
15.42.30 0.13 FINISHED : 2 LISTFILES
BUDGET        USED      LEFT
TIME(P)         15       -13
MONEY           20      4980

***** ***************************************************************************************************
```