NOVEL POLYMERIC MATERIALS FROM RENEWABLE RESOURCES : PHENOLIC RESINS BASED ON CROTONALDEHYDE

Submitted to the
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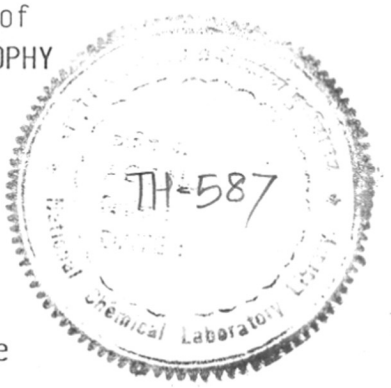

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FORM A

Certified that the work incorporated in the thesis **'Novel Polymeric Materials From Renewable Resources : Phenolic Resins Based On Crotonaldehyde'** submitted by Mr. R.N. Dongre was carried out by the candidate under my supervision. Such material as has been obtained from other sources has been duly acknowledged in the thesis.

DR. V.M. NADKARNI
Research Guide

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R.N. DONGRE

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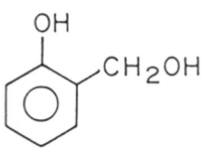
INTRODUCTION

1.1 HISTORICAL BACKGROUND

The generic term 'Phenolic Resins' describes a wide variety of resinous product formed by acid and base catalysed reactions between aromatic hydroxy compounds and various aldehydes. Phenol and formaldehyde are the most widely used ingredients. Other hydroxy compounds such as resorcinol, alkyl-substituted phenols, hydroquinone and aldehydes like acetaldehyde, furfuraldehyde have also been investigated.

The earliest work in this field is due to the efforts of Von Bayer in 1872. He observed the formation of a colourless resinous substance together with a red oxidation product when pyrogallic acid was heated with benzaldehyde[1]. Similar results were obtained with resorcinol and benzaldehyde using sulfuric acid as catalyst. Bayer also showed that phenol reacts with acetaldehyde in presence of sulfuric acid as catalyst.

In 1884, Michael[2] found that the resinous mass can be obtained by reacting benzaldehyde and phenol using catalytic amount of hydrochloric acid or a base. The first systematic investigation of the reaction of formaldehyde with phenols was conducted by Kleeberg[3] in 1891. Similar experiments were carried out by Claisen[4]. Kleeberg observed that in the presence of high concentration of strong acids, phenol reacts vigourously with excess of formaldehyde to yield rose coloured cross-linked, insoluble viscous resin. Hosaeus[5] obtained a crystalline product in the reaction of formaldehyde and β-napthol with acetic acid as catalyst. Similar findings are reported by Abel[6] using napthols and formaldehyde. In 1894, Lederer[7] and Manasse[8] independently prepared o-hydroxybenzyl alcohol (Saligenin) by base catalysed reaction of phenol and formaldehyde at low temperature.



(SALIGENIN)

The first patent on phenolic resins describing a cast cured resin substitute for hard rubber was granted in 1899 to Smith[9]. Speier, Smith and Luft[10] were the first to identify the technical applications of curable phenolic

resins. Luft reinvestigated the reaction between phenol and an excess of formaldehyde catalysed by strong acids[9]. Around the same time Blumer[11] independently reported for the first time the generation of non-reactive resins by the reaction of phenol with less than stoichiometric amount of formaldehyde. Further improvements to the preparation of phenolic resins were made by Fayolle[12] and Story[13].

The major advances in phenolic resins are related to the research of Backeland. Backeland started a systematic and exhaustive investigation of phenolic resins in 1905 on the basis of the then available data :

- Phenols and formaldehyde react to form resionous products in the presence of acidic and alkaline catalysts. The resin properties may be controlled to produce fusible (thermoplastic) or heat-curable (thermoset) by altering the reaction parameters.
- Phenolic resins could substitute shellac, ebonite, horn and celluloid. The resins were thermally moldable into specific shapes of the molds with the incorporation of fillers.

By 1907, Backeland could differentiate between acid and base catalysed reactions. He showed that the resins formed differed markedly in their properties dpending on whether the phenol to formaldehyde mole ratio was less than or greater than one. The first patent filed by Backeland[14] described the reaction of phenol, formaldehyde and catalyst at elevated temperatures and also the incorporation of fibrous cellulosic material. He also patented the process for preparation of phenolic resins using alkaline catalysts[15]. This patent was the first description of the resin manufacture. This commercial practice is followed even today. The salient points of the patent are summarised below :

- The reaction is performed in a closed vessel with a reflux condenser to prevent loss of volatile materials.
- The reaction is interrupted on attaining the desired viscosity.
- Vaccum distillation is then initiated and continued till a solid product, still soluble in alcohols is obtained.

A number of patents[16-30] were filed after industrial trials on the specific applications of phenolic resins.

Two research communications were published on alkali catalysed resinification (Bakelite)[31] and fusible products from acid catalysed phenol - formaldehyde reaction products (novolaks)[32] were critically acclaimed. The chemical investigations of these resins resulted in the identification of cross-linking agents such as Hexamethylenetetramine (Hexa) and Trioxymethylene to post cure the resins into useful commercial products.

1.2 PROPERTY VARIATIONS VS CHEMICAL MODIFICATIONS

In some formulations phenol has been partially or completely replaced by substituted phenols with electron donating groups such as o-cresol; industrial cresol; xylenols; m-, p-tert-butylphenol; p-phenyl phenol; resorcinol; cardanol and m-, p-isopropylphenol for property manipulation.

The reactivity of phenol is related to the position of the substituents at the ortho, meta or para position and its electron donating power. The most reactive phenol is 3,5-xylenol. It is followed, in the order of descending reactivity, by 2,4-xylenol, m-cresol, phenol, 3,4-xylenol,

2,5-xylenol, p-cresol and o-cresol. Substitution by the electron donating groups in the ortho or para position deactivates the phenol ring to one third of its original reactivity. However, meta substitution increases the electron density and hence the reactivity of the ortho and para positions towards electrophilic substitution. Thus, m-cresol reacts very rapidly with formaldehyde. The resins obtained are structurally linear and cannot be easily cross-linked. The curing is slower than that of phenol based resins. The m-substituted resins show greater thermoplasticity, better resistance to moisture and better electrical properties under humid conditions and are suited to applications as laminates.

Introduction of an additional hydroxyl group on the benzene ring increases the condensation rate with formaldehyde. The increase in the reactivity is more dramatic than those observed with the alkyl substitution. Formaldehyde reacts readily with resorcinol in the absence of a catalyst even at room temperature. It is extremely difficult to isolate the first condensation product, resorcinol alcohol, as the polycondensation rate is very rapid[33]. When less than stoichiometric equivalence of formaldehyde is reacted with resorcinol under acidic

conditions, only a liquid resin is obtained. Solid, hard, cured resins were obtained when formaldehyde is replaced by paraformaldehyde[34]. The resins show better water resistance. The resorcinol based resins display better electrical properties, high impact strength, less thermoplasticity and lower flammability than corresponding phenol based resins.

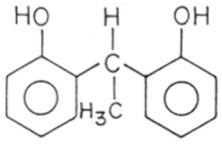
Paraform has also been reacted with pyrogallol in presence of gum arebic to produce a red, fusible resin[35]. Internal plasticization is observed with phenols having bulkier side chain such as m- and p-isopropyl phenol and m-tert-butylphenol[36]. Resins with substituted phenols such as p-phenylphenol[37] and p-tert-butylphenol[38] alone and in combination with phenol have better solubility in drying oils and are used as varnishes.

Under alkaline or acidic conditions at 100° - 200°C, cardanol self-polymerizes as well as condenses with formaldehyde to yield a wide variety of curable resins[39].

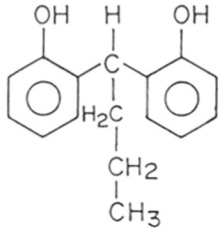
Aromatic carboxylic acids condense with aldehydes resulting in resins[40] soluble in mild alkalies. These find use in leather finishing and treating felts used

in hat manufacture. Chemically inert resins from chlorinated phenols and formaldehyde have been blended with phenolic resins to impart flame retardance[41]. The property profile of these resins is similar to the traditional novolak resins[42].

In certain formulations formaldehyde is also replaced to achieve the desired properties. The higher homologues condense with phenols in a manner similar to formaldehyde but at a slower rate. Among the resins formed with higher aldehydes only those due to acetaldehyde (I), butyraldehyde (II) alone or in combination with formaldehyde have found commercial acceptance. The cured resins are less



(I)

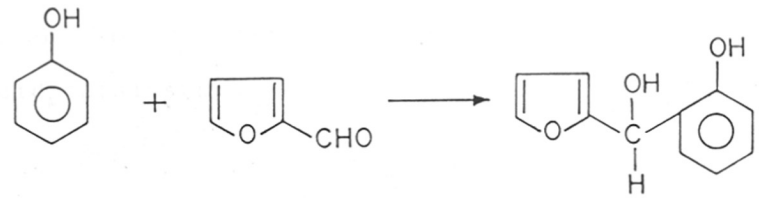


(II)

rigid due to the larger group in the carbon chain between phenol rings. Bayer observed that the reaction of phenol with acetaldehyde yields a crystalline product[43]. Phenol condenses with acetaldehyde, paraldehyde, metaldehyde

or tetraldehyde in presence of acids, bases, neutral, basic or acidic salts to yield soluble, fusible hard resins[44-51].

Furfural reacts with phenol in the presence of sodium carbonate to form a α- (o- or p-hydroxy phenyl) furfural alcohol [52] (III). Under acidic conditions, self-condensation of furfural proceeds rapidly to the gel state[53].



PHENOL FURFURAL

(III)

The acid catalysed reaction of phenol and butyraldehyde at high temperatures results in a viscous brown resin[54], curable with furfural/potassium carbonate or hexa. End uses are in hot and cold moldings, varnishes, adhesives and impregnators[54,55].

The reaction of phenol and substituted phenols with benzaldehyde generates dark brown resins[56,57] which are hardened thermally or in the presence of small quantities of acids, acid salts or methylene-engendering bodies[58]. p-nitrobenzaldehyde has also been shown to condense with phenol, resorcinol, thymol, o-nitrophenol, or o-methylanisole to yeild amorphous solids[59].

The reaction of phenols with unsaturated aldehydes such as acrolein, methacrolein, crotonaldehyde, aldol have been investigated in acidic and alkaline medium[60]. With acid catalysts,

$CH_2 = CH\text{-}CHO$	$CH=C(CH_3)\text{—}CHO$	$CH_3\text{-}CH=CH\text{-}CHO$
Acrolein	Methacrolein	Crotonaldehyde

maximum rate of polycondensation was observed at a phenol to acrolein ratio of 1:5.0. While for base catalysts, the maximum rate was observed at the ratio of 1:2.5. The resins compared well with phenol-formaldehyde resins as lacquers. Acid catalysed reaction of phenol and acrolein (mole ratios 1:1.3 to 4.0) in the temperature range of

52°-105°C yields water soluble, moldable resins[61]. The resins prepared at lower temperatures were light coloured under neutral and basic conditions but dark coloured under acidic conditions[62-65]. Under acidic conditions the polycondensation proceeds by aldol condensation. The maximum number average molecular weight obtained was 650. Resins prepared under acidic conditions from a less than stoichiometric equivalence of phenol to acrolein (mole ratio 1:0.25 to 1.0) are similar to novolak resins and can be cured with hexa[66,67]. Anionic or cationic resins have been prepared by modification of phenol - acrolein resins with sodium hydrosulfite and aromatic diamine[68]. Epoxy resins can be prepared by modifying with epichlorohydrin [69,70]. Phenol acrolein resins have also been prepared by reacting polyacrolein oligomer with phenol using acid catalyst[71,72].

1.3 REACTION MECHANISM

The phenolic hydroxyl group is electron donating. It activates the ring to electrophilic reactions at ortho and para positions by increasing the relative electron

densities at these positions. Phenol is trifunctional, with the two ortho and one para position being active. Formaldehyde has a functionality of two. Thus, phenol and formaldehyde can react to a three-dimensional cross-linked structure. Ortho and para substituted phenols such as o- and p-cresol have a functionality of two. Reaction products of these phenols with formaldehyde result in linear structures without cross-links. Meta substituted phenols such as m-cresol are trifunctional and can form cross-linked products. Megson and Holligdale[73] calculated the structural complexity of the phenolic resins from reactions at three positions of the phenyl nucleus. For an average phenolic resin molecule comprising of eight phenyl rings, there exist at least 1485 unbranched and 1200 branched isomers. This molecular complexity results in amorphous resins and explains the enormous difficulty in elucidating the exact structure. It also opens up the scope of preparing resins to meet a wide variety of specific property and performance requirements.

Thus, the polymerization of phenol and formaldehyde (both being small in size) yields a rather tightly knit

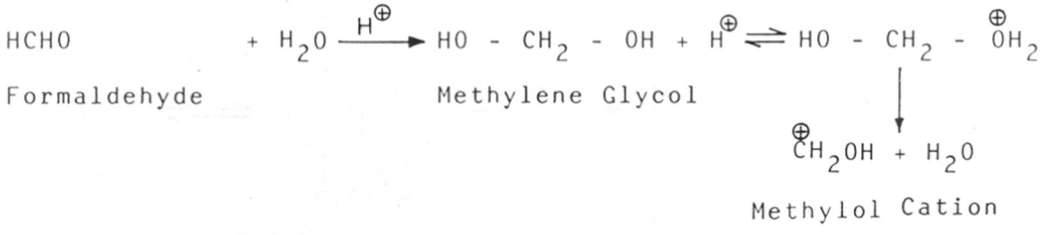
structure with low degree of flexibility and good high temperature strength. The primary reaction variables determining the resin structure and the physical properties are [74]:

- The pH of the reaction mixture, and
- The mole ratio of phenol to formaldehyde.

The pH of an equimolar mixture of phenol and formaldehyde (37-40 weight % in water) is 3.0-3.1. This is taken as the reference or neutral point. The rate of the phenol-formaldehyde reaction at pH 1.0 to 4.0 is proportional to the hydrogen ion concentration, above pH 5.0 it is proportional to the hydroxyl ion concentration, indicating the change in reaction mechanism. Thus, a shift in pH to either side of reference point results in reaction rate enhancement. For acid catalysed reactions, the ideal pH range is between 0.5 to 1.5. The resins obtained are called Novolaks. Two mechanistically differing reactions are observed at pH above the reference point, one at the intermediate pH of 5.0 to 7.0 and other in alkaline range with pH from 7.0 to 11.0. The resins formed in intermediate range are called High ortho novolaks and Resols in the alkaline range.

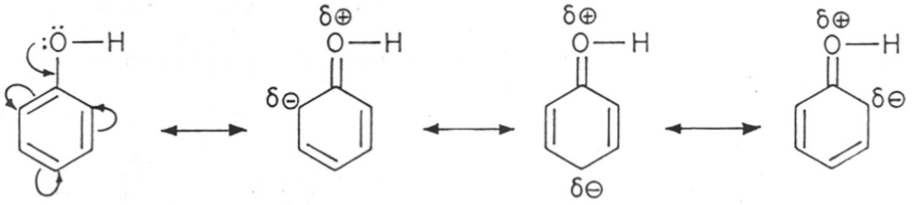
1.3.1 Acid Catalysed Condensation

In acidic medium (pH of 0.5 to 1.5), formaldehyde condenses with phenol over the mole ratio range from 0.5 to 0.8 to form solid, thermoplastic resins. With excess of formaldehyde the product formed is infusible. If excess of phenol is present a fusible product, termed Novolak, is formed. With a large excess of phenol, the main product formed is dihydroxyphenyl methane. On increasing the relative ratio of formaldehyde, larger molecules with 15 to 20 phenyl rings are formed. The molecular weight of the resin is governed by the relative amounts of formaldehyde and phenol in the reaction mixture. The resin chain ceases to grow after the consumption of formaldehyde. The condensation is an electrophilic substitution reaction. It involves the protonation of formaldehyde or of its methylene glycol to form methylol cation.

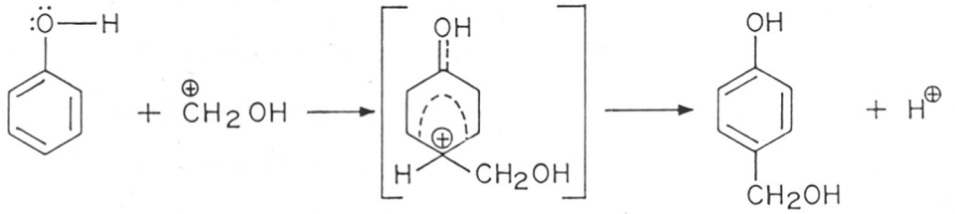


The hydroxyl group on phenol increases the electron density

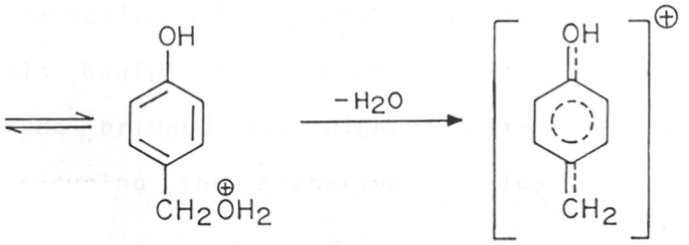
at the ortho and para positions of the ring.



The protonated formaldehyde (methylol cation) electrophilic attacks the ring at either one of the two ortho or at the para position forming methylol phenol.

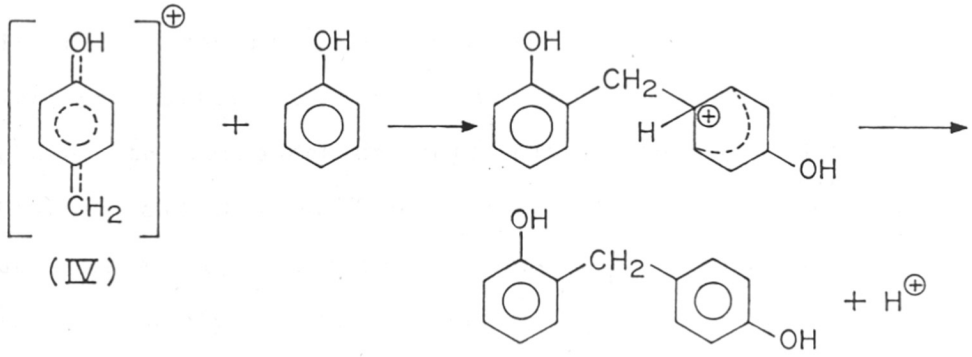


Methylol Phenol



(IV)

The hydrated carbonium ion, in equilibrium with the alcohol loses water to form (IV) or reacts with phenol generating a proton and forming dihydroxydiphenyl methane.



(IV)

Dihydroxydipheyl methane

The intermediate form may be quinone methide[75]. The phenyl ring of the methylol phenol formed is less active (relative to phenol) to further electrophilic substitution reaction by formaldehyde. The dihydroxyphenyl methane is not as strongly ortho or para directive as phenol. In the initial course of the reaction, phenol and formaldehyde condense to form predominently diphenols. The concentration of diphenols increases rapidly before polyphenols begin to be formed. At higher conversions formaldehyde bridges two diphenols to form polyphenols, thereby reducing the formation of low molecular weight

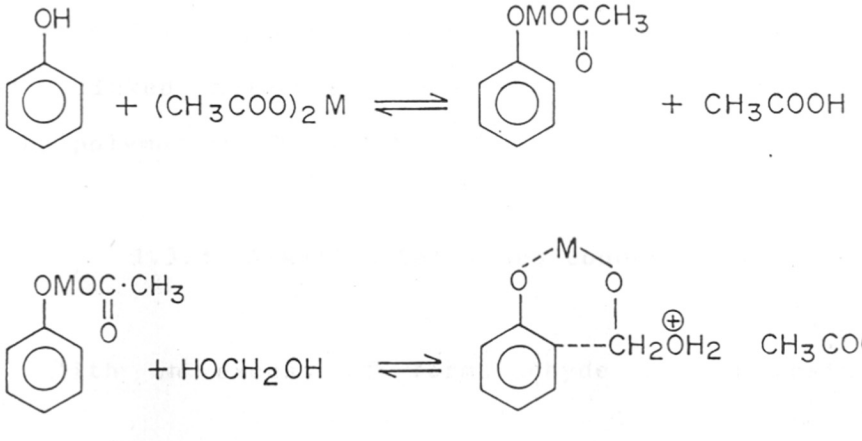
adducts. This molecular growth ends when formaldehyde is completely consumed and a final molecular weight distribution results. In addition to the linear growth, branching is also observed to a less extent indicating that the third position in the benzene nucleus of phenol molecules is not extensively deactivated or sterically hindered. The probability of branching and gelation increases as phenol to formaldehyde mole ratio tends to 1.0 : 1.0. Dijksta and DeJonge[76] used the gel formation during the acid catalysed reactions to show that generalised polymer theories apply to this reaction[77,78].

The rate of reaction is proportional to the concentration of the catalyst and the reactants formaldehyde and phenol. It is inversely proportional to the concentration of water. In an excess of phenol, the reaction kinetics is first order with respect to formaldehyde. The most commonly used acid catalysts are sulfuric acid, hydrochloric acid, p-toluene sulfonic acid, phosphoric acid and oxalic acid.

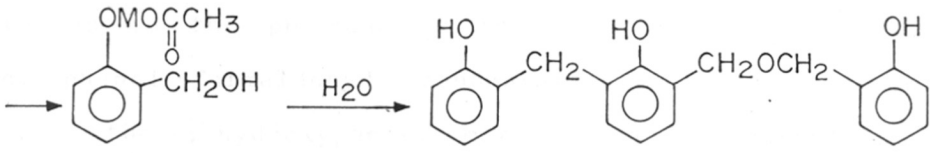
1.3.2 Catalysed Condensation At Intermediate pH Range

In addition to mineral acids and bases, metal salts catalyse the phenol-formaldehyde reaction in the pH range of 4.0 to 7.0. The solid resins obtained have a high concentration of O, O'-repeat units[79]. Hence the term 'High Ortho Novolaks' is ascribed to this pH range. Any electropositive bivalent metal ion can be used. The effective ones are manganese, cadmium, zinc and cobalt[80,81].

In this pH range, formaldehyde adds slowly to phenol and the condensate reacts with a second phenol molecule to form diphenol. The phenolic hydroxyl and methylol glycol chelate with metal to form the moiety (V) which hydrolyses to give the resin.



(V)



Resin

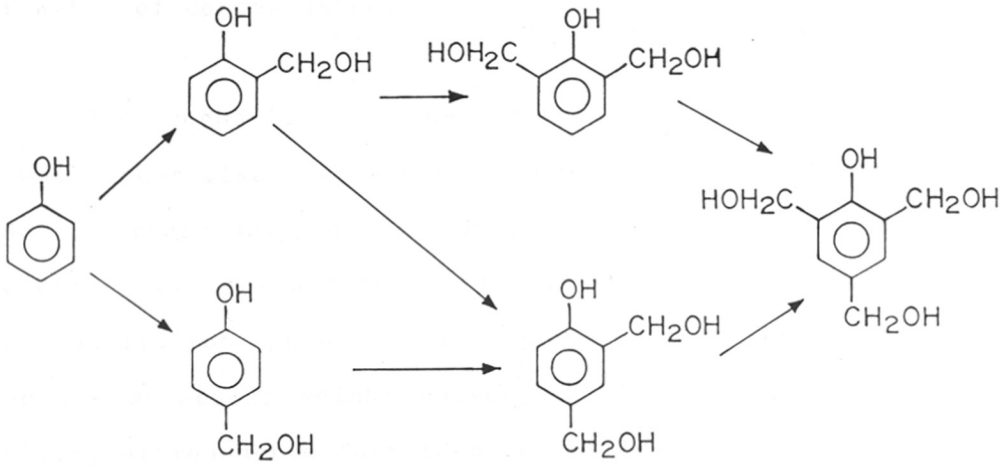
Thus in these resins para positions are relatively unsubstituted. The resins also have a small concentration of methylene ether groups that decompose when contacted with acids.

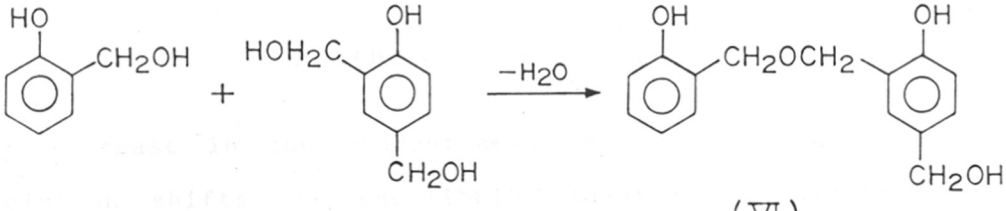
Resins with excellent property profile are obtained when the formaldehyde to phenol molar ratio is less than 0.9. In general practice a 15-30% excess of phenol over formaldehyde is used. Structural effects such as hydrogen bonding are also present due to the hyperacidity effect. The resins also exist in pure ortho trimers and tetramers[82]. Intermolecular hydrogen bonding have been found between ortho linked molecules depending on the concentration of the polymer in the solution[83].

1.3.3 Alkaline Catalysed Condensation

With an excess of formaldehyde liquid resins are

formed in the pH range 7 to 11. The initial products of phenol-formaldehyde condensation reaction, at pH $\geqslant$ 8 are ortho, p-hydroxyphenyl methylol and dimethylols[84-86]. Further reaction leads to two possibilities : (a) formation of methylene ether (VI) and (b) independent or subsequent formation of diarylmethane (VII).





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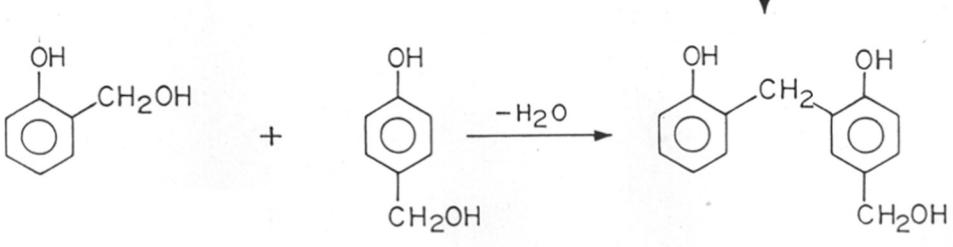


(VII)

Monomers and dimers condense on further heating to increase the average molecular weight of the resin. If reaction is not discontinued at an appropriate time, a cross-linked, infusible product results. The reaction is terminated when a semisolid resin results after the distillation of water of condensation.

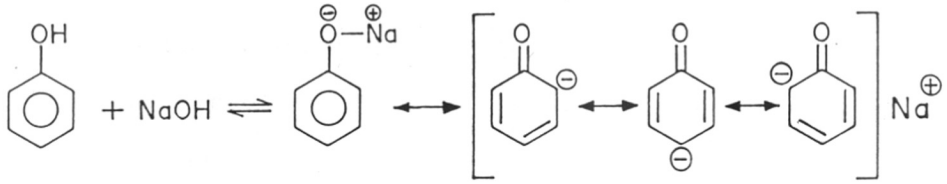
The mechanism of the addition of formaldehyde to phenol under alkaline conditions have been studied extensively and is reasonably well understood. Commercial aqueous solution of formaldehyde (37-40% by weight) exist as an equilibrium between the reactive methylene glycol[87] and low molecular weight polyoxymethylene glycols. Availability of monomeric formaldehyde is limited by its equilibria with its hemiformals.

$$HO - CH_2 - OH \rightleftharpoons {}^{\delta\oplus}CH_2 - {}^{\delta\ominus}O + H_2O$$

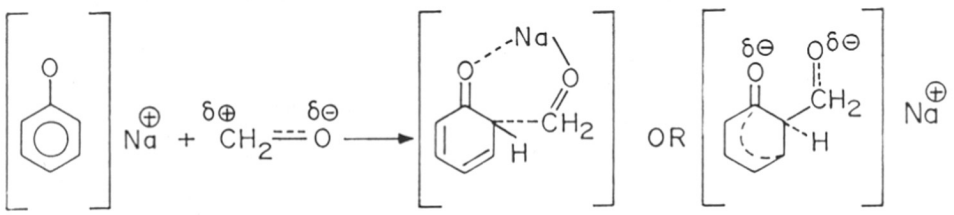
An increase in the concentration of formaldehyde in the solution shifts the equilibrium towards polyoxymethylene glycol.

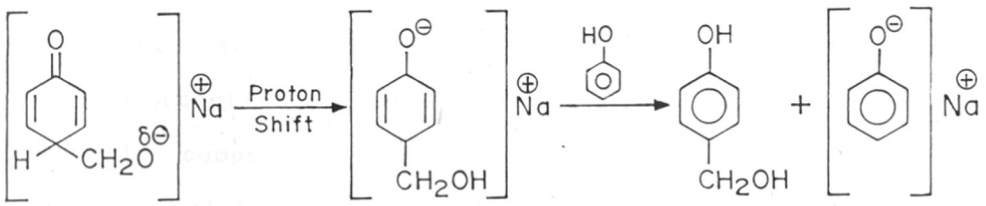
$$3HO - CH_2 - OH \rightleftharpoons HO - CH_2O - CH_2OH + 2H_2O$$

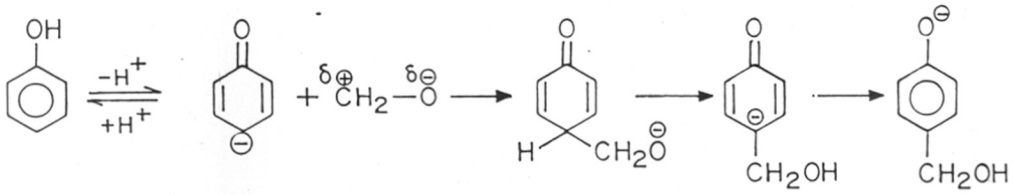
In alkaline pH, phenol deprotonates to form resonance stabilized phenoxide ion.



In dilute solutions the two consecutive reactions namely substitution followed by proton shift leads to the formation of methylol phenol[87,88].







Yeddanapalli and Gopalkrishna[89] suggest that the para substitution depends on the formation of the activated complex from the quinonoid form.

Martin studied the characteristics of 147 different mono- and dinuclear phenol alcohols, as reference compounds. It was borne out that in phenol the para position is not as active as the sum of the two ortho positions[90]. A higher concentration of ortho methylol phenol is formed in the initial phase of the condensation. Unlike in acid catalysis, in alkaline conditions, substitution of phenol enhances its reactivity relative to phenol. The reaction therefore diverges from that under acidic conditions after the first condensation. The reaction results in the formation of dimethylol phenol rather than in ring fusion to form dihydroxydiphenylmethane. The concentrations of each of the possible alcohols and unreacted phenol change progressively during the course of the reaction. The reactions summerised earlier are mutually competing. No specific concentration of each can be cited as the universal limit.

Thus, under alkaline conditions, phenol and formaldehyde react to give di- and tri-methylol or methylene-ether containing resins and to a limited extent diarylmethane structures. These resins are liquids, solutions or solids. The product of commercial importance are formed at phenol to formaldehyde ratios greater than 1 : 1.5. The catalysts used are sodium hydroxide, barium hydroxide, calcium hydroxide, sodium carbonate and organic amines.

1.4 APPLICATIONS OF PHENOLIC RESINS

Phenolic resins have been extensively used as bonding materials. The resins may be used either in solid or liquid form. They also find uses as adhesives, coatings and as matrix materials for glass fibre reinforced molding compounds. In recent years phenolic resins have found application in microencapsulation.

Phenolic resins are used to bond wood composites[91] as in plywood, particle board, fibre board, wafer board, macroscopic wood composites like beams, arches, etc. Phenolic resins exhibit better resistance to humidity

than urea-formaldehyde and malemine-formaldehyde resins[92,93].

Phenolic resins are used in thermal acoustical insulation mats and carpet underlay. In these applications, low molecular weight, highly functional, water soluble resoles are sprayed on glass, rockwool and then compression molded. Alternatively high ortho novolaks or a blend of one-step and two-steps resins are used.

Phenolic resins are used in decorative and industrial laminates. The resin is coated on paper, cloth or glass substrate. The end uses of decorative laminates are in furniture, wall panelling, home and office furnishings. The commercial laminates are used as electronic circuit boards, gears, rods, bearings and as tubes.

Phenolic resins are used in 2-3% weight/weight as binders for sand consolidation in foundries. Molten metals are cast into numerous intricate finished parts such as machine housings, automotive transmissions and cylinder heads using phenolic resin bonded sand molds[94]. The foundry process dictates the type of phenolic resin

used, whether one-step resin or novolak/hexa composition. Casting can be done by Hot-box process[95], No-bake process[96] and Cold-box process[97,98].

Phenolic resins are used as bonding agents for abrasive grinding wheels[99,100] and snagging wheels and for coated abrasive sand papers, discs and belts[101,102]. Bonded abrasives display greater strengths compared to ceramics or vitrified compositions. The materials are used in metal grinding. Synthetic alumina and silicon carbide are used as the abrasives. For special applications, boron carbide and diamond are used. Coated abrasives are used at high temperatures requiring water cooling. The abrasive materials used include ground glass, flint, emery, aluminium oxide and silicon carbide.

In the automobile industry, phenolic resins find applications in brake linings, clutch facings and transmission bands[103-105]. In the automotive brake lining application, good performance at high temperature and better adhesion to semimetallic additives are desired. The phenolic resins used are either novolak or a liquid-solid resole with fillers, friction granules such as cross-linked

particles based on alkenylphenol form, cashew-nut shells, asbestos or semimetallic fibres.

Electrical devices such as sockets, switch gears and circuit breakers utilize the good mechanical and electrical properties offered by phenolic molding powders[106,107]. The important properties of the cured products are thermal stability with modulus retension, good electrical insulation, solvent resistance and gloss. The modulus retention and thermal stability are used advantageously in applications such as automotive distribution caps, relays, brake pistons, coffee makers, utensile handles and general appliance parts[108]. The properties of molding materials depend on the formulation including the type and amount of the resin and fillers used. Recently molding materials with superior mechanical performance have been achieved with addition of certain fibrous fillers[109].

A blend of phenolic resins with a number of thermoplastic and thermosetting polymers have found use as coatings, additives and tackifiers. The end applications are as automotive primers, can coatings, drum linings,

anticorrosive paints, printing inks, wire enamels and varnishes. Other polymers used are epoxies, drying oils, poly (vinyl formals), poly (vinyl butyrals) and acrylics. Recent developments in coating applications include the use of polyether amide-imide/t-butylphenolic resin blend as powder coating for high temperature wire insulations[110]. Polypropylene glycol-maleic anhydride/phenolic copolymer to impregnate and coat cellulosic fibres to obtain rapid wetting battery seperators[111] and oil modified, water-soluble phenolics with lower cure temperature[112]. Modified phenolic resins generally display good solvent resistance, abrasion resistance, thermal stability and electrical insulating properties.

Phenolic resins offer good flame retardance, low smoke density and the by-product of combustion are relatively non-toxic. These properties are of critical importance to the recently developed glass fibre-reinforced phenolics[113], phenolic fibres[114] and phenolic foams[115] for applications in the transport sector.

1.5 CROTONALDEHYDE BASED PHENOLIC RESINS

Phenol and crotonaldehyde (PC) resins are reported in the patent literature as highly viscous, resinous mass useful as tackifiers, lacquers and tanning agents.

Herrmann and Deutsche[116], in 1928, reacted crotonaldehyde with polyphenols, such as resorcinol and pyrogallol to give resinous materials. A process for preparing PC resin with acid catalyst was described by G. Balle and A. Steindroff[117]. These PC resins were transformed into an infusible, insoluble mass by the addition of PF resoles and a basic catalyst[118]. The acid catalysed condensation was carried out in the presence of solvents such as carbon tetrachloride and chloroform[119]. Antoine Poulverel[120] prepared PC resins in the presence of strong bases and protective colloids.

Maksorov and Andrianov[121] reported in 1933 the acid and base catalysed condensation reactions of phenol with crotonaldehyde. Equimolar ratios of the two reactants were used in condensation. The catalyst concentration was 1 weight percent of phenol. The course of the conden-

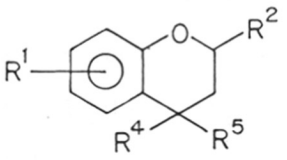
sation was monitored by withdrawing samples after predetermined times and checking the viscosity of 10% resin solution in acetone, by an ostwald viscometer. The relative merits of hydrochloric acid, β-napthalene sulfonic acid, boric acid, sulfuric acid, phosphoric acid, potassium hydroxide, silica gel, potassium sodium tartarate (seignette salt), aluminium trichloride, ferric chloride were evaluated as catalysts. Hydrochloric acid, sulfuric acid, β-napthalene sulfonic acid and phosphoric acid were found to be the most efficient catalysts.

The effect of molar ratio of phenol to crotonaldehyde on the final product properties were also investigated[121]. 1 weight% β-napthalene sulfonic acid and potassium hydroxide were used as catalysts. The mole ratios used were (phenol to crotonaldehyde) 1 : 0.33, 1 : 0.5, 1 : 1 and 1 : 2. The temperature was maintained at 100°C and the reaction time exceeded 7 hours. On the basis of viscosity data it was concluded that for both acid and base catalysts the most effective phenol to crotonaldehyde molar ratio was 1 : 3.

Resins of crotonaldehyde with cresols and xylenols were also synthesised and characterised under identical experimental conditions[121]. It was deduced that cresols react faster with crotonaldehyde than xylenols.

The mode and rate of condensation in acidic medium was compared with that in basic medium[121]. In acid catalysed condensation reactions, the initial polycondensation is rapid with gradual decceleration with increasing conversion. In base catalysed reactions, polymerization is slow in the initial phase and accelerates as it proceeds especially near the final stage. It was concluded on the basis of viscosity measurements that cresols react faster than phenol. These resins were useful in preparing lacquers, particularly for electrical insulations.

Platt et al[122] observed that phenols condense with α, β -unsaturated compounds in the presence of acids to give six membered heterocyclic compounds. The reaction between resorcinol and acrolein or crotonaldehyde under acidic conditions leads to chroman derivative (VIII).



R^1 = 7-OH
R^2, R^4 = H
R^5 = CH_3

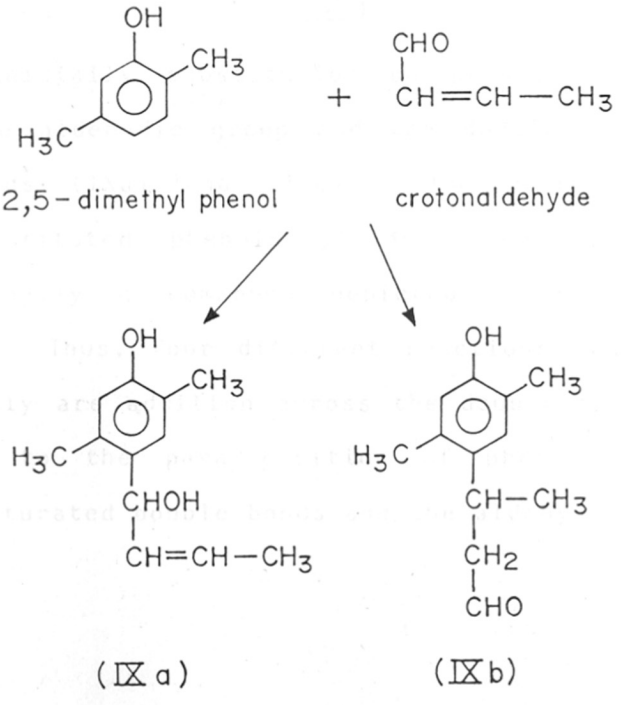
(VIII)

Bayer[68] reported the formation of a solid resin intermediate when 2 moles of rescorcinol react in presence of mineral acid with 1 mole of α , β -unsaturated aldehyde such as acrolein and crotonaldehyde. The resin reacts with sodium bicarbonate, polyhydric phenols or salts of aromatic amines to form water soluble anionic or cationic resins useful as tannines.

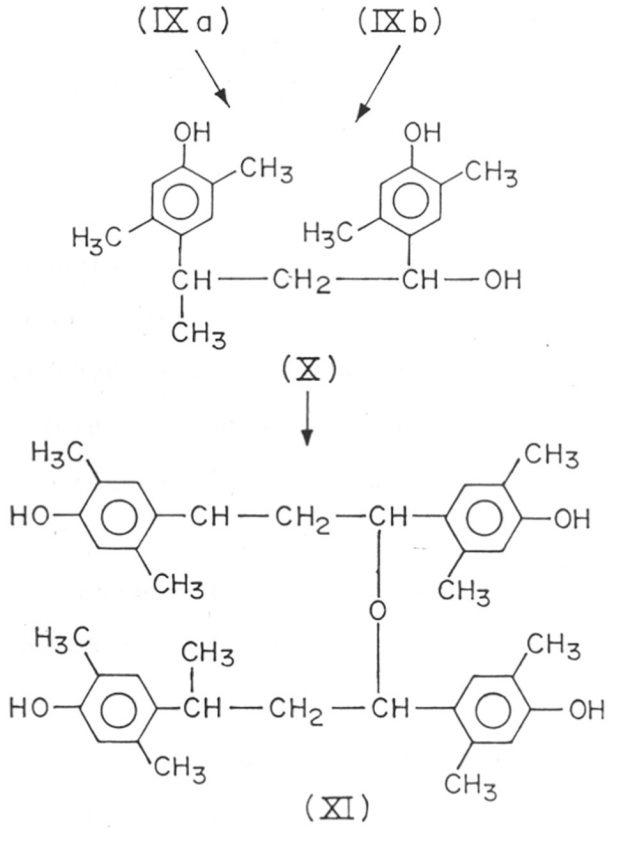
Winguist[123] reacted phenol, alkyl-phenol and poly-nuclear phenols with 2-alkenals such as crotonaldehyde using 0.1 to 1.0 weight % equimolar mixture of boric acid and monohydroxy carboxylic acid as catalyst. PC resins, obtained by acid catalysed (sulfuric acid) reaction of crotonaldehyde with p-octyl phenol, resorcinol or p-dodecylphenol have found use as tackifiers for rubber[124].

Vizovisek et al[125] analysed the acid and base catalysed polycondensates of phenols such as o-, m-, p-cresols; 2,5-, 3,5-dimethylphenol with crotonaldehyde using ^{13}C NMR

spectroscopy and gel permeation chromatography. The condensation was shown to involve the double bond of the unsaturated aldehyde, in addition to the aldehyde group. The addition of the double bond to free ortho and para positions of phenols is dominant in case of 3,5- and 2,5-dimethyl phenol. Cresols are marginally more reactive than the addition of aldehyde groups. The reaction proceeds stepwise to form two, three and four benzene ring systems and finally to high molecular weight polymers as per the reaction scheme given below :



(IX a) (IX b)



Initially substitution on phenol ring takes place via the aldehydic group and the double bond forming the compounds (IXa) and (IXb). The condensation of this monosubstituted phenols yields diphenolic compound (X) and finally a compound depicted by structure (XI) is formed. Thus, four different reactions that occur simultaneously are addition across the double bond and aldehyde groups to the para position of phenol, polymerization of unsaturated double bonds and the aldehyde group.

Chambers et al[126] prepared phenolic resins from substituted phenols and acetaldehyde, crotonaldehyde, propionaldehyde etc. A mixture of oxalic acid and hydrochloric acid was used as catalyst. Resins with high softening temperatures were formed.

The condensates of resorcinol and 4-alkyl-resorcinol with crotonaldehyde under alkaline conditions are also reported[127]. These resins were useful as adhesives on cellulosic fibres e.g. viscose rayon. These fibres are bonded to rubber.

Bauer[128] has reported the reaction of phenol and crotonaldehyde. The reactions were carried out at 95°C for 3-4 hours with sulfuric acid as catalyst. The resins were useful as tanning agents. Resins were also prepared by condensing the sulfonated mixture of polyhydric phenols or their homologues with unsaturated aldehydes such as crotonaldehyde which find use as tanning agents[129].

Stamler and Nebe[130] studied the tanning action of different phenolic resins. The resins were prepared

by reacting sulfonated phenol or 2-napthol with formaldehyde, aldol, acrolein, benzaldehyde, paraldehyde, crotonaldehyde and furfural between 50° and 110°C. Tanning agents of high light-resistance[131] were prepared by introduction of alkyl or 2-butenyl groups into molecules of syntans using crotonaldehyde, acrolein, higher unsaturated aldehydes or acetaldehyde.

CHAPTER 2

SCOPE OF THE PRESENT WORK

CHAPTER 2

SCOPE OF THE PRESENT WORK

Phenolic resins were the first synthetic polymers introduced commercially. The chemistry and technology of phenolic resins are well documented. Major research efforts directed towards phenolic resins have been invariably product oriented. Due to their dimensional stability and excellent thermal and electrical properties, phenolic resins are used in electrical and high temperature applications. The most important fields of application are the wood working industry, molding and insulation compounds. Over the years, a wide variety of phenolic resins have been synthesised exhibiting a broad spectrum of properties to suit the end requirements. In the synthesis of phenolic resins, formaldehyde may be replaced either partially or completely by other aldehydes. Similarly, in certain formulations, phenol is replaced by other alkyl-phenols or polyhydric phenols. Recent efforts in the field have been directed towards development of noval thermoplastic and thermoset compositions for specific end applications.

The present work deals with the synthesis and characterization of acid catalysed novolak resins from phenol and crotonaldehyde. The objective of using crotonaldehyde in place of formaldehyde is to utilise one of the by-products of the sugar industry, an agrobased renewable resource, which is abundantly available in India. In literature, there is little published information on the synthesis of phenol-crotonaldehyde (PC) resins, their chemical structure and properties.

In this Ph.D. research work, the possibility of synthesising novel thermoplastic resins from phenol and crotonaldehyde, has been explored. Thermoplastic solid resins were prepared by condensing one mole of phenol with crotonaldehyde, over a range of molar amounts of crotonaldehyde (0.4 to 1.4 moles), using sulfuric acid as catalyst. Two sets of phenol - crotonaldehyde (PC) resins were synthesised from crude and distilled crotonaldehyde. As reference material, phenol-formaldehyde (PF) novolak resins were prepared over phenol to formaldehyde ratio of 1:0.4 to 1:0.75 under identical experimental conditions. The resins were characterised for solubility,

softening temperature range, Norton flow length and number average molecular weight. The chemical structure analysis involved infra-red spectroscopy (IR), thin layer chromatography (TLC), column chromatography and micro-analysis.

The novolak resins are cured by addition of hexamethylenetetramine (hexa) and heating at elevated temperatures. The curing behaviour of PC resins was found to be different from that of PF novolak resins. PC resins remain thermoplastic after curing at 120°C for 15 minutes, even at a loading of hexa as high as 20% by weight. These semi-cured thermoplastic resins are transformed into infusible, insoluble thermoset material on post-cure heat treatment at elevated temperatures (about 200°C). The retention of thermoplastic nature and concurrent increase in softening temperature range of the PC resins combine the processability of thermoplastics and the desirable thermal and dimensional stability of thermosets. This peculiar curing behaviour was observed for resins from both crude and distilled crotonaldehyde over a range of phenol to crotonaldehyde mole ratios.

The PC resins were characterised for their non-isothermal degradation in air by thermogravimetric analysis (TGA) in comparison with PF novolak resins. The thermograms show degradation in three distinct stages similar to the conventional PF resins. The degradation kinetics was studied using methods of Horowitz et al and Coats et al. It was found that the degradation follows first order kinetics.

The phenolic resins (both PC and PF) were compounded with fillers, additives and compression molded into tensile test specimens. The temperature conditions of compression molding were defined on the basis of thermal data. The curing cycle was defined after preliminary molding trials and inspecting the molded pieces visually. The tensile strength measurements of the molded specimens were made on Instron mechanical tester at a deformation rate of 0.05 mm/min. Both PC and PF resins behave similarly. The specimens exhibited plastic flow and strain hardening for both PC and PF resins. The modulus values were calculated in the elastic and strain hardening regions. The toughness was calculated by measuring area under the stress-strain curves.

The dynamic mechanical behaviour of the PC and PF resins was investigated on a dynamic spectrometer. The storage moduli of both PC and PF resins were found to be comparable. The variation of loss modulus with temperature was studied to elucidate viscoelastic behaviour.

Thus, the thesis consists of three major elements as per details given below :

(1) Synthesis of PC Resins

* Acid catalysed condensation reaction of phenol and crotonaldehyde to yield resins over a wide range of phenol to crotonaldehyde mole ratio.
* Effect of purity of crotonaldehyde on the resin characteristics.

(2) Characterization of PC Resins

* Solubility, softening temperature range, Norton flow length, number average molecular weight by VPO, IR, TLC, column chromatography and micro-analysis.
* Effect of mole ratio on resin characteristics.

(3) Thermal and Mechanical Behaviour of PC Resins

* Effect of mole fraction and purity of croton-

aldehyde on curing behaviour and thermal stability of the PC resins.

* Effect of mole ratio on the mechanical behaviour of the PC resins.
* Effect of mole ratio on the dynamic mechanical behaviour of the PC resins.

Thus, the scope of the work illustrates the interdisciplinary nature of polymer science and technology that involves aspects of polymer chemistry, processing and mechanical testing of materials leading to specific product development.

CHAPTER 3

SYNTHESIS AND CHARACTERIZATION : EXPERIMENTAL

CHAPTER 3

SYNTHESIS AND CHARACTERIZATION : EXPERIMENTAL

3.1 CHEMICALS USED

PHENOL : Emperical Formula - C_6H_6O

Molecular Weight - 94.11

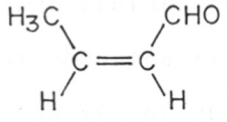
Structural Formula - 

Laboratory grade phenol was obtained from S.D. Chemicals (India). The purity of phenol was checked using a Nucon (AIMIL, Model 5500) series gas chromatograph. A SE-30 column and thermal conductivity detector (TCD) were used. The oven temperature and injection temperature were set at 140°C and the flow rate of the carrier gas, hydrogen, was maintained at 50 ml/min. The purity was found to be greater than 99.5%. The phenol obtained was used as such without further purification.

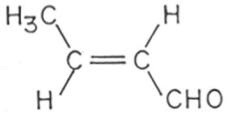
CROTONALDEHYDE : Emperical Formula - C_4H_6O

Molecular Weight - 70.09

Structural Formula



(cis isomer)



(trans isomer)

The crotonaldehyde (2-Butenal) used was a crude by product of Sugar Industry obtained from Deccan Sugar Institute, Pune (India). Gas chromatographic analysis of the crotonaldehyde indicated the following composition:

Crotonaldehyde	$\simeq$	80.0%
Water	$\simeq$	15.0%
Low Boiling Fractions (two)	$\simeq$	2.5%
High Boiling Fractions (two)	$\simeq$	2.5%

The following parameters were used for gas chromatographic analysis : SE-30 column

Thermal conductivity Detector (TCD)

Oven Temperature - 140°C

Injection Temperature - 180°C

Flow rate of carrier gas, hydrogen - 50 ml/min. The crude crotonaldehyde was dried repeatedly over anhydrous calcium chloride till it was free from water, and then used for synthesis of PC resins (Set I, hereafter called as PCC Resins).

The pure crotonaldehyde was obtained by fractional distillation of dried, crude crotonaldehyde and was used for the synthesis of PC resins (Set II, hereafter called as PCD Resins). The four fractions, boiling in the temperature ranges 65°-95°C, 95°-101.5°, 101.5°-102°C and 102.5°C above were separated. The colourless fraction, boiling in the temperature range of 101.5°-102°C (90%) was redistilled. The middle fraction boiling at 101.5°C was analysed by gas chromatography, using the same parameters as in crude crotonaldehyde. It was found to be $> 99.5\%$ pure and used as purified crotonaldehyde for synthesis of PCD resins.

SULFURIC ACID : Emperical Formula - H_2SO_4

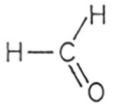
Molecular Weight - 98.08

Sulfuric acid was used as the catalyst for the phenol - crotonaldehyde condensation reaction. Analytical reagent grade sulfuric acid was obtained from Ranbaxy Labs. Pvt. Ltd. (India) and was used as received.

FORMALDEHYDE : Emperical Formula - CH_2O

Molecular Weight - 30.03

Structural Formula -



Formalin containing 37-40% formaldehyde was used for the preparation of PF novolak resins. The formalin solution obtained from Hindustan Organic Chemicals Ltd. (India) was filtered, analysed for the free formaldehyde content and used.

CALCIUM CHLORIDE : Emperical Formula - $CaCl_2$

Molecular Weight - 110.79

Commercial grade anhydrous calcium chloride was used for drying crude crotonaldehyde.

3.2 EXPERIMENTAL PROCEDURE/POLYMERIZATION SET-UP

3.2.1 Phenol - Crotonaldehyde Polycondensation

The polycondensation reactor assembly is schematically shown in Figure 1. It consisted of a four-necked round bottom flask (1 litre capacity) fitted with mechanical stirrer, reflux condenser and thermowell. The heating mantle used to heat the reactants was connected through a variac to a temperture controller. A Nickel-chromium thermocouple connected to the temperature controller was inserted into the thermowell to monitor and control the reaction temperature.

Phenol was melted in a warm water-bath (kept at 40°C) and one mole (94.11 gms) was transferred to the round bottom flask quantitatively. The temperature was set at 60°C. Concentrated sulfuric acid (0.9411 gms; 1 weight % of phenol) was weighed accurately, dissolved in 10 ml. of distilled water and added to phenol. The temperature was raised to 65°C. The desired weight of crotonaldehyde was then added gradually to the reaction flask over a period of 30 minutes. There was no exotherm observed as indicated by no change in temperature of the reaction mixture during this addition. The colour of the reactants, however, changed from colourless to brownish black during the addition. The reaction temperature was set at 84°C, which corresponds to the reflux temperature of crotonaldehyde-water azeotrope. The polycondensation was carried out for 4 $\frac{1}{2}$ hours. The reaction mixture remained homogeneous throughout this reaction time.

After 4 $\frac{1}{2}$ hours of reaction, the reflux condenser was replaced with a water cooled distillation condenser.

Unreacted monomers, phenol and crotonaldehyde and water from sulfuric acid and water of condensation were distilled out under reduced pressure. Two separate layers were noted in the distillates. The water cooled distillation condenser was replaced with an air cooled distillation condenser and the final traces of unreacted phenol were distilled out under reduced pressure. The volumes of the different distillate fractions were recorded exactly. The composition of the distillate fractions were analysed by gas chromatography using a SE-30 column, and thermal conductivity detector. The injection and column temperature were set at 180°C and 140°C respectively. The flow rate of hydrogen, carrier gas, was maintained at 50 ml/min. From the volume of the unreacted phenol and crotonaldehyde the composition of the PC resins was estimated.

The molten resin mass was poured into clean enamel trays and air cooled to room temperature. The nature of the resin, whether solid or liquid, was noted. Solid resins were crushed to a fine powder and stored in stoppered bottles in a cool, closed, dry place.

A series of resins were prepared by varying the mole ratio of phenol to crotonaldehyde between 1:0.4 to 1:1.4. Two sets of PC resins were prepared using a anhydrous crude crotonaldehyde (PCC resins) and distilled pure crotonaldehyde (PCD resins). The quantitative details of resin synthesis is shown in Table 1.

3.2.2 Phenol-formaldehyde Polycondensation

A series of PF novolak resins were synthesised under identical reaction conditions using the experimental set up shown in Figure 1. Formalin solution was analysed for the formaldehyde content and appropriate volume was added gradually. An exotherm was noted during the addition to phenol and sulfuric acid mixture. Instant change in the colouration from colourless to pinkish was also noted during the addition. During the reaction, phase separation of resin from the aqueous phase was clearly seen. The reaction was run at 84°C. The course of the reaction was monitored by analysing the unreacted formaldehyde content in the reaction mixture at any

specific time. The reaction was discontinued when the concentration of formaldehyde was found to be less than 0.5%. The aqueous layer was decanted off and the unreacted phenol was distilled off using air cooled distillation condenser at reduced pressure and analysed to estimate the phenol to formaldehyde composition in the resin formed.

3.2.3 Formaldehyde Analysis[132]

A sample of resin, about 0.1-0.5 gms was taken out and weighed accurately. To this, 10 ml of freshly prepared hydroxylaminehydrochloride solution in water (10% by weight) was added and stirred. In the reaction equivalent amount of hydrochloric acid is set free as indicated below :

$$CH_2 = O + [NH_2\text{-}OH].\ HCl \longrightarrow H_2C = N\text{-}OH + H_2O + HCl$$

The mixture was then titrated against sodium hydroxide solution of known concentration. The free formaldehyde content was computed using the following formula :

$$\text{Free formaldehyde content \%} = \frac{(B-S) \times N_{NaOH} \times 3.002}{W}$$

where, B = Burette reading for blank titration

S = Burette reading for sample titration

N_{NaOH} = Normality of sodium hydroxide solution

W = Weight of resin taken

3.2.4 Soxhlet Extraction

All the powdered resins prepared were further purified by soxhlet extraction technique using distilled water to remove the final traces of phenol, crotonaldehyde and formaldehyde. The finely powdered resin (about 50 gms) was placed in a circular box made up of porous paper and clipped from both the ends. It was placed in the soxhlet extraction tube (see Figure 2) mounted on a round bottom flask containing distilled water. Traces of the unreacted monomers, namely, phenol and crotonaldehyde were extracted with warm water for 24 hours. The resin pocket was then removed, dried, finely powdered and used for characterization.

3.3 CHARACTERIZATION OF PC RESINS

3.3.1 Appearance

The resins synthesised were solid, dark brown in colour and brittle. These were easily ground to fine powder passing through 300-400 mesh.

3.3.2 Solubility

Finely powdered resins were checked for their solubility in common organic solvents such as acetone (δ value = 10.0), (Cal. $cm^{-3})^{1/2}$, methanol (δ value = 14.5), ethanol (δ value = 12.7), toluene (δ value = 8.9), benzene (δ value = 9.2), ethyl acetate (δ value = 9.1) and petroleum ether. The resins were readily soluble in polar solvents such as acetone, methanol, ethanol, ethyl-acetate, etc. They were partially soluble in non-polar or less polar solvents such as toluene, benzene, petroleum ether and insoluble in water.

3.3.3 Softening Temperature Range

The PC and PF resins are amorphous solids with no clear melting point. The temperature range over which the opaque resin changed into a mobile phase was noted as the softening temperature range. Finely powdered resin was tightly filled in a glass capillary fused at one end (Figure 3 a) and placed in an electrically heated melting point apparatus. The softening temperature was determined from the digital indicator as well as a mercury thermometer. The temperature at which the resin starts to melt along the capillary wall was noted as the lower end (Figure 3 b) and the temperature at which the resin attains complete mobility was noted as the upper temperature (Figure 3 c).

3.3.4 Flow Length Measurement

The curing behaviour of the resins was studied by evaluating 'the Norton flow length'[133], a conventional quality control parameter used for phenolic resins in the industry.

The finely powdered resin (0.5 gms) was mixed with required quantity of hexamethylenetetramine (hexa), a curing agent for phenolic resins (0.02 gm, 4 weight % of the resin and 0.04 gm, 8 weight % of the resin). The mixture was reground to intimately mix the resin and hexa. Exactly 0.5 gm of this mixture was pelletized with a 1.2 cm diameter Perkin-Elmer cylindrical die at 3.5 tons force. The flow length apparatus is shown in Figure 4. It consists of a detachable horizontal glass plate, 15 cm x 15 cm x 2 mm in dimension. The plate can be tilted to 60° angle by mechanical arrangement.

The flow length apparatus was thoroughly cleaned and placed in an air circulating oven set at 120°C with the glass plate in horizontal position for 10 minutes. The pellets were placed on the glass plate and allowed to rest in the horizontal position for 5 minutes at 120°C, for melting the resin. The glass plate was then tilted quickly to 60° angle (as shown in figure) and kept for 10 minutes (the change over was carried out in less than 5 seconds). The apparatus was then taken out of the oven and allowed to cool to room temperature.

As the resin starts to flow in the inclined position, curing of the resin by cross-linking reaction retards this flow. The length of the flow is thus inversely related to the rate of curing. The total length of flow, in millimeters, from tip to tip of the deformed pellet was measured and recorded as the flow length. The experiment was repeated at different temperatures.

3.3.5 Infra-red Spectroscopy

The infra-red spectrum of the resins were recorded in the frequency range from 4000 cm^{-1} to 600 cm^{-1} either in nujol or in potassium bromide using a Pye Unican (model SP-300) infra-red spectrometer.

3.3.6 Vapour Pressure Osmometry

The number average molecular weights ($\overline{M}n$) of the resins were determined by vapour pressure osmometry (VPO). VPO is an efficient method to determine the Mn below 30,000. In VPO, droplets of a polymer solution and pure solvent are placed on two thermistors suspended

in the thermostated chamber of the vapour pressure osmometer, saturated with the solvent vapour. Since the vapour pressure of the solvent in the solution is less than that of pure solvent, condensation takes place on the solution droplet. It thus becomes both diluted and heated by latent heat of vaporization of the solvent. The temperature of the solution droplet increases, until the vapour pressure of the solvent in it, at the new higher temperature, reaches that of the pure solvent at the original temperature. The difference in the temperature of the two droplets is sensed by the thermistors and is indicated as the difference in the resistance of the two thermistors. Since lowering of vapour pressure is a colligative property, its value depends on the number of molecules of solute in the solution. The variation of the colligative property of the polymer solution with concentration can be represented as follows:

$$\frac{\Delta R}{K.C} = \frac{1}{\overline{Mn}} \left[1 + \mathfrak{Z}_2 C + g\mathfrak{Z}_2^2 C^2\right] \qquad (1)$$

where ΔR = the difference in the resistance of the two thermistors caused by thermal difference. It is directly read from the instrument;

K = calibration constant. It varies with the nature of the solvent and chamber temperature;

$\mathcal{J}_2$ = second virial coefficient;

g = polymer solvent interaction function;

C = concentration.

The last term in the above equation is insignificant at low concentrations and can be neglected. Therefore,

$$\frac{\Delta R}{C} = \frac{K}{\overline{Mn}} + \frac{K\mathcal{J}_2}{\overline{Mn}} C \qquad (2)$$

Thus, a plot of $\Delta R/C$ versus C should be linear and Mn can be computed from the slope knowing K and $\mathcal{J}_2$.

The molecular weights of the resins were determined by using five dilute solutions ranging in the concentration from 2 to 6 gm/lit. The Knaur vapour pressure osmometer was used. The following values of the instrumental parameters were used :

Thermostate reading	:	260
Temperature of the chamber	:	50°C
Time for one reading	:	4 minutes
Sensitivity	:	16
Zero balance	:	10
Bridge voltage	:	100%

Benzil was used as the standard and ethyl acetate (spectroscopic grade, > 99.99% pure) was used as solvent. Since lowering of vapour pressure is a colligative property, any low molecular weight impurity in the solvent would give misleading results. Therefore the solvent to be used must be highly pure, spectroscopic grade.

3.3.7 Thin Layer Chromatography (TLC)

TLC analysis of phenol, both crude and distilled crotonaldehyde and the resins were carried out. Silica gel was used as the stationary phase. Various solvent systems widely varying in their polarities were used to differentiate the different molecular species present in the resins. Glass plates of dimensions 15 cm x 4 cm x 2 mm were thoroughly cleaned, dipped in a slurry of silica

gel (98% by weight) and clay (2% by weight) in petroleum ether and air dried. An alcoholic solution of the resin was spotted on the plate with a fine glass capillary and allowed to dry. The dried plate was placed in a solvent chamber consisting of 70% (volume/volume) petroleum ether and 30% (volume/volume) ethyl acetate solvent mixture. The solvent front was allowed to rise to 80% of the height of the plate (roughly 10 cm). The plate was taken out and dried in air at room temperature. The dried plate was then kept in iodine chamber to spot the chromatograms.

3.3.8 Column Chromatography

The different chemical constituents with varying polarities in the resins were separated by column chromatography. A glass column 50 cm in length and 1 cm in diameter was used. The loading ratio of stationary phase (silica gel) to resin was 30:1. The column was neatly packed. Precautions were taken to keep the column wet throughout the experiment. Different solvent systems were used to fractionate the different species present

in the resins. The solvents used in order of increasing polarity and volumetric compositions were :

Petroleum ether (60-80 fraction)	- 100%;
Petroleum ether/Benzene	- 75/25%, 50/50% and 25/75%;
Benzene/ethyl acetate	- 100/0%; 90/10%, 80/20%, 70/30%, 60/40% and 20/80% ; and
Ethylacetate/ethanol	- 100/0%, 90/10%, 80/20%, 50/50%, 20/80% and 0/100%.

The eluents were checked by TLC for the presence of resin fractions. Fractions displaying same Rf value based on TLC were pooled together, the solvents were distilled off to collect the separated resin fractions. The resin fractions were further analysed by infra-red spectroscopy.

3.3.9 Microanalysis

Conventional elemental analysis was used to determine the carbon, hydrogen, oxygen and sulfur content in the resins.

TABLE 1

QUANTITY INPUT IN RESIN SYNTHESIS

Resin Code	Phenol		Crotonaldehyde	
	Moles	Grams	Moles	Grams
PCC 1 and PCD 7	1	94	0.4	28
PCC 2 and PCD 8	1	94	0.6	42
PCC 3 and PCD 9	1	94	0.8	56
PCC 4 and PCD 10	1	94	1	70
PCC 5 and PCD 11	1	94	1.2	84
PCC 6 and PCD 12	1	94	1.4	98

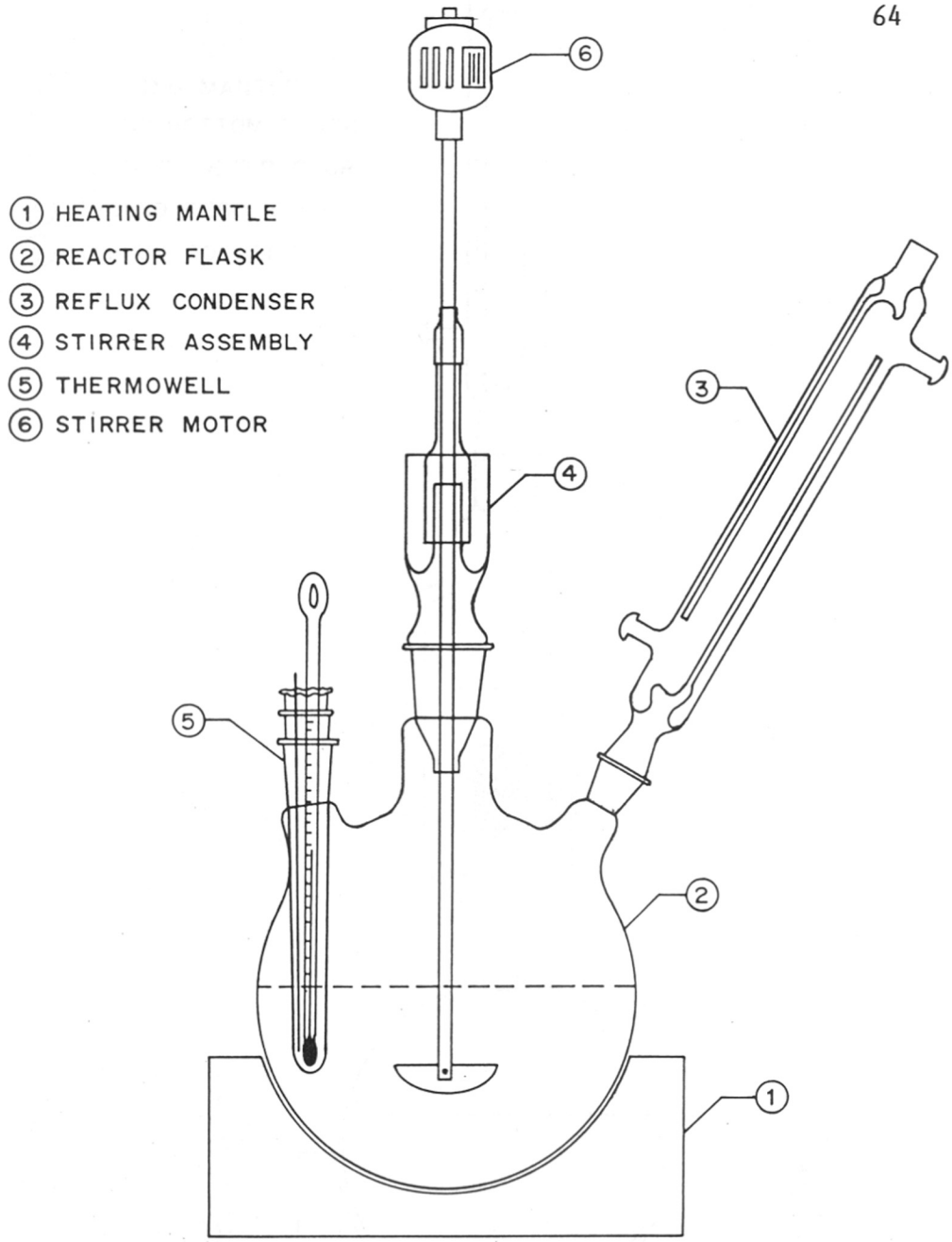


FIGURE 1: LABORATORY REACTOR ASSEMBLY FOR RESIN SYNTHESIS

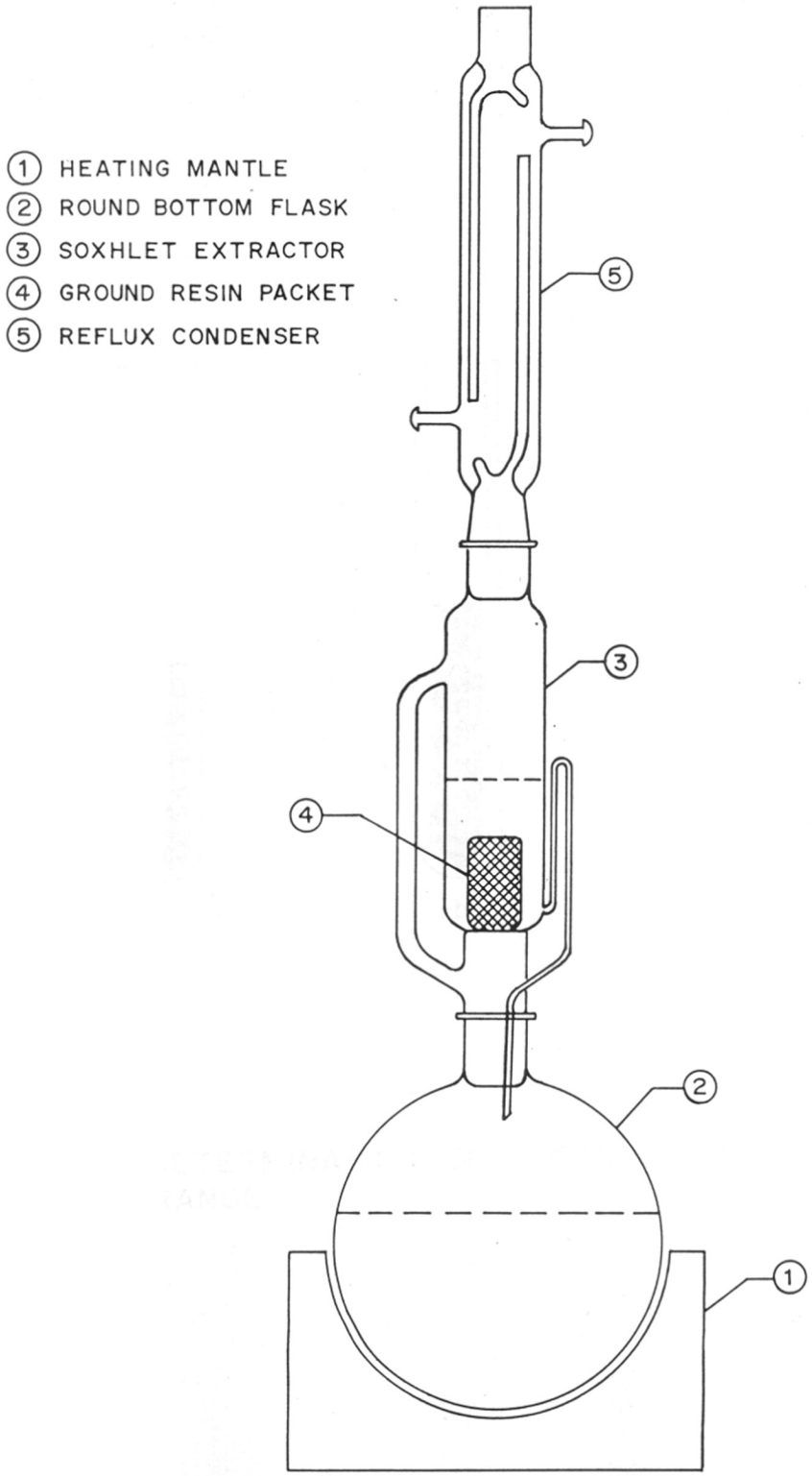


FIGURE 2: SOXHLET EXTRACTION ASSEMBLY

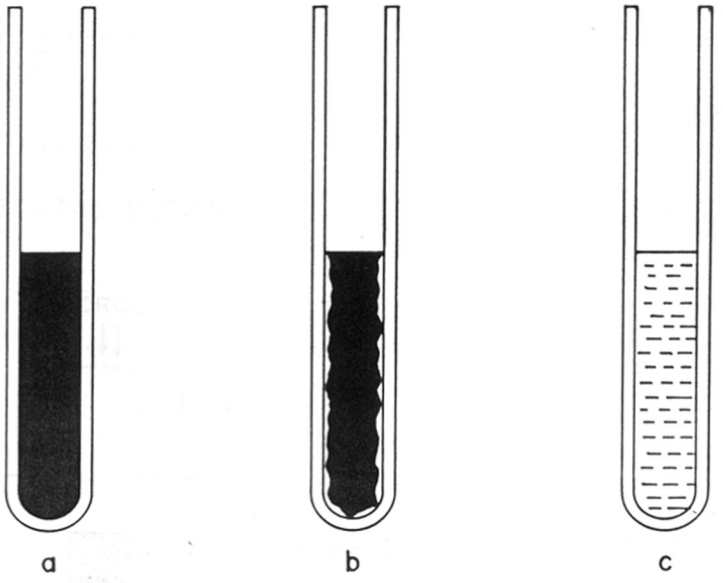
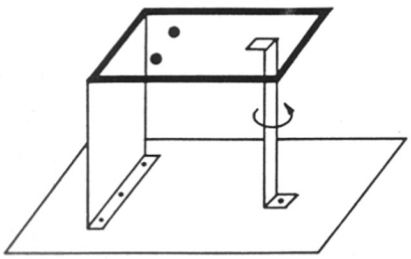
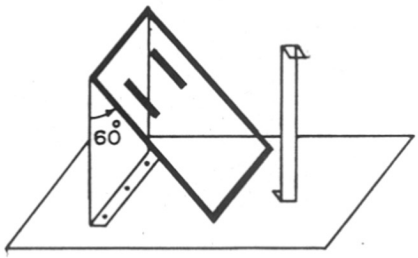


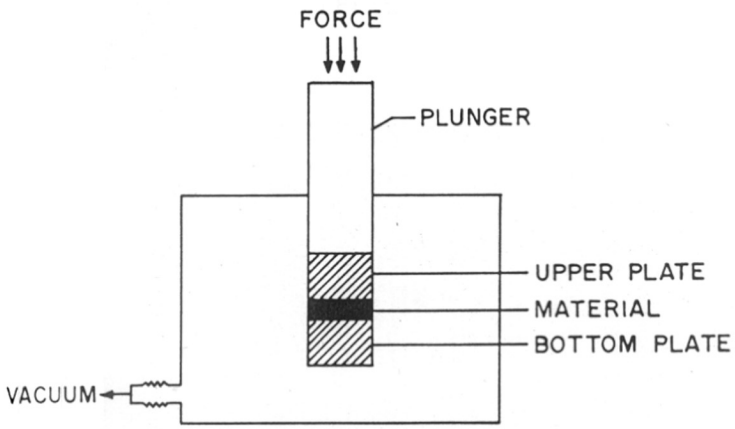
FIGURE 3: DETERMINATION OF SOFTENING TEMPERATURE RANGE



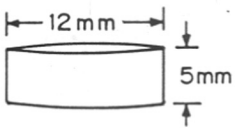
HORIZONTAL POSITION



TILTED POSITION



DYE



PELLET

FIGURE 4 : FLOW LENGTH APPARATUS

CHAPTER 4

EFFECT OF MOLE RATIO AND PURITY ON RESIN CHARACTERISTICS

CHAPTER 4

EFFECT OF MOLE RATIO AND PURITY ON RESIN CHARACTERISTICS

The two sets of solid, fusible, thermoplastic resins were prepared from polycondensation of phenol with dry, crude crotonaldehyde (PCC Resins), and with dry, distilled crotonaldehyde (PCD Resins). In both the sets six different resins were synthesised varying phenol to crotonaldehyde mole ratio from 1:0.4 to 1:1.4. The resins synthesised were characterised and the properties were compared with conventional PF novolak resins.

All the PC resins were brittle, thermoplastic solids, soluble in organic solvents such as acetone, ethanol, methanol, ethyl acetate, etc. irrespective of the mole ratio of phenol to crotonaldehyde and purity of the croton-aldehyde.

The amount of unreacted phenol and crotonaldehyde at the end of the reaction time was a small fraction

of that used initially and computed qualitatively by gas chromatography using following parameters :

SE 30 column
Thermal Conductivity Detector (TCD)
Oven Temperature - 110°C
Injection Temperature - 155°C
Detector Temperature - 160°C
Flow rate of carrier gas, hydrogen - 0.5 kg/cm^2

In the resins synthesised in both the sets, some quantity of unreacted crotonaldehyde and phenol distilled out irrespective of the purity of the crotonaldehyde and the mole ratio (see Table 2). Thus reaction occurs between phenol and crotonaldehyde. The phenol to crotonaldehyde mole ratios and mole fractions were calculated on the basis of the weights of the unreacted monomers which were computed quantitatively by gas chromatography. These are presented in Table 3.

In both sets, the mole fraction of crotonaldehyde in the resin increased linearly, but not proportionally,

with its mole fraction in the feed (Figure 5), indicating that the incorporation of crotonaldehyde in the condensation product is governed not only by kinetic effects of the feed composition but also by reactivity. At lower feed mole fractions, crotonaldehyde adds to phenol to a marginally greater extent. At higher mole fractions, crotonaldehyde encounters a greater concentration of less reactive, more sterically hindered substituted phenols. This, perhaps, accounts for the decreased incorporation of crotonaldehyde at higher feed mole fractions.

Referring to Figure 5 it is clearly noted that, at any feed compositions, a greater fraction of croton-aldehyde was incorporated when distilled crotonaldehyde was used. The apparent decreased reactivity of crude crotonaldehyde is probably due to the impurities present in the crotonaldehyde. These were found to be about 5% by gas chromatography comprising of traces of ethanol, acetaldehyde, acetic acid, acetaldol, dimer and trimer of crotonaldehyde. It is known that acetaldehyde reacts more rapidly with phenol, thereby leaving fewer sites for crotonaldehyde in the course of the reaction[43,44,134].

It is also well understood that in these types of reactions, when the substiution takes place on phenyl ring, it deactivates the ring to 1/3rd of the original reactivity[135].

In comparison, under highly acidic conditions, the phenol-formaldehyde polycondensation reaction results in thermoplastic solid resins termed novolaks. The polycondensation rates are much higher[135]. However, the thermoplasticity of the resins is retained only over a narrow range of formaldehyde mole ratio, 0.45 to 0.72. Below 0.45 moles of formaldehyde the resins are viscous liquids and above 0.72 the resins are solids, infusible[136]. PC resins, on the other hand, retain their thermoplasticity over a much wider range of the crotonaldehyde mole fraction, irrespective of the purity of the crotonaldehyde. This could be well explained by taking into consideration the molecular size of the reacting species. As compared to formaldehyde, having only one carbon atom, crotonaldehyde with four carbon atoms, is larger in size which could result in the steric hindrance in the substitution reaction. As discussed earlier at lower feed mole ratios, crotonaldehyde mole fraction in the polymer is more than

that in case of higher feed mole fractions. This again explains that once the monosubstitution has taken place on the phenyl ring, due to bulkier groups in the side chain, having four carbon atoms, it sterically hinders the further substitution. Phenol and crotonaldehyde both are known to be trifunctional in these polycondensation reactions[125,137]. Interestingly, the resin formed with a crotonaldehyde mole fraction of 0.48 was still thermoplastic solid. The trifunctionality of phenol and crotonaldehyde is perhaps only partially utilized due to the steric factors associated with such a reaction.

The resins were soxhlet extracted for 24 hours with distilled water to remove the final traces of phenol and crotonaldehyde. The dried resins were used for characterization.

Elemental analysis of the resins indicated presence of sulfur in the resin corresponding almost quantitatively to that of sulfuric acid added as the catalyst (see Table 4). Thus sulfuric acid gets incorporated in the structure besides catalysing the polycondensation reaction. The

incorporation of sulfur in the polymer structure may either be sulfonic acid or as sulfate by addition across the crotonaldehyde double bond. There is no marked difference in the amount of carbon, hydrogen, oxygen present in the resins synthesised both from crude as well as distilled crotonaldehyde and the feed mole ratio of phenol and crotonaldehyde.

The TLC of the PCC and PCD resins are very similar (see Figure 6). TLC of phenol showed one major constituent (Rf value 5.5) and a slight impurity (Rf value 5.8). In case of crude crotonaldehyde two major constituents (Rf values 3.9 and 4.9) along with the impurities (Rf values 0.9, 2.2 and 6.6) were noted while for distilled crotonaldehyde only one prominent spot (Rf value 3.9) alongwith very low amount of impurity (Rf value 4.9) was seen. The resins showed extensive tailing with dark spots at Rf values 1.0, 3.0 and 3.7. A slight tailing was observed uptil a faint spot at Rf value 5.3. The extensive tailing observed indicate the presence of structurally similar species differing in the molecular weight and polarity. The tailing is very prominant at

the bottom part of the TLC plate indicating that the reaction has taken place between phenol and crotonaldehyde and that species with varying polarities but similar in structure are present.

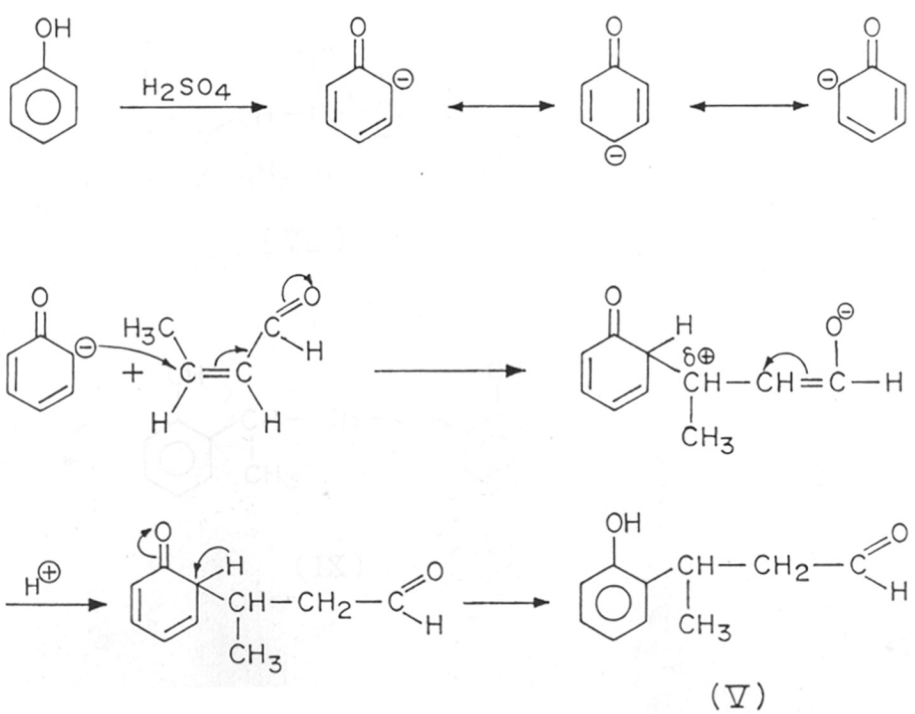
The representative resins from both the sets were fractionated by column chromatography into chemical moieties that showed single spots on TLC. The infrared absorption bands of these fractions were broad and almost identical. The various resin fractions are structurally complex and similar, invarient to the phenol to crotonaldehyde mole ratio and purity of the crotonaldehhyde.

The number-average molecualr weights of the resins (see Table 5) indicate that the resins are essentially oligomers, consistent with other reports on acid-catalysed phenol-aldehyde reactions[138]. For any given phenol to crotonaldehyde ratio, the resins synthesised with distilled crotonaldehyde exhibit a higher molecular weight than those prepared with crude crotonaldehyde. Phenol is perhaps involved in non-polymeric side reactions with impurities present in crude crotonaldehyde, such

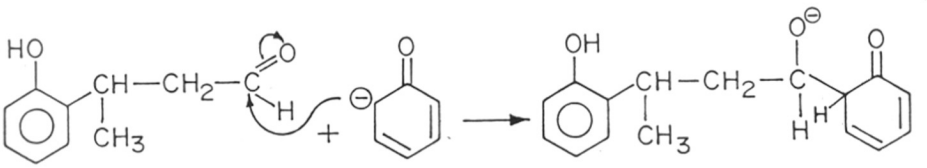
as dimer and trimer. Also, crotonaldehyde can form acetal with the alcoholic impurities under the reaction conditions[139]. Such low molecular weight side products would decrease the molecular weight of the resins.

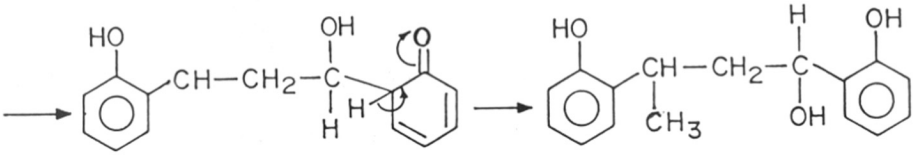
The prominent infra-red frequencies of phenol, crotonaldehyde (crude and distilled) and represented PCC and PCD resins are presented in Table 6. Crotonaldehyde absorbs at frequencies corresponding to the trans C=C double bond (1640, 1310 and 970 cm^{-1}) and C=O (1680 cm^{-1}) (see Figure 7). The infra-red spectrum of phenol is represented in Figure 8. The prominent absorption frequencies are at 3400-3300 cm^{-1} for -OH stretching; at 1600, 1500 and 1480 cm^{-1} for aromatic C-C in plane skeleton vibrations and at 760 and 690 cm^{-1} for aromatic monosubstitution vibrations. The representative PCC resins and PCD resins do not absorb at these frequencies (see Figure 9 and 10). All the PC resins exhibit almost identical infra-red spectra irrespective of the mole ratio and purity of the crotonaldehyde. Therefore, crotonaldehyde reacts in the polycondensation reaction probably by the addition across C=C double bond and

condensation across the aldehydic C=O group. This very fact is supported by the literature also. The occurance of such reactions in acid-catalysed polycondensation of alkyl-phenols with crotonaldehyde has recently been studied and demonstrated by ^{13}C NMR studies[125,137]. The various structures proposed for the reaction products are shown in Figure 11. Interestingly, the molecular weights of the proposed structures, in particular structure III and IV fall in the range observed in the present study. However, the exact sequence of events in this reaction leading to such structures is still not clear. We can hypothesize concerning the probable reaction mechanism and the structural development as follows:



(V)





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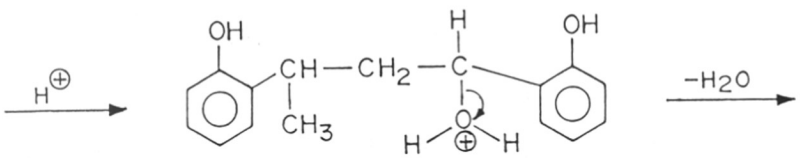

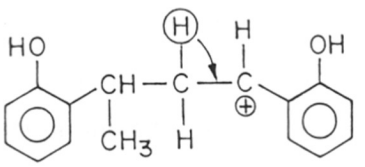

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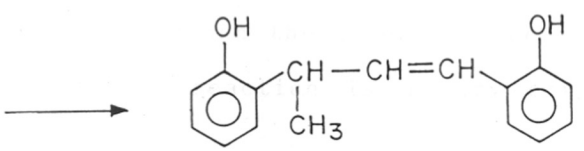


(Ⅸ)

Thus, the reaction proceeds like conventional phenol-formaldehyde condensation reaction as per the above hypothesis. The above hypothesis is based on Micheal addition reaction. However, the infra-red spectra indicate little concentration of C=C double bond is present in the resins synthesised. Also the infra-red spectra indicate absorption at 1250 cm^{-1} corresponding to =C-O-C, aryl-alkyl ether vibrations and at 830, 750 and 695 cm^{-1} corresponding to aromatic ring substitutions at 0; 0,0'; 0,0',p positions. In the above discussed reaction mechanism no ether linkage is seen. This clearly tells us that the reaction may not proceed through the structure VII and it may be possible that a very little amount of compounds like structures VIII and IX are present in the final product. Also the reported structures of a alkyl-phenol crotonaldehyde condensation products do not show a double bond and has a ether group in between (see Figure 11). It may be possible that the reaction proceeds through addition across the double bond of crotonaldehyde molecule. This means that the reaction mechanism and the structural development of phenol-croton-aldehyde reaction is a very complex in nature and some

more detailed study must be done, which is beyond the scope of present work. The complexity of the reaction mechanism can be explained by the factors like stearic hindrance, functionality of the monomers, bulk of the crotonaldehyde molecule, decrease in the reactivity after the substitution on phenyl ring, etc.

The softening temperature ranges of the resins are presented in Table 7 and are plotted in Figure 12 as function of the crotonaldehyde mole fraction in the polymer. At a given mole ratio of the reactants, the resins prepared from distilled crotonaldehyde manifested a higher softening temperature than those prepared from crude crotonaldehyde, in part due to their higher molecular weights. The oligomeric side-products present in the resins based on crude crotonaldehyde could also lower their softening temperature range by acting as plasticizers. This plasticizing effect may also be due to the formation of resins with inferior thermal properties by the poly-condensation between phenol and dimer and/or trimer of crotonaldehyde.

TABLE 2

DISTILLATION ANALYSIS

Resin code	Feed Mole ratio	Distillate collected, ml		
		Phenol	Crotonaldehyde	Water
PCC 1	1:0.4	12	2	7
PCC 2	1:0.6	20	5	5
PCC 3	1:0.8	4	10	16
PCC 4	1:1	0	15	10
PCC 5	1:1.2	0	18	19
PCC 6	1:1.4	0	27	19
PCD 7	1:0.4	38	5	21
PCD 8	1:0.6	20	5	26
PCD 9	1:0.8	19	4	24
PCD 10	1:1	10	9	20
PCD 11	1:1.2	19	10	30
PCD 12	1:1.4	12	10	30

TABLE 3

RESIN COMPOSITION-FEED AND POLYMER

No.	Crotonaldehyde Mole Fraction				
	PCC Resins		PCD Resins		
	Resin code	Feed	Polymer	Resin code	Feed	Polymer
1	PCC 1	0.27	0.29	PCD 7	0.27	0.32
2	PCC 2	0.36	0.39	PCD 8	0.36	0.38
3	PCC 3	0.43	0.40	PCD 9	0.43	0.47
4	PCC 4	0.48	0.43	PCD 10	0.48	0.48
5	PCC 5	0.53	0.47	PCD 11	0.53	0.55
6	PCC 6	0.57	0.50	PCD 12	0.57	0.58

TABLE 4

MICROANALYSIS DATA

Resin code	Mole fraction of crotonaldehyde in the polymer	Microanalysis data			
		C	H	O	S
PCC 1	0.29	76.07	7.03	16.05	0.50
PCC 2	0.39	77.38	6.98	14.71	0.93
PCC 3	0.40	75.37	7.17	17.21	0.34
PCC 4	0.43	76.38	7.24	15.08	0.50
PCC 5	0.47	72.89	7.17	18.84	1.10
PCC 6	0.50	78.07	7.18	14.21	0.54
PCD 7	0.32	78.79	7.08	13.89	0.55
PCD 8	0.38	77.28	6.95	14.83	0.94
PCD 9	0.47	78.37	6.94	14.21	0.58
PCD 10	0.48	78.64	7.33	13.04	0.99
PCD 11	0.55	77.68	7.54	13.26	1.52
PCD 12	0.58	75.43	7.03	17.06	0.48

TABLE 5

NUMBER AVERAGE MOLECULAR WEIGHT DATA

Resin code	Mole fraction of crotonaldehyde in in the polymer	Number average molecular weight, $\overline{Mn}$
PCC 1	0.29	380
PCC 2	0.39	285
PCC 3	0.40	285
PCC 4	0.43	380
PCC 5	0.47	370
PCC 6	0.50	531
PCD 7	0.32	570
PCD 8	0.38	557
PCD 9	0.47	425
PCD 10	0.48	629
PCD 11	0.55	519
PCD 12	0.58	562

TABLE 6

PROMINENT INFRA-RED FREQUENCIES

Frequency, cm^{-1}					Remarks
Phenol	Crotonaldehyde[a]		Resins[b]		
	Crude	Distilled	PCC 3	PCD 9	
1	2	3	4	5	6
3400-3300	-	-	3400-3300	3400-3300	-OH; stretching frequency
-	2740	2740	-	-	-CH; stretching frequency of aldehyde
-	1680	1680	-	-	-C=O; stretching frequency of α, β - unsaturated aldehydes
1600, 1500, 1480	-	-	1600, 1500, 1460	1600, 1500, 1460	Aromatic C-C in plane skeleton vibrations
-	1640, 1310, 970	1640, 1310, 970	-	-	C=C (trans) double bond vibrations

1	2	3	4	5	6
-	-	-	1250	1250	=C-O-C; aryl-alkyl ether vibrations
760,690	-	-	-	-	Aromatic ring substitution (mono) vibrations
-	-	-	830,750, 695	830,750, 695	Aromatic ring substitution at O, O,O'; O,O', P position on phenyl ring

a : spectrum obtained neat on KBr salt plates

b : spectrum obtained in Nujol

TABLE 7

THERMAL BEHAVIOUR OF THE RESINS

Resin code	Mole fraction of crotonaldehyde in the polymer	Softening temperature range, °C
PCC 1	0.29	69±2
PCC 2	0.39	92±2
PCC 3	0.40	82±2
PCC 4	0.43	86±2
PCC 5	0.47	90±2
PCC 6	0.50	132±2
PCD 7	0.32	96±2
PCD 8	0.38	97±2
PCD 9	0.47	102±2
PCD 10	0.48	110±2
PCD 11	0.55	102±2
PCD 12	0.58	107±2

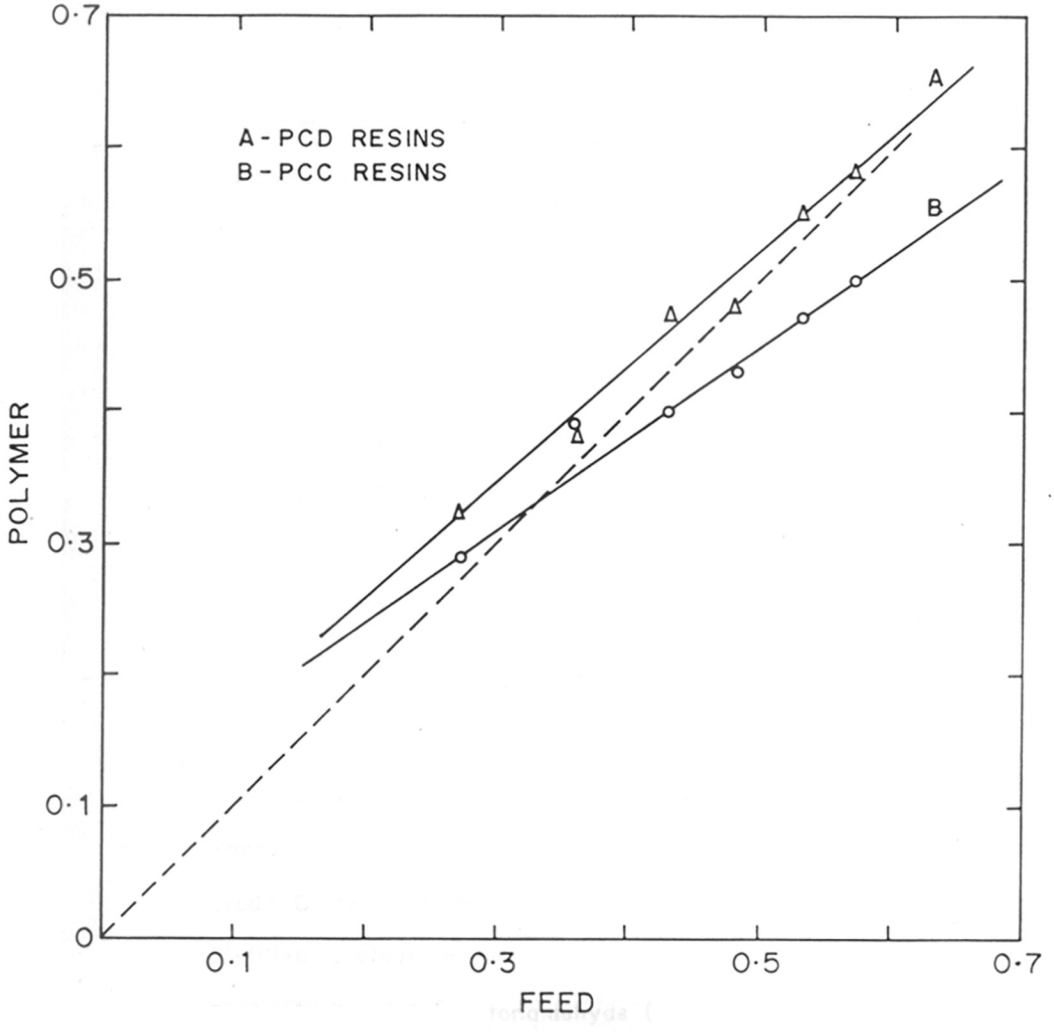
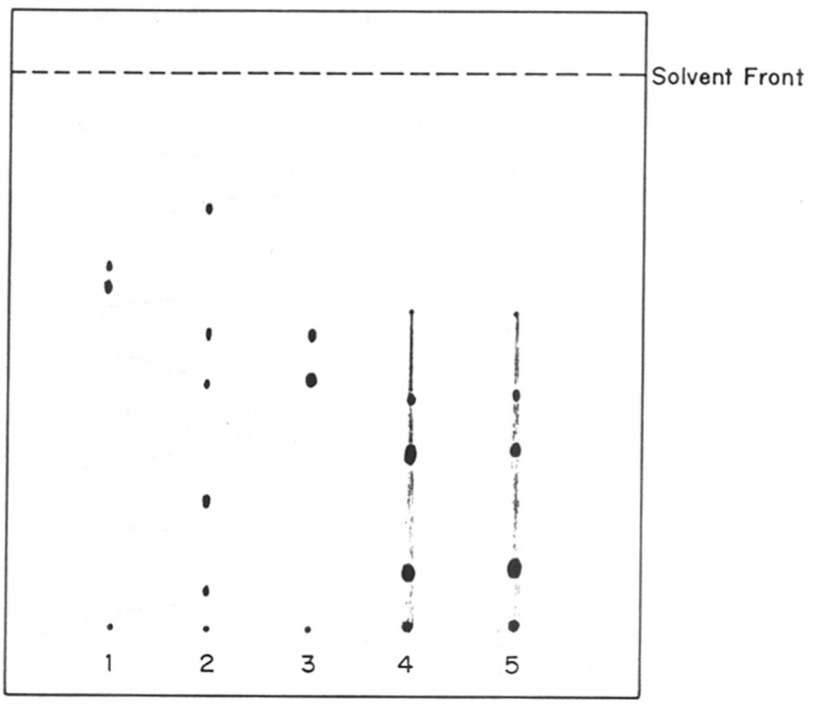


FIGURE 5 : MOLE FRACTION OF CROTONALDEHYDE IN THE RESIN AS A FUNCTION OF THAT IN FEED



1 Phenol

2 Crude Crotonaldehyde

3 Distilled Crotonaldehyde

4 Resin from crude crotonaldehyde (PCC 3)

5 Resin from distilled crotonaldehyde (PCD 9)

Solvent system : 70% Pet. Ether + 30% Ethyl acetate (V/V)

FIGURE 6: TLC OF PHENOL, CROTONALDEHYDE AND RESINS

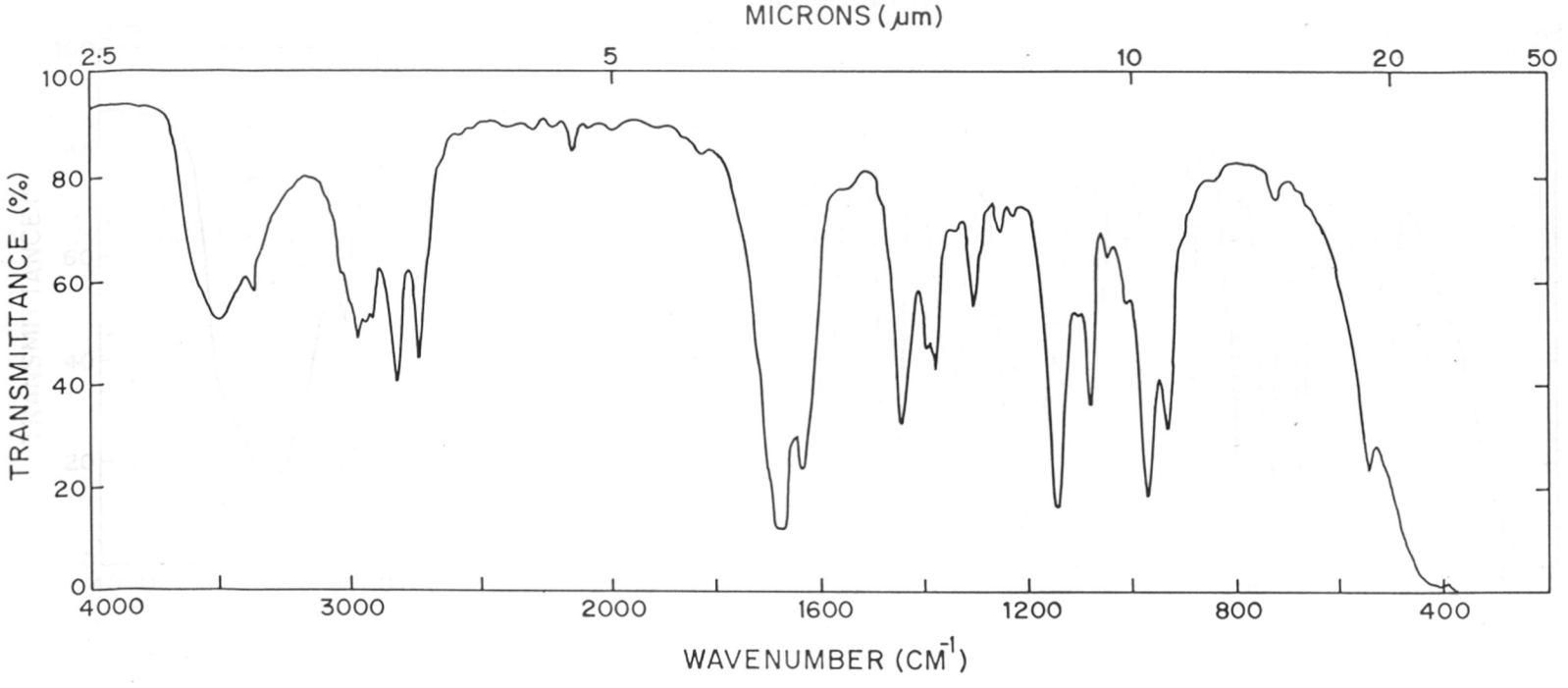


FIGURE 7: INFRA-RED SPECTRUM OF CROTONALDEHYDE

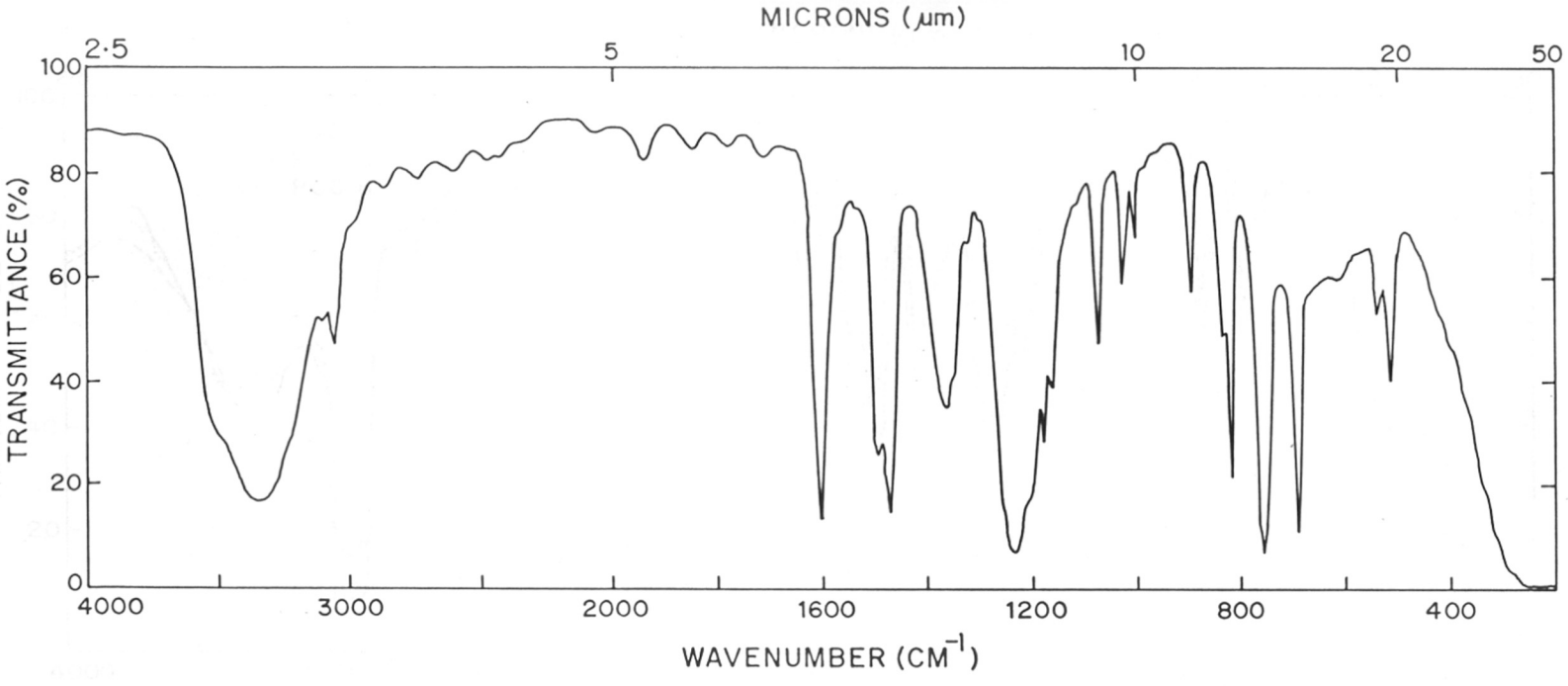


FIGURE 8: INFRA-RED SPECTRUM OF PHENOL

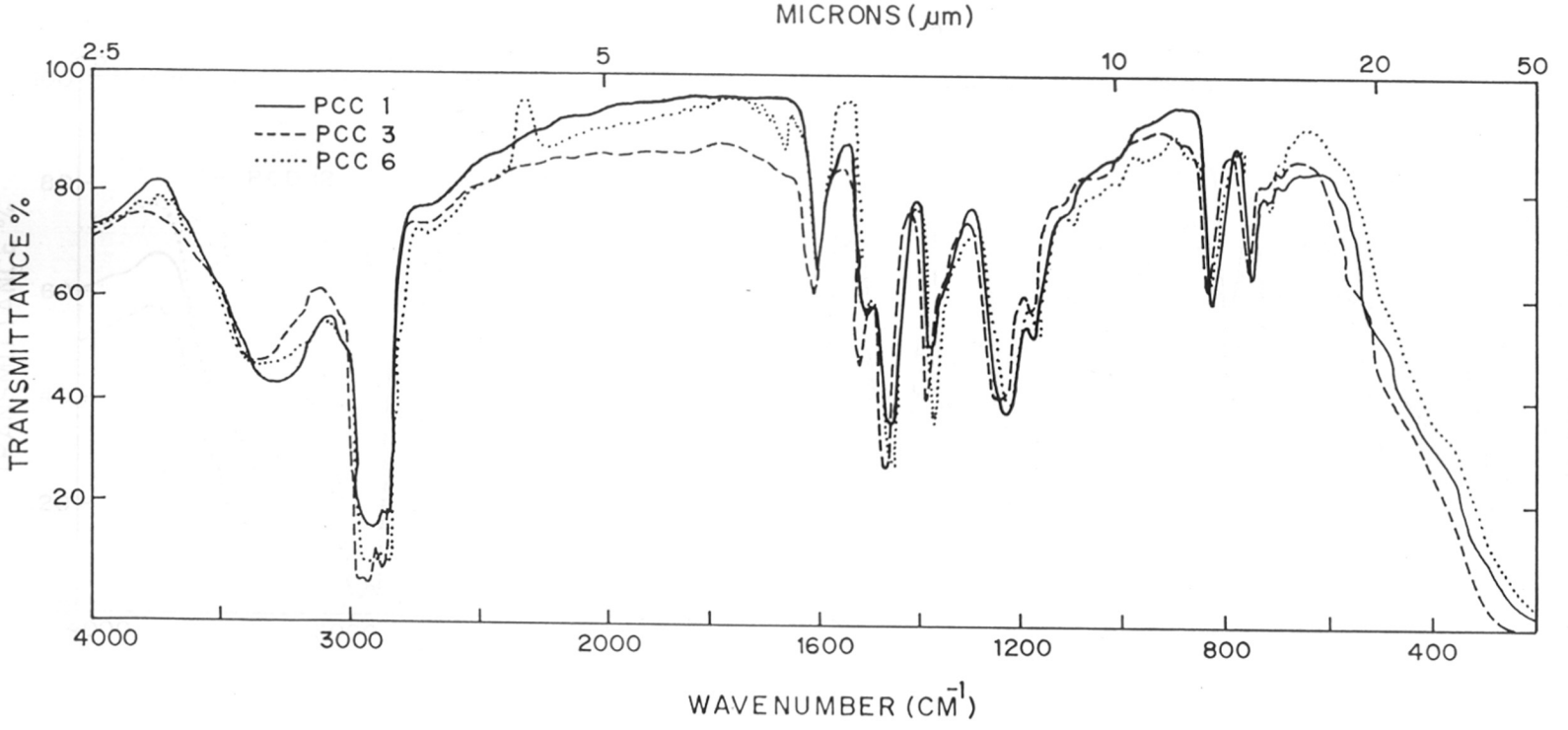


FIGURE 9: INFRA-RED SPECTRA OF PCC RESINS

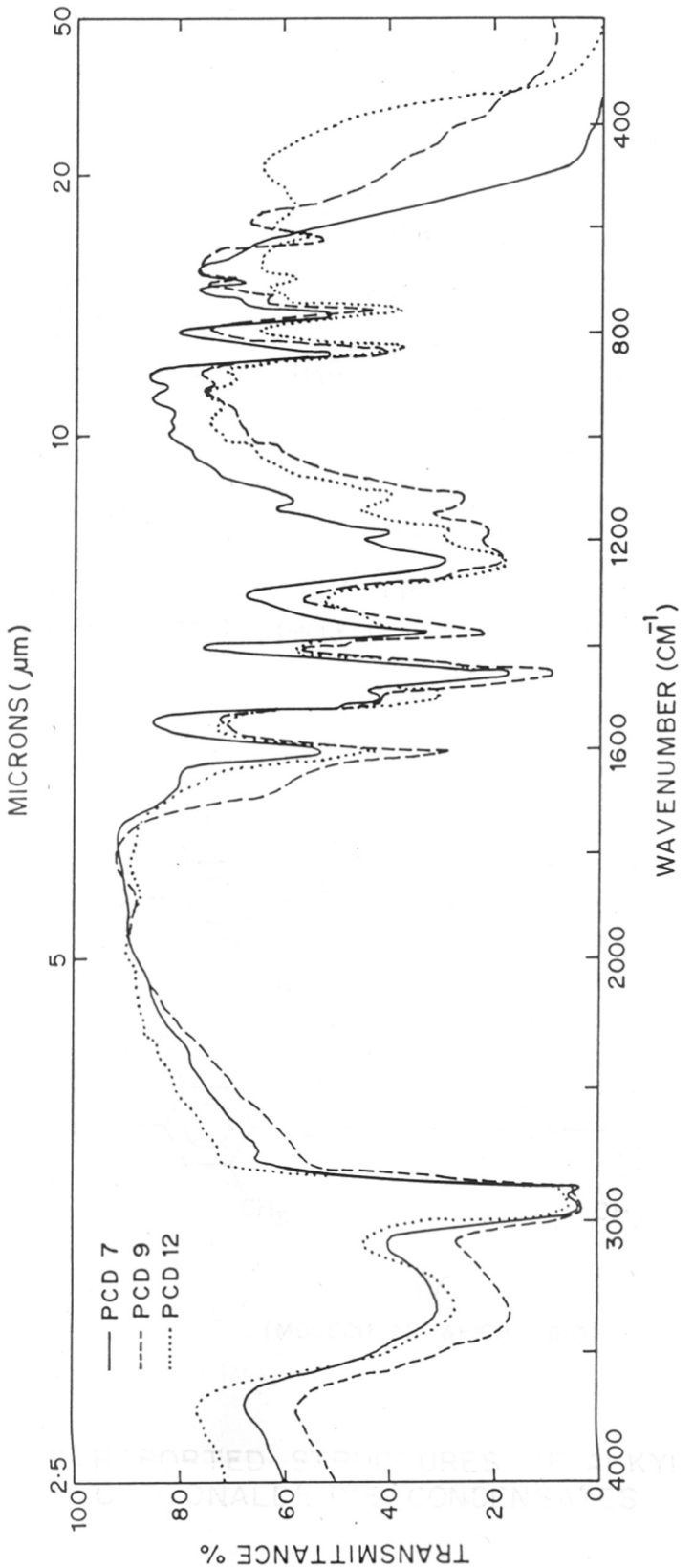
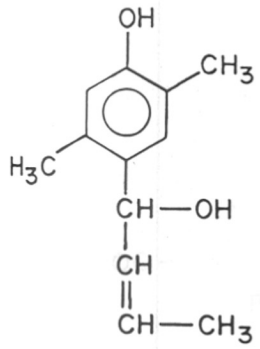


FIGURE 10 : INFRA-RED SPECTRA OF PCD RESINS



(I)

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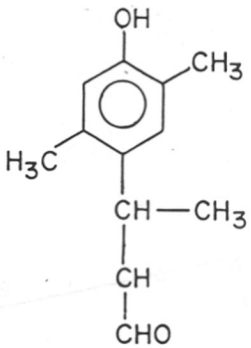

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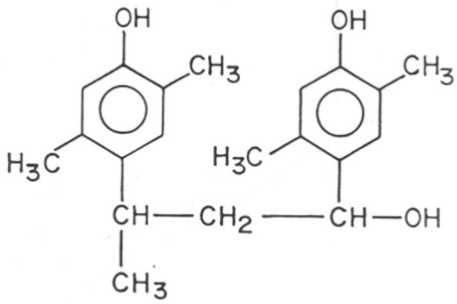

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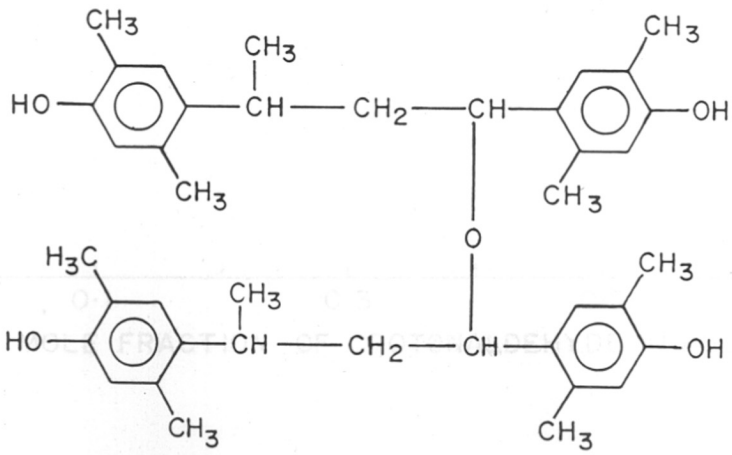

IV

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FIGURE 11 : REPORTED STRUCTURES OF ALKYL PHENOL – CROTONALDEHYE CONDENSATES

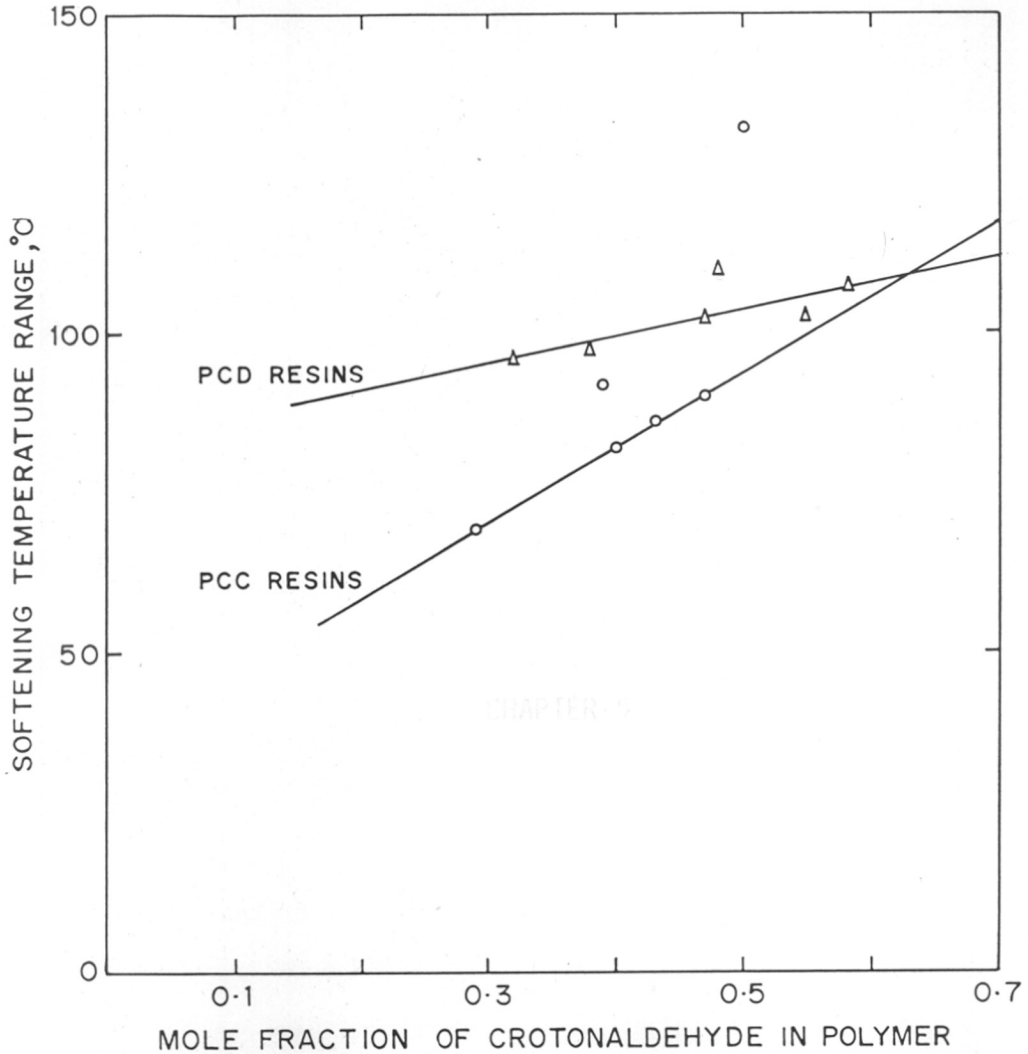


FIGURE 12: EFFECT OF CROTONALDEHYDE MOLE FRACTION ON SOFTENING TEMPERATURE RANGE OF THE RESINS

CHAPTER 5

CURING BEHAVIOUR

CHAPTER 5

CURING BEHAVIOUR

The acid-catalysed condensation of phenol and crotonaldehyde results in solid thermoplastic resins similar to the conventional PF novolak resins. Although the softening temperature range of the PC resins is comparable to that of the PF resins, the curing behaviour of the PC resins has been found to be different. Conventional PF resins, when cured with 8-15 weight % hexa at elevated temperatures, set into infusible, insoluble solids[74].

However, PC resins, on curing with hexa under identical conditions, did not form a thermoset but gave soluble, higher melting thermoplastic products. This peculiar behaviour offers interesting processing possibilities. It may be possible to process the PC resins containing hexa (8-12 weight %) on thermoplastic injection molding equipment into intricate product shapes, followed by postcuring of the molded part in ovens to impart

to them the desirable thermoset characteristics. This was the driving force for the detail study of curing behaviour, which includes the effect of amount of hexa, curing temperature, and postcuring heat treatment on the thermal and solubility characteristics of PC resins in comparision with the PF resins.

Conventional PF novolak resins, which are thermoplastic in nature, are generally cured by the addition of a chemical cross-linking agent. The most widely used cross-linking agent is hexa. Paraformaldehyde and trioxane are also used for curing but these are of limited importance. The novolaks manufactured from phenol and formaldehyde at a phenol to formaldehyde mole ratio of 1:0.8 may be cured by the addition of 8-15 weight % hexa. In general practice the most commonly employed hexa level which yields the best overall performance is 9-10 weight %.

Hexa is prepared from formaldehyde and ammonia according to equation (1).

$$\underset{\text{Formaldehyde}}{6CH_2O} + \underset{\text{Ammonia}}{4NH_3} \longrightarrow \underset{\text{Hexa}}{(CH_2)_6N_3} + \underset{\text{Water}}{6H_2O} \qquad (1)$$

The reaction is reversible. Hexa is split at elevated temperatures, generally above 115°C, depending on the medium[140]. The generated formaldehyde is used for curing novolaks. Also in aqueous solutions hexa can be easily hydrolysed. The small amount of water which is always present in novolak resins (about 0.1-0.5 weight %) leads to hydrolysis of hexa and formation of amino-methylol compounds[141]. Due to the acidic nature of the free phenol in the resins, carbonium ions are generated from these α-amino alcohols, which then interact with phenol to form a secondary and tertiary benzyl-amine containing chain molecules. At decreasing pH the reaction rate increases considerably clearly indicating this as a homogeneous acid catalysis[142]. Thus free phenol and traces of moisture enhance the rate of curing to great extent. Thus the novolak resins, on heating with 8-15 weight % hexa at elevated temperatures, cure into infusible, insoluble thermoset solids[74]. While the

cross-linking reaction the formation of oligomers is accompanied by the liberation of considerable amount of gas, which consists of at least 95% of ammonia[133]. The hardened resin may contain upto 6% chemically bound nitrogen.

Thus by considering the nature of PC resins, they were cured using hexa as cross-linking agent. However, PC resins on heating with hexa under the similar conditions, used for conventional PF novolak resins, did not form a thermoset but yielded a soluble, fusible thermoplastic material with higher softening range[143]. The effect of the following parameters on the thermal and solubility characteristics of PC resins was investigated and compared to PF novolak resins:

* The amount of hexa,
* The curing temperature, and
* The post-curing heat treatment.

The softening temperatures of the resins and the resin-hexa mixtures were determined by the capillary method, as described in Section 3.3.3 of Chapter 3.

The curing behaviour was studied by evaluating the Norton 'flow length' of the resin pellet at different temperatures as described in Section 3.3.4 of Chapter 3.

Three sets of curing experiments were carried out. In the first, the effect of the amount of hexa on solubility and fusion characteristics of the cured PC and PF resins was studied. The curing temperature was set at 120°C for the PF and PCC resins and at 140°C for the PCD resins. The curing time was 15 minutes for all resins.

The objective of the second set of curing experiments was to investigate the effect of curing temperature on the cured resin characteristics at a fixed hexa level. The PC resins were mixed with 8 weight % hexa and cured for 15 minutes. The results of this set would have a bearing on the temperature of injection molding and also on the conditions of postcure heat treatment.

On the basis of the results of the second set, postcuring heat treatment experiments were carried out with the PC resins containing 8 weight % hexa cured at 140° and 160°C. The postcuring treatment was at 160°,180° and 200°C for 15 minutes.

The use of hexa as a cross-linking agent is necessary for curing PC resins. When the PC resins were heated at elevated temperature (120°C for 15 minutes) without the addition of hexa, the resin turned into a free-flowing liquid and did not solidify. Therefore, the flow length could not be measured. There was no change in the softening temperature range of the PC resins when heated without hexa. It is thus concluded that PC resins require the addition of hexa for curing, as do conventional PF resins.

The effect of the amount of hexa on the flow length of the PF and PCC3 resins (at 120°C) is illustrated in Figure 13. Generally, at a fixed amount of hexa, a shorter flow length is indicative of a faster rate of curing. Thus, the PF resin appears to cure faster

than the PCC 3 resin. Also, the curing of the PF resin is more sensitive to the amount of hexa than the PCC 3 resin, as illustrated by the slopes of the lines in Figure 13. The curing behaviour of the PC resins (PCC 3 and PCD 9) is markedly different from that of the PF resins (Table 8). The thermoplastic PF resin turned into infusible, insoluble thermoset on curing at 120°C for 15 minutes even at low loading (4 weight %) of hexa, whereas the cured PC resins remain thermoplastic even at high loadings of hexa. The thermoplastic nature of the cured PC resins was further confirmed by checking their solubility in common solvents. The cured PC resins were found to be soluble in acetone, ethanol, methanol and ethylacetate, whereas the cured PF resins were insoluble.

To study the curing behaviour in details the resins were mixed with 4 and 8 weight % of hexa. It was observed that the softening temperature range of the resin mixture with 4 and 8 weight % hexa was only marginally higher (5-9°C) than that of pure resins (Table 9, Figures 14 and 15). As a general trend the softening

temperature range of the resins and their mixtures with hexa increased with an increase in the crotonaldehyde mole fraction.

The flow length data at 140° and 160°C are presented in Table 10. The resins prepared from distilled crotonaldehyde cure faster than resins prepared from crude crotonaldehyde, indicated by shorter flow lengths. Similarly, resins cure faster at 160°C than at 140°C. As expected, the curing rate increases with increasing temperature and amount of crosslinking agent (Figures 16 and 17). In case of PCC resins the flow length increases with increasing crotonaldehyde mole fraction both at 140°C and 160°C whereas in case of PCD resins it decreases with increase in crotonaldehyde mole fraction at 140° and 160°C. The difference in the curing of PCC and PCD resin must be due to impurities in the crude crotonaldehyde. The purity of crude crotonaldehyde and distilled crotonaldehyde were 80% and 99.5%, respectively. Infrared spectroscopic analysis showed that both are in trans form (very little amount of cis isomer is present)[143]. The only difference between crude and distilled croton-

aldehyde was found to be the presence of 5% impurities, such as ethanol, acetaldehyde, acetic acid, acetaldol, as well as the dimer and trimer of crotonaldehyde[143]. These could take part in the polycondensation reaction and thereby influence the resin properties.

In comparision, there is a difference between the curing rate and behaviour of PF novolak resins than PC resins (Table 11). In case of PF resins, viscous liquid resins are formed below 0.4 moles of formaldehyde in the polymer whereas in case of PC resins, irrespective of amount of crotonaldehyde, solid resins are formed. Commercially, novolak resins are cured by stepwise heating for varied times at different temperatures in the temperature range 60°-180°C to yield a thermoset product which is not the case with PC resins. It is known that PF resins cure at a slower rate compared to urea-formaldehyde (UF) and melamine-formaldehyde (MF) resins. The curing rate of PF resin is enhanced by mixing with either UF or MF resin. However, at high temperature end, phase separation occurs at the final stages of curing cycle.

Secondly, it was observed that the curing rates of PF and PC resins are almost comparable. If PC resin is mixed with PF resin, it was observed that the curing rate is enhanced and no phase separation is seen. For detailed study PF (1:0.75) resin was used and it was mixed with different amounts of PCC 3 resin (Table 12). The mixed resin system behave as thermoset after curing upto a PC loading of 20% by weight. At higher PC loading the cured mixed resins are practically thermoplastic in nature. This may be due to the incomplete cross-linking of PF and PC resins because of the steric hindrance of the bulkier moieties on phenyl ring of PC resin. All the cured resins were found to be infusible.

It is interesting to note that the softening points of the PC resins increased substantially on curing with hexa at 140° and 160°C. The PC resins even after curing with hexa at elevated temperatures remained thermoplastic as indicated by fusibility and solubility in organic solvents. With the exception of PCD 1 and PCD 2 resins cured with 8 weight % hexa at 160°C, all the cured resins were soluble and fusible. However, the

softening points of the cured resins were considerably higher as indicated by ΔT values in Table 13. This indicates that the resins do react with hexa to form only linear linkages. Thus the resins remain soluble and fusible (thermoplastic) after curing for short times (15 minutes) with low amounts of hexa (4-8 weight %) at 140°-160°C. This unusual behaviour offers interesting processing possibilities. It may be possible to process the PC resins containing 8-12 weight% hexa on thermoplastic injection molding equipment into intricate product shapes, since the molding times would be short. The thermoplastic molded parts may be further postcured in ovens to impart the desired thermoset characteristics to them.

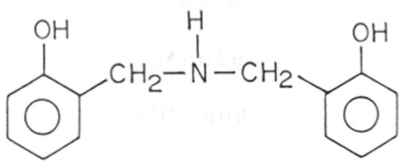
The enhancement in softening temperature, ΔT, increases with increasing hexa and curing temperature. Resins cured at 160°C with 8 weight % hexa showed the highest ΔT values. It is interesting to note that the cured PCD resins with lower crotonaldehyde mole fraction (PCD 1 and PCD 2) were insoluble and did not soften upto 250°C. Also, the mole fraction of croton-

aldehyde in the resin appears to exert an influence on the increase in the softening temperature, mainly in case of PCD resins. Thus, there is a decreasing trend in ΔT with increasing mole fraction of croton-aldehyde, except for the cure at 140°C with 4 weight % hexa. As such, the resins with low mole fraction of crotonaldehyde cured at 160°C with 8 weight % hexa are infusible upto 250°C. The increase in the softening temperature is associated with an increase in the number average molecular weight, $\bar{M}n$, as shown in Table 14. PCC 3 resin was cured at 120°C for 15 minutes with varied amounts of hexa. This clearly indicates that there is some sort of reaction taking place between the resin and hexa.

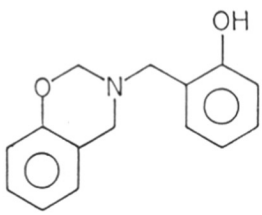
This unique curing behaviour of the PC resins was confirmed over a broad range of phenol to croton-aldehyde ratios (Table 15). The softening point of the base resin and its reactivity increases (as indicated by shorter flow lengths) with increasing amount of croton-aldehyde in the resin. However, the cured resins were

all soluble and their softening points were comparable, independent of the phenol to crotonaldehyde ratio[144].

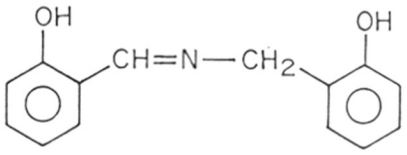
The mechanism of curing of conventional PF resins is not fully understood although there are literature reports proposing possible steps that can occur during the reaction of novolak resins with hexa[133-135]. One of the proposed reactions involved hydrolysis of hexa by trace amounts (0.1-0.5 weight %) of moisture in the resin, generating formaldehyde. The acidic nature of phenol may also lead to the generation of -amino alcohols[141,142]. It is known that the predominent moiety bridging the phenyl rings in novolak resins is the methylene group, although the presence of other bridging structures, such as dibenzylamines, benzoxazines, and azomethines, has also been reported[145-147] as shown in structures I, II and III respectively.



(I)



(II)



(III)

For PC resins, the nature of the bridging group would be other than the short methylene group. It is reported that the side chain in the acid-catalysed reaction between alkyl-phenol and crotonaldehyde contains three or four carbon atoms[125,137] as shown in Figure 11, Chapter 4. The presence of such bulky groups on the benzene ring of the PC resins may sterically limit the bridging sites on the ring to the positions ortho to phenolic hydroxyl. This may lead to predominantly linear structures on reaction with hexa. The bridging groups may be similar to the structures I, II and III in addition to methylene group which crosslink on curing at elevated temperatures.

The observation that the PC resins are not thermosetting under these conditions deserves comment. Crotonaldehyde, both crude and distilled, absorbs at infrared frequencies corresponding to C=C double bond (at 1640, 1310 and 970 cm^{-1} for trans isomer) and C=O (at 1680 cm^{-1}), whereas the resins prepared from both crude

and distilled crotonaldehyde do not absorb in these regions[144], indicating that there is a very little or no unsaturation. Therefore, the crosslinking reaction with hexa may be taking place by the conventional route, as in PF novolak resins.

The effect of curing temperature on the fusion characteristics of the cured PC resins was investigated to determine the upper limit on the temperature of thermoplastic processing. A representative resin from PCC and PCD series was used for this study (Table 16). It is evident from Table 16 that the extent of crosslinking increases with increasing the loading of hexa and with raising the curing temperature. Also, the reduction of flow length indicates that the reactivity of the resin increases with rising temperatures. Below 140°C, the PC resins remained totally thermoplastic after curing, while above 140°C, it showed partial thermoset properties. Thus, the upper limit on temperature for thermoplastic processing of PC resins appears to be 140°-160°C at hexa loading of 8 weight %.

The results of postcuring heat treatment experiments are given in Table 17.. The cured PC resins were further heated at 160°, 180° and 200°C and checked for their nature, solubility and fusion characteristics. It was noted that the heat treatment at 180°-200°C transformed the cured yet thermoplastic resins into thermosets. Thus, the technical feasibility of the processing concept involving thermoplastic molding followed by postcure has been demonstrated.

TABLE 8

EFFECT OF THE AMOUNT OF HEXA ON THE FUSION CHARACTERISTICS OF PHENOLIC RESINS

Hexa weight %	Softening temperature range, °C					
	PF resin (1:0.72)		PCC 3 resin		PCD 9 resin	
	Before curing	After curing (120°C/15 min)	Before curing	After curing (120°C/15 min)	Before curing	After curing (140°C/15min)
0	72-76	-	80-84	80-84	100-103	100-103
4	80-84	Infusible	90-94	112-116	104-108	134-139
8	86-89	Infusible	93-97	120-123	109-113	149-153
12	90-94	Infusible	95-98	125-128	114-118	153-157
16	93-97	Infusible	99-101	130-133	120-124	156-160
20	98-102	Infusible	100-103	139-142	123-127	161-165

TABLE 9

THERMAL BEHAVIOUR OF THE RESINS

Resin Code	Mole fraction of crotonaldehyde in polymer	Softening temperature range, °C	Softening temperature range with hexa, °C	
			4 weight %	8 weight %
1	2	3	4	5
PCC 1	0.29	69±2	78±2	82±2
PCC 2	0.39	92±2	98±2	101±2
PCC 3	0.40	82±2	92±2	95±2
PCC 4	0.43	86±2	90±2	93±2
PCC 5	0.47	90±2	95±2	97±2
PCC 6	0.50	132±2	138±2	140±2
PCD 7	0.32	96±2	99±2	104±2
PCD 8	0.38	97±2	101±2	106±2

1	2	3	4	5
PCD 9	0.47	102±2	107±2	111±2
PCD 10	0.48	110±2	114±2	118±2
PCD 11	0.55	102±2	107±2	111±2
PCD 12	0.58	107±2	112±2	118±2

TABLE 10

CURING BEHAVIOUR OF RESINS

Resin code	Mole fraction of crotonaldehyde in polymer	Softening temperature range, °C	Flow length with hexa, mm			
			At 140 °C		At 160 °C	
			4 weight %	8 weight %	4 weight %	8 weight %
1	2	3	4	5	6	7
PCC 1	0.29	69±2	38	35	24	20
PCC 2	0.39	92±2	26	21	16	13
PCC 3	0.40	82±2	42	38	26	22
PCC 4	0.43	86±2	42	39	27	22
PCC 5	0.47	90±2	43	39	28	24
PCC 6	0.50	132±2	-	-	20	18

1	2	3	4	5	6	7
PCD 7	0.32	96±2	31	27	22	17
PCD 8	0.38	97±2	29	25	21	18
PCD 9	0.47	102±2	28	25	25	22
PCD 10	0.48	110±2	21	17	19	16
PCD 11	0.55	102±2	26	24	20	18
PCD 12	0.58	107±2	22	18	19	16

TABLE 11

CURING BEHAVIOUR - COMPARISON OF PCC AND PF RESINS

PCC Resins							PF Resins		
Resin code	Mole fraction of crotonaldehyde in polymer	Softening temperature range, °C	Softening temperature range with hexa, °C		Flow length (120°C/15 min), mm		Mole ratio in the polymer	Softening temperature range, °C	Flow length (120°C/15 min), mm
			4 weight %	8 weight %	4 weight %	8 weight %			
PCC 1	0.29	67-71	76-80	80-84	47	43	1:0.4	Liquid Resin	
PCC 2	0.39	90-94	96-100	99-104	32	28	1:0.67	50-54	> 127
PCC 3	0.40	80-84	90-94	93-97	54	49	1:0.72	72-76	60
PCC 4	0.43	84-88	88-92	91-95	55	49	1:0.75	82-86	38
PCC 5	0.47	88-92	93-97	95-99	53	44			

TABLE 12

CURING BEHAVIOUR OF MIXED RESINS

No.	Resin composition (% W/W)	Softening temperature range, °C	Flow length with 8 weight % hexa at 120°C, mm	Solubility of the cured resins in acetone
1	PF (1: 0.75) (100%)	102-107	38	Insoluble
2	PF (90%) + PCC 3 (10%)	96-99	36	Insoluble
3	PF (80%) + PCC 3 (20%)	97-101	34	Insoluble
4	PF (70%) + PCC 3 (30%)	99-103	33	Sparingly soluble
5	PF (60%) + PCC 3 (40%)	100-104	31	Sparingly soluble
6	PF (50%) + PCC 3 (50%)	102-106	30	Slightly soluble

TABLE 13

THERMAL BEHAVIOUR OF THE CURED RESINS

Resin code	Mole fraction of crotonaldehyde in polymer	Softening temperature range before curing, °C		Softening temperature range after curing, °C							
				140°C/15 mins				160°C/15 mins			
		4 Weight % hexa	8 Weight % hexa	4 Weight % hexa	ΔT	8 Weight % hexa	ΔT	4 Weight % hexa	ΔT	8 Weight % hexa	ΔT
1	2	3	4	5	6	7	8	9	10	11	12
PCC 1	0.29	78±2	82±2	113±2	35±2	123±2	41±2	132±2	54±2	161±2	80±2
PCC 2	0.39	98±2	101±2	133±2	35±2	142±2	41±2	175±2	77±2	190±2	91±2
PCC 3	0.40	92±2	95±2	130±2	38±2	140±2	45±2	165±2	73±2	222±2	127±2
PCC 4	0.43	90±2	93±2	121±2	31±2	131±2	34±2	155±2	65±2	171±2	78±2
PCC 5	0.47	95±2	97±2	134±2	39±2	144±2	47±2	165±2	70±2	176±2	79±2
PCC 6	0.50	138±2	140±2	-	-	-	-	178±2	40±2	191±2	51±2
PCD 7	0.32	99±2	104±2	123±2	24±2	153±2	49±2	178±2	79±2	a	-

1	2	3	4	5	6	7	8	9	10	11	12
PCD 8	0.38	101±2	106±2	127±2	26±2	161±2	56±2	184±2	83±2	a	-
PCD 9	0.47	107±2	111±2	137±2	30±2	151±2	40±2	180±2	73±2	230±2	119±2
PCD 10	0.48	114±2	118±2	132±2	18±2	142±2	24±2	168±2	59±2	201±2	83±2
PCD 11	0.55	107±2	111±2	126±2	19±2	137±2	25±2	173±2	66±2	194±2	84±2
PCD 12	0.58	112±2	118±2	135±2	23±2	145±2	27±2	153±2	41±2	172±2	54±2

a : Does not melt upto 250°C

TABLE 14

MOLECULAR WEIGHT DATA FOR CURED PCC 3 RESIN

Hexa Wt.%	Softening temperature range with hexa (before curing), °C	Characterization after curing (120 °C/15 minutes)		
		Softening temperature range, °C	Increase in the softening temperature range, °C	$\overline{Mn}$
0	80-84	80-84	-	285
4	90-94	112-116	22±2	400
8	93-97	120-123	27±2	405
12	95-98	125-128	30±2	390
16	99-101	130-133	31±2	450
20	100-103	139-142	39±2	540

TABLE 15

CURING BEHAVIOUR OF PCD RESINS

Resin code	Mole fraction of crotonaldehyde in polymer	Softening temperature range, °C	Softening temperature range with 8 weight % hexa, °C	Flow length (140°C/15 min) mm	After curing (140°C/15 min)	
					Softening temperature range, °C	Solubility in acetone
PCD 7	0.32	94-97	102-106	27	152-155	Soluble
PCD 9	0.47	100-103	109-113	25	149-153	Soluble
PCD 12	0.58	105-109	116-120	18	143-146	Soluble

TABLE 16

EFFECT OF TEMPERATURE ON CURING OF PC RESINS

Resin code	Curing temperature, °C	Flow length (15 minutes), mm	Cured resin characteristics	
			Softening temperature range, °C	Solubility in acetone
PCC 3	120	49	120-123	Soluble
	140	38	138-142	Soluble
	160	22	220-224[a]	Slightly soluble
	180	20	235-239[a]	Slightly soluble
PCD 9	120	-	-	-
	140	25	149-153	Soluble
	160	22	228-232[a]	Slightly soluble
	180	19	250-254[a]	Slightly soluble

a : Resin softens but does not melt into clear liquid

TABLE 17

POSTCURING HEAT TREATMENT OF PC RESINS

Resin code	Posturing temperature °C	Cured at 140°C/15 min with 8 weight % hexa		Cured at 160°C/15 min with 8 weight % hexa	
		Softening temperature range after 15 min. postcure, °C	Solubility in acetone after postcure	Softening temperature range after 15 min. postcure, °C	Solubility in acetone after postcure
PCC 3	160	171-175	Soluble	220-223[a]	Soluble
	180	205[a]	Insoluble	225[a]	Insoluble
	200	Infusible	Insoluble	Infusible	Insoluble
PCD 9	160	190-194	Soluble	228-230[a]	Soluble
	180	215[a]	Insoluble	235[a]	Insoluble
	200	Infusible	Insoluble	Infusible	Insoluble

a : Resin softens but does not melt into clear liquid.

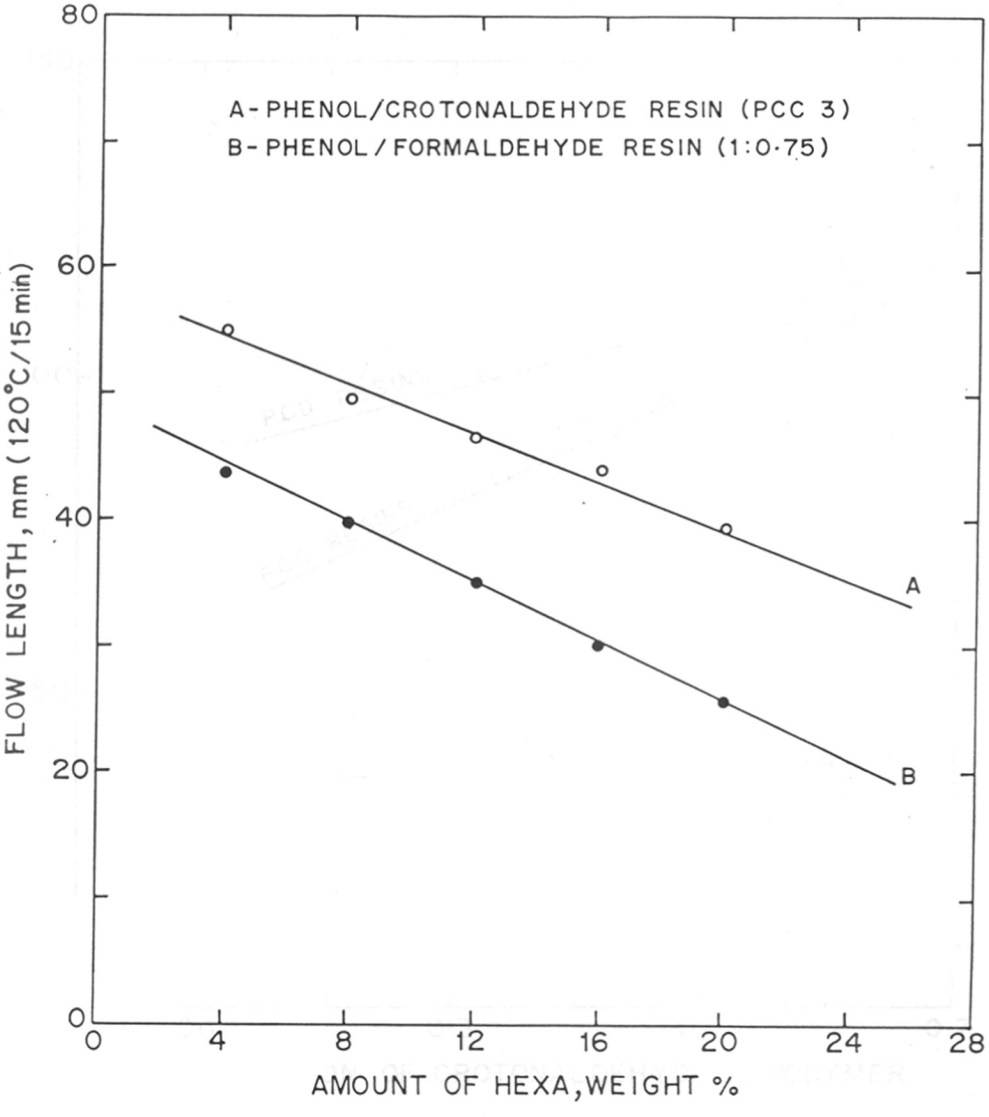


FIGURE 13 : DEPENDENCE OF THE CURING BEHAVIOUR ON AMOUNT OF HEXA

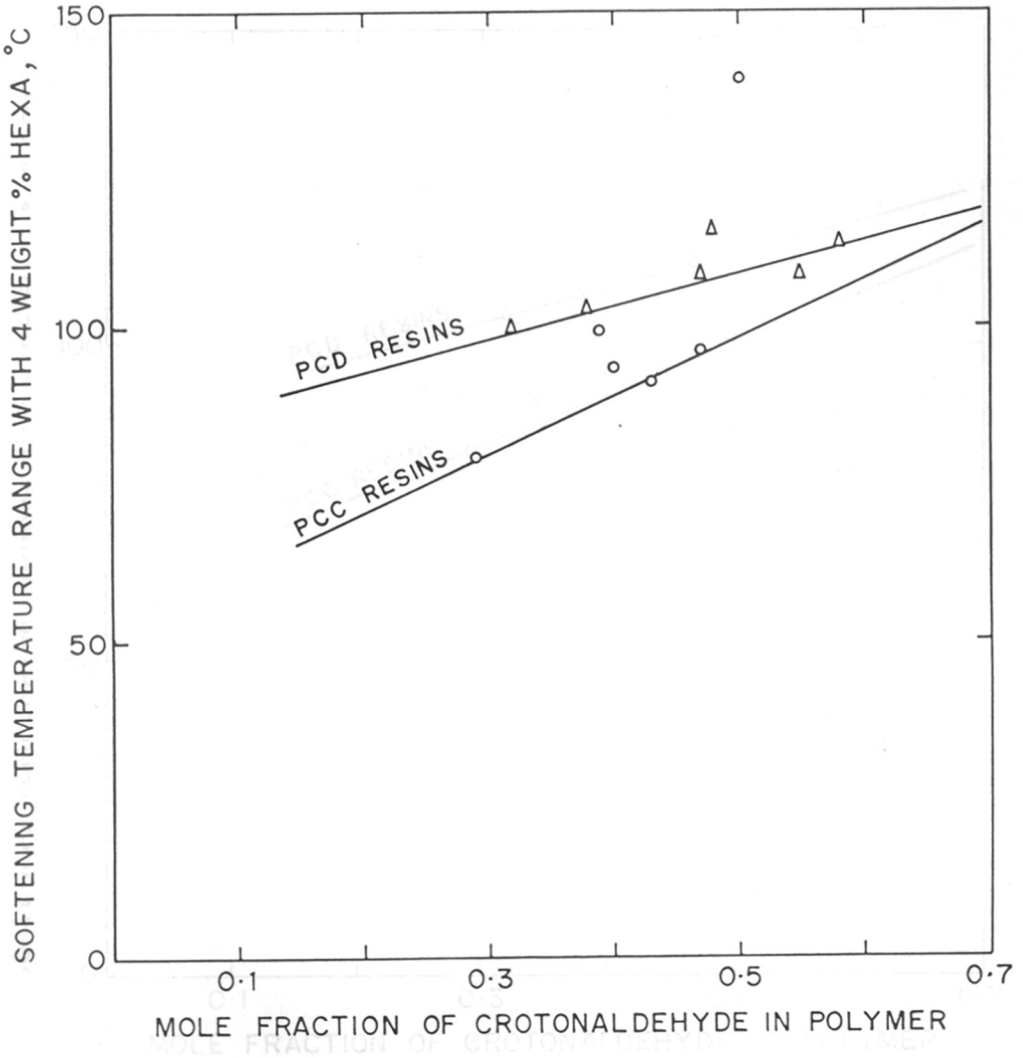


FIGURE 14: EFFECT OF CROTONALDEHYDE MOLE FRACTION ON SOFTENING TEMPERATURE RANGE OF RESINS WITH 4 WEIGHT % HEXA

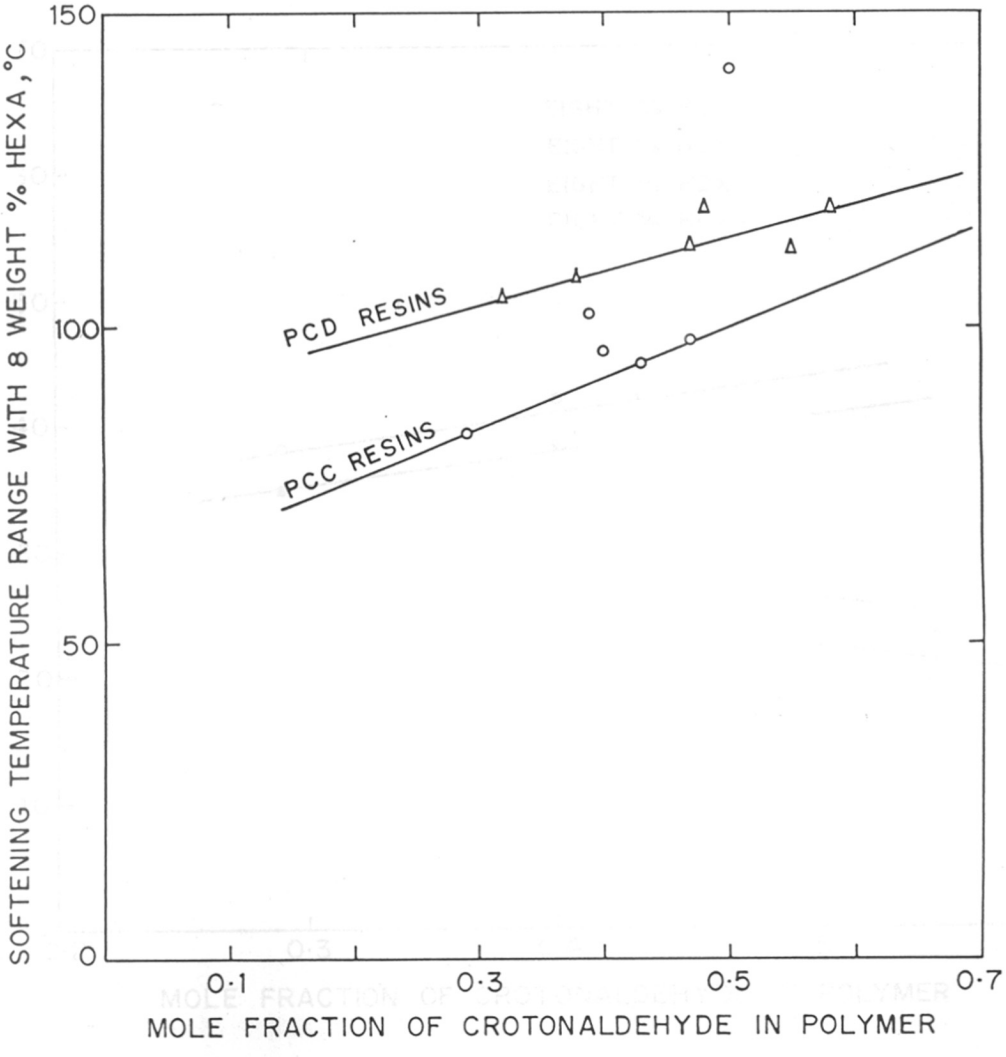


FIGURE 15: EFFECT OF CROTONALDEHYDE MOLE FRACTION ON SOFTENING TEMPERATURE RANGE OF RESINS WITH 8 WEIGHT % HEXA

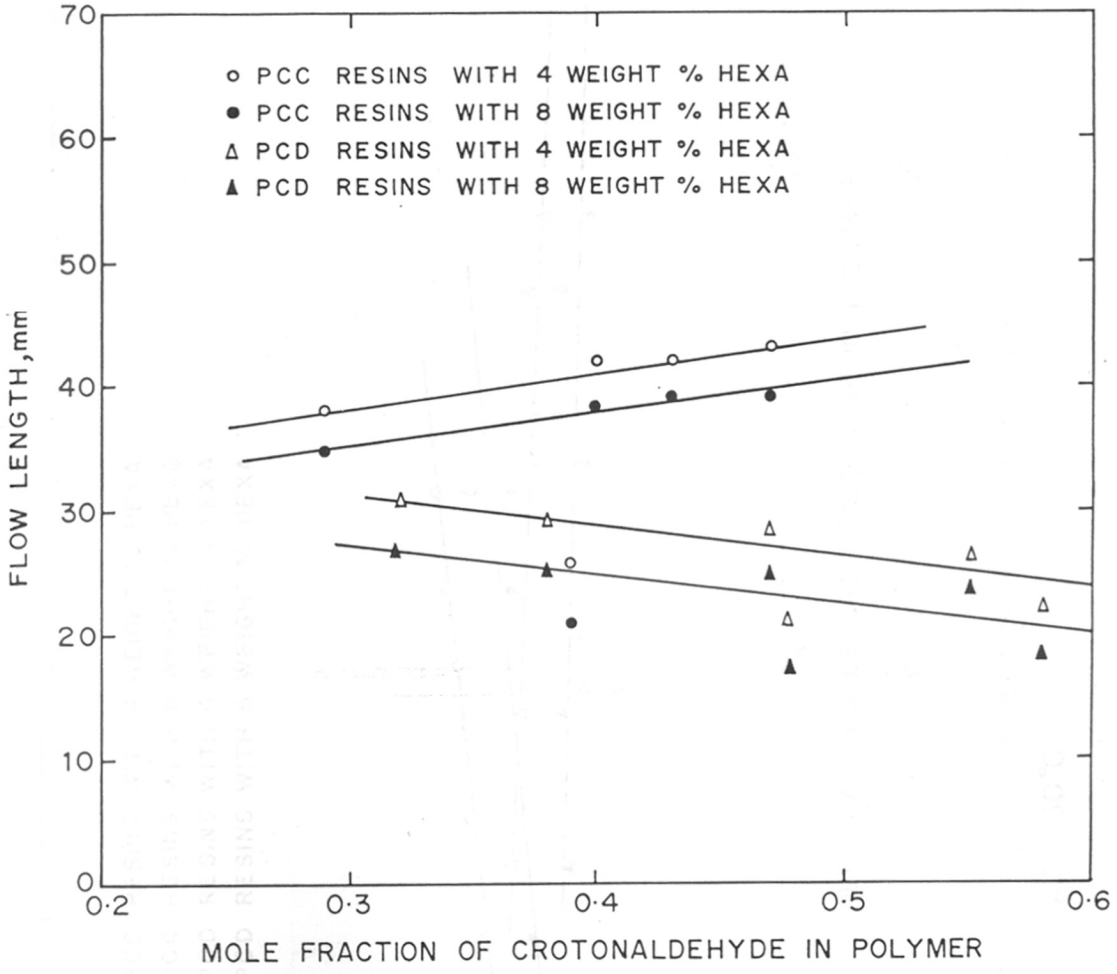


FIGURE 16: EFFECT OF CROTONALDEHYDE MOLE FRACTION ON CURING OF RESINS AT 140°C

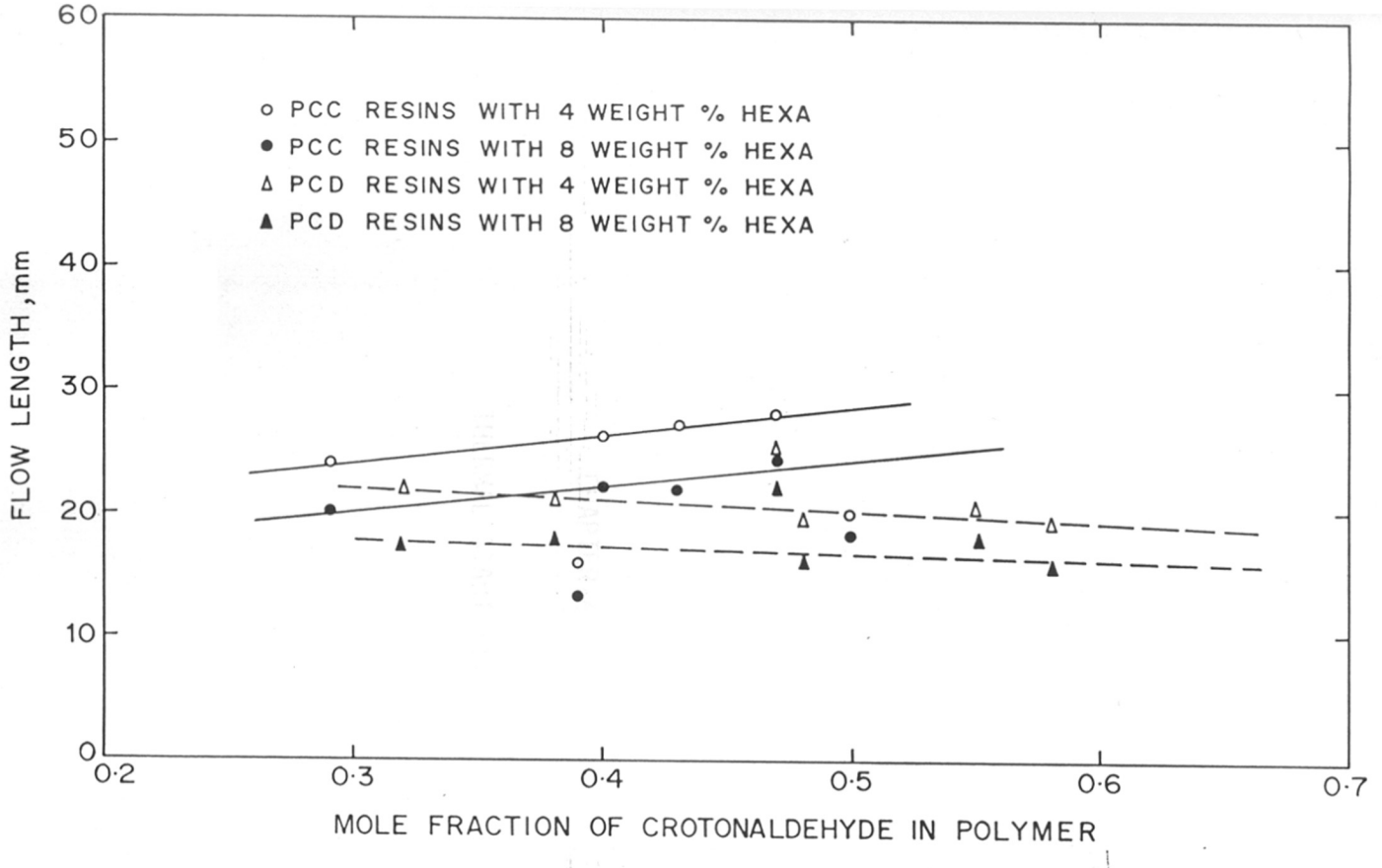


FIGURE 17 : EFFECT OF CROTONALDEHYDE MOLE FRACTION ON CURING OF RESINS AT 160°C

CHAPTER 6

THERMAL STABILITY

CHAPTER 6

THERMAL STABILITY

6.1 INTRODUCTION

A knowledge of the thermal stability of polymeric materials is required for the selection of proper processing and fabrication conditions, for optimising the mechanical performances and for identifying suitable end uses. The highest permissible processing temperature is dictated by the thermal stability of the polymer. Thermogravimetric analysis (TGA) is a dynamic technique used to determine and to analyse the thermal degradation resistance of polymers.

In this technique, the change in the mass of the polymer is monitored continuously as the specimen is heated at a constant rate. Alternatively, the sample is heated quickly to a predetermined temperature, maintained at this temperature and the loss in the mass is estimated as a function of time. The resulting thermograms provide information on the rate and modes of degradation, the activation energies, etc.

The thermal stability is defined as a general term indicating ability of a substance to maintain its properties as nearly unchanged as possible on heating. From a practical point of view, thermal stability needs to be considered in terms of the environment to be imposed on the material and the function it has to perform. The thermobalance is a useful technique for studying the inherent resistance of a material to chemical degradation on exposure to high temperatures. The resistance would vary depending on whether the environment contains oxygen (air) or an inert gas like nitrogen.

Studies on the thermal degradation of polymers[148,149] give vital information on :

(i) the strengths of the various bonds holding together the polymer molecules,

(ii) the kinetics of depolymerization,

(iii) the effect of time, temperature, pressure and other variables on the rates and products of degradation.

Similarly, this study is of great importance from a practical point of view because it explains the behaviour of the polymer at high temperatures relevant to their processing. The general term polymer thermal stability

is not always exact. It is mostly used with reference to the changes in one or more physical properties as a result of thermal history (temperature/time). In general, all thermochemical and physical impacts must be taken into consideration.

Phenolic resins are known for their heat resistance and give high yield of residue on pyrolysis. They are, therefore, used as ablative materials, friction materials, grinding wheels, and high temperature moldings. The high temperature oxidative degradation of PF resins is studied extensively[150-153]. The oxidative degradation of PF resins occurs in three stages, as indicated by weight loss and volume change[154-156]. In the first stage (upto 300°C) the polymer essentially remains intact. Small quantities of gaseous components (1-2 weight %) are released comprising of water and unreacted monomers. In the second stage, ranging from 300°C to 600°C, decomposition gets initiated. The major quantity of gaseous components are split off during this stage. The degradation reaction rate reaches a maximum within this range. In this stage, random chain scission occurs, yet no depolymerization to monomer takes place, the shrinkage

is relatively low and the density decreases. In the third stage above 600°C, the degradation products may include carbon dioxide, methane, water, benzene, toluene, phenol, cresols and xylenols. Considerable shrinkage is observed in this stage and the density increases. The mechanism of the thermo-chemical degradation of phenolics was thoroughly investigated by Conley[157] and Gautherot[158]. It was stated that there is always a thermo-oxidative process taking place regardless of whether the pyrolysis reaction occurs in oxidative or inert atmosphere. The high oxygen content of phenolic resins is the reason for this process.

6.2 DEGRADATION REACTION KINETICS (NON-ISOTHERMAL METHODS)

Thermogravimetric data are used to evaluate the kinetic parameters of reactions involving weight loss/or gain of the following four types[159-162]:

$$As \longrightarrow Bs + Cg$$

$$As + Bs \longrightarrow Cs + Dg$$

$$As + Bg \longrightarrow Cs$$

$$As \text{ or } Al \longrightarrow Ag$$

where A, B,C and D are different chemical moieties, and the suffixes s,g, and l are solid, gaseous and liquid forms of the substances.

The non-isothermal methods of estimating the kinetic parameters offer certain advantages :

(i) minimal experimental data is required,

(ii) kinetics can be probed over an entire temperature range in a continuous manner,

(iii) when a sample undergoes considerable degradation in being raised to the required temperature in case of isothermal method, the results obtained are often questionable.

The earliest attempt to use TGA curves for kinetic data is by Van Krevelen et al[163]. They derived an approximate equation to estimate graphically the order of the reaction (0, 1 or 2 order).

The foundation for calculations of kinetic data from a TGA curve is based on the formal kinetic equation[164]

$$-\left(\frac{dX}{dt}\right) = KX^n \qquad (1)$$

where X = the amount of sample undergoing the reaction,

n = the order of the reaction, and

K = the specific reaction rate expressed by the Arrhenius equation as :

$$K = Ae^{-E/RT} \qquad (2)$$

where

A = the pre-exponential factor,

E = the activation energy,

R = the gas constant, and

T = the absolute temperature.

In case of polymeric materials dynamic thermogravimetry can not predict the exact reaction mechanism and the structural development because of the higher functionality of the monomers. An extension of TGA is derivative thermogravimetry (DTG). In this technique, the rate of mass change with respect to time, t, or temperature, T (dm/dt) is monitored versus time or temperature. The thermogram thus contains a series of peaks instead of stepwise curves. The areas under the peaks are proportional to the total mass-change of the sample. A horizontal plateau in TG curve gives a corresponding

horizontal plateau in DTG curve since dm/dt = 0. A maximum in DTG curve is obtained at a point in the TG curve where the rate of mass loss is maximum observed.

A schematic representation of the thermogravimetry (TG) and derivative thermogravimetry (DTG) scans is given in Figure 18. For each step of degradation in the TG curve a corresponding peak is observed in the DTG curve. The onset temperatures for each degradation stage are marked as T_1, T_2, T_3 etc. and the final degradation temperature as T_F. The temperature at which a maximum in the rate of weight loss is observed is termed as T_{max} (See Figure 18).

The information obtained by DTG and its applications have been summerized by Dunn[165]:

1. The DTG curve presents this information in a form that is most visually accessible, whereas DTG curve contains no more information than does the TG curve.
2. The DTG curve allows the ready determination of the temperature at which the rate of mass-change

is maximum, T_{max}, and this provides additional information to the extrapolated onset temperature Ti and the extrapolated final temperature, T_F.

3. The area under the DTG curve is directly proportional to the extent of mass-change.

4. The height of the DTG peak at any temperature is a measure of the rate of mass-change at that temperature. These values can be used to obtain kinetic information since the equations can be written in the form [166]

$$-\left(\frac{dX}{dt}\right) = Ae^{(-E/RT)} \cdot f(X) \qquad (3)$$

where X = the amount of sample undergoing the reaction,

A = the pre-exponential factor,

E = the activation energy,

R = the gas constant, and

T = the absolute temperature

A number of methods have been developed to compute the kinetic parameters from DTG thermograms. These are the methods formulated by Newkirk[167], Freeman and Carroll[159], Horowitz and Metzger[168], Coats and Redfern[169],

Doyle[162,170], Ingraham and Marier[171], Vachuska and Voboril[172], Reich and Stivala[173], Ozawa[174] and the steady state parameter jump method. Of these the methods suitable for investigating degradation kinetics of polymers are those proposed by Coats and Redfern, and Horowitz and Metzger.

The mathematical treatment of kinetic equations makes use of differential, integral or approximation methods of evaluation. In the present study, we have used the Coats and Redfern method for evaluation of the kinetic parameters, which is based on the integral evaluation technique. The integral methods use the integrated form of the equation (1). The exact mathematical steps which leads to the final expression is beyond the scope of present work and therefore not discussed in details. Coats and Redfern derived the following expression for a reaction in which the order is unknown :

$$\log\left\{\frac{1-(1-\alpha)^{1-n}}{T^2\,(1-n)}\right\} = \log\frac{AR}{aE}\left[1-\frac{2RT}{E}\right] - \frac{E}{2.3RT} \qquad (4)$$

where α = the fraction of sample decomposed at time t,

a = the heating rate,

A = the pre-exponential factor,

E = the activation energy

R = the gas constant,

T = the absolute temperature, and

n = the order of the reaction

A plot of either $\log \left\{ \frac{1-(1-\alpha)^{1-n}}{T^2 (1-n)} \right\}$ against 1/T or when n = 1, $\log [-\ln (1-\alpha)]/T^2$ against 1/T should result in a straight line of slope - E/2.3R for the correct value of n[175]. The quantity $\log \left[\frac{AR}{aE}\right] \left[1 - \frac{2RT}{E}\right]$ appears to be reasonably constant for most values of E and in the temperature range over which most reaction occur.

6.3 EXPERIMENTAL

The thermogravimetric analysis in air (oxidative degradation) was conducted on a Netzsch Thermal Analyser STA 409 keeping the sample weight almost same ($\simeq$ 21 mgm). The Soxhlet extracted, purified PCC, PCD and PF resins

were run at three heating rates, 5°C/min, 10°C/min and 20°C/min. The instrument settings were as follows:

TG	:	25 mgm	=	25 cms,
DTG	:	0.2 mV	=	25 cms,
DTA	:	0.2 mV	=	25 cms,
Temperature range	:	12.5 mV	=	25 cms,
Chart speed	:	120 mm/min		

The reaction kinetics were studied using the Coats and Redfern method. For computing the rate of reaction, thermograms run at the heating rate of 10°C/min were considered. All the mathematical calculations were done on a PCL model (IBM PC/AT Type).

6.4 RESULTS AND DISCUSSIONS

6.4.1 Qualitative Analysis of Thermograms

Literature search reveals that phenolic resins show three distinct stages in oxidative degradation. A similar trend was observed in PC resins irrespective of the molar ratio of phenol to crotonaldehyde and the

purity of the crotonaldehyde. The temperature from where the degradation starts were recorded as the starting degradation temperature for various stages of degradation (see Figure 18). Table 18 gives the onset temperatures of degradation of PC and PF resins for the different stages of degradation. The TG of PCC 3, PCD 9, PF (1:0.45), and PF (1:0.75) are shown in Figure 19. The thermograms are almost identical except the one for PF(1:0.45) which is a semisolid resin. The degradation starts around 150°C and ends around 700°C for PC resins. The three stages of degradation can be roughly marked as :

Stage 1 : from 150°C to 300°C,

Stage 2 : from 300°C to 500°C, and

Stage 3 : from 500°C to 700°C.

In the case of PF resins, these temperatures were upto 300°C for stage 1, from 300°C to 600°C for stage 2, and from 600°C to about 800°C for stage 3. It is interesting to note that PF (1:0.45) resin starts degrading from about 100°C which is lower than other resins under study. It is observed that the degradation starts at higher temperature in case of PC resins irrespective of mole ratio and purity of crotonaldehyde when compared to

the conventional PF resins. Alternatively it can be stated that PC resins are thermally more stable than PF resins. But the pattern of the thermograms indicated in Figure 19 are almost similar in nature thereby it may be concluded that the degradation mechanism is similar in both resin types. Also it is observed that the mole fraction of crotonaldehyde in the polymer does not have a major influence on the degradation mechanism.

The data on weight loss and percent weight loss in the three stages are summerized in Table 19. The stagewise percent degradation of PCC resins was about 19-30% for first stage, 34-48% for second stage and 26-32% for third stage whereas for PCD resins it was 12-27%, 38-58% and 26-30% for stage 1,2 and 3 respectively. As discussed earlier, in the first stage of degradation mainly water and unreacted monomers split off. In case of the PCC resins the percent degradation in the first stage of degradation is more as compared to the PCD resins. This may be due to the impurities present in crude crotonaldehyde or it could be explained on the basis of the formation of low molecular weight side

products in the condensation reaction. It may be possible that these products degrade at a lower temperature thereby reducing the thermal stability of the PCC resins. In the second and third stages of degradation, mainly chain scission and depolymerization takes place. The percent degradation in the second and third stages are comparable for both PCC and PCD resins. This indicates that the resins are similar in chemical structure as per discussion in Chapter 4. In contrast, conventional PF resins exhibit extent of degradation of 16-20% in the first stage, 17-28% in the second stage and 48-60% in the third stage (see Table 19). The difference in the percent degradation in each stage between PF and PC resins may be explained on the basis of their chemical structure. As discussed in earlier chapters, the reactivity of crotonaldehyde is less than that of formaldehyde. The resins prepared from both crude and distilled crotonaldehyde are oligomeric in nature with maximum number average molecular weights of about 600, whereas it is wellknown that the conventional PF novolak resins exhibit a molecular weight of about 1500 or more irrespective of the molar composition[133]. Secondly the bridging moiety in PF resins is methylene

group and in case of PC resins it consists of a chain with atleast four carbon atoms. This may enhance the degradation at lower temperatures in case of PF resins. Because of the tightly knit chemical structure of PF resins, the chain scission or depolymerization would occur at higher temperature and thus the percent decomposition in the first and second stages is low for PF resins as compared to PC resins.

The degradation of PC resins was completed around 650° to 700°C whereas for PF resins the temperature for complete degradation was above 800°C. This difference may also be attributed to the differences in the molecular weights of the PC and PF resins as discussed earlier.

The amount of residue was about 3-5% for all the resins under study (see Table 19).

6.4.2 Quantitative Analysis : Kinetic Study

The degradation reaction kinetics was studied using Coats and Redfern method. This method is based

on the integral approximation and the derived equation can be fitted for any order of reaction. When the correct order of reaction is substituted in Equation (4), a straight line graph results. Thus, the order of reaction can be determined by curve fitting expression (4) written in section 6.2 at different values of n until a straight line plot is obtained.

The determination of kinetic parameters involves the use of DTG curves. The DTG curves of PCC 3, PCD 9, PF (1:0.45) and PF (1:0.75) are shown in Figure 20. The DTG curves show peak corresponding to maximum rate of degradation for a particular stage of degradation. The peak temperature for first stage for PCC and PCD resins is observed around 300°C whereas for PF (1:0.45) and PF (1:0.75) it was around 265°C and 310°C respectively. For second stage the peak temperature for all the resins is around 425°C except the PF (1:0.75) resin which showed the peak at 450°C. In the third stage of degradation the peak is observed at 620°C for PC resins and around 650°C for PF resins. It is observed that the DTG curves of PC resins both from crude and distilled crotonaldehyde

show a high and sharp peak in the temperature range of 340°-520°C. The peaks are of greater height and area as compared to conventional PF resins under study. It is reported that these types of sharp and high peaks are observed for alkyl-substituted phenolic resins in the temperature range of 430°-470°C[176]. As the chain length of the alkyl substituent increases, so does the maximum rate of weight loss. Several possible explanations were offered for these sharp peaks. They are : (a) due to the restricted rotation of the alkyl group, some or all the side chains may break away from the aromatic ring, (b) degradation of side chain may occur, (c) the resins degrade at the bridges and the polymer further degrades into smaller fragments which volatilize at the particular temperature. As discussed earlier in this temperture range the chain scission occurs and no deploymerization takes place. Due to bulkier side chains the rate of mass-loss increases considerably thereby giving high peaks. In case of PC resins, the bridging group consists of four carbon atoms and thus play a similar role as side chain giving the high peak in DTG. In case of conventional PF novolak resins these

sharp peaks are not observed because of the smaller bridging group. As discussed earlier, the onset temperatures for each stage in case of PC resins are higher than that of PF resins which reflects in the shifting of the DTG peaks.

The mathematical parameters for calculating the order of reaction of each stage of degradation using Coats and Redfern method are summerized in Tables 20, 21 and 22 for first, second and third stage respectively. For calculations, a number of points were selected in each stage and the fraction of sample decomposed at a particular time, t, was calculated and corresponding temperature, T, was measured. Using expression (4) and plotting a graph of $\log\left\{\frac{1-(1-\alpha)^{1-n}}{T^2\ (1-n)}\right\}$ against 1/T it was found that linear plots are obtained at a value of n of unity for both the PC and PF resins, for all the stages of degradation (see Figures 21,22 and 23). Thus, it is clear that the degradation follows first order kinetics. To confirm this hypothesis, the plots of log $[-1n\ (1-\alpha)]/T^2$ against 1/T were plotted for orders

other than one for all the three stages. These plots were not linear as shown in Figures 24 and 25 for third stage. Figure 24 is for the plot of order zero and figure 25 is for the plot of order two. This confirms that the degradation reaction follows first order kinetics for both the PC and PF resins for all the three stages of degradation.

TABLE 18

ONSET TEMPERATURES OF DEGRADATION

Resin code	Mole fraction of crotonaldehyde in polymer	Sample weight mgm	Starting temperature of degradation stages, °C			
			T_1	T_2	T_3	T_F
1	2	3	4	5	6	7
PF (1:0.45)	-	20.8	98	366	506	791
PF (1:0.75)	-	21.1	138	345	499	882
PCC 1	0.29	21.1	162	322	477	675
PCC 2	0.39	21.1	146	322	499	691
PCC 3	0.40	21.1	152	321	510	691
PCC 4	0.43	21.1	131	323	533	697
PCC 5	0.47	21.1	169	323	516	697

1	2	3	4	5	6	7
PCC 6	0.50	21.1	175	312	493	688
PCD 7	0.32	21.1	160	339	518	706
PCD 8	0.38	21.1	178	334	516	683
PCD 9	0.47	21.1	181	331	521	683
PCD 10	0.48	21.15	166	318	521	683
PCD 11	0.55	21.1	173	319	537	679
PCD 12	0.58	21.1	151	323	519	676

TABLE 19

WEIGHT LOSS IN THE DEGRADATION

Resin code	Mole fraction of crotonaldehyde in the polymer	Sample wt;mgm	Weight loss in degradation stages						Residue	
			Stage 1		Stage 2		Stage 3		Wt, mgm	%
			Wt, mgm	%	Wt, mgm	%	Wt, mgm	%		
1	2	3	4	5	6	7	8	9	10	11
PF (1:0.45)	-	20.8	4.15	19.95	5.90	28.37	9.80	47.12	0.95	4.56
PF (1:0.75)	-	21.1	3.70	17.54	3.50	16.59	12.95	61.37	0.95	4.50
PCC 1	0.29	21.1	6.75	31.99	7.23	34.27	5.73	27.16	1.40	6.58
PCC 2	0.39	21.1	4.60	21.80	9.70	45.97	5.70	27.01	1.10	5.22
PCC 3	0.40	21.1	4.75	22.51	9.90	46.92	5.60	26.54	0.85	4.03
PCC 4	0.43	21.1	4.05	19.19	10.25	48.58	6.00	28.44	0.80	3.79
PCC 5	0.47	21.1	4.40	20.85	9.90	46.92	5.90	27.96	0.90	4.27

1	2	3	4	5	6	7	8	9	10	11
PCC 6	0.50	21.1	4.40	20.85	8.95	42.42	6.75	31.99	1.00	4.74
PCD 7	0.32	21.2	5.80	27.36	8.18	38.58	6.42	30.28	0.80	3.78
PCD 8	0.38	21.1	4.98	23.60	9.55	45.26	5.67	26.87	0.90	4.27
PCD 9	0.47	21.1	3.80	18.00	10.60	50.24	6.00	28.44	0.70	3.32
PCD 10	0.48	21.15	2.45	11.58	12.10	57.21	5.80	27.42	0.80	3.79
PCD 11	0.55	21.1	3.13	14.83	11.50	54.50	5.82	27.58	0.65	3.09
PCD 12	0.58	21.1	3.15	14.93	11.48	54.41	5.82	27.58	0.65	3.08

Note : For PC Resins : Stage 1 = 150°-300°C
Stage 2 = 300°-500°C
Stage 3 = 500°-700°C

For PF Resins : Stage 1 = upto 300°C
Stage 2 = 300°-600°C
Stage 3 = 600°-about 800°C

TABLE 20

COATS AND REDFERN METHOD (STAGE 1)

Resin code	Parameters					
	Temp. at start, °C	Temp. at end, °C	Temp. at R max, °C	Temp. at 1/e, °C	Analysis from decomp., %	Analysis to decomp., %
1	2	3	4	5	6	7
PF (1:0.45)	175	356	266	285	1.24	58.02
PF (1:0.75)	111	374	312	291	21.84	66.43
PCC 1	149	342	297	291	7.06	68.01
PCC 2	155	355	298	305	6.01	69.48
PCC 3	149	309	295	277	5.50	66.94
PCC 4	161	335	292	283	18.05	69.90
PCC 5	157	337	277	276	19.59	63.88

1	2	3	4	5	6	7
PCC 6	175	344	313	319	9.29	54.16
PCD 7	172	343	312	303	8.22	72.33
PCD 8	175	339	279	291	15.18	78.69
PCD 9	181	332	302	298	12.58	68.28
PCD 10	169	338	292	300	14.84	71.20
PCD 11	170	318	259	274	19.92	77.09
PCD 12	169	341	298	295	20.41	78.51

TABLE 21

COATS AND REDFERN METHOD (STAGE 2)

Resin code	Parameters					
	Temp. at start, °C	Temp. at end, °C	Temp. at R max, °C	Temp. at 1/e, °C	Analysis from Decomp., %	Analysis to Decomp., %
1	2	3	4	5	6	7
PF (1:0.45)	356	495	425	445	44.53	81.22
PF (1:0.75)	374	526	457	469	15.21	78.14
PCC 1	342	504	396	410	30.41	84.94
PCC 2	355	511	420	434	34.65	84.61
PCC 3	309	507	402	416	30.42	82.17
PCC 4	335	521	402	422	29.36	84.91
PCC 5	337	515	433	435	23.01	84.07

1	2	3	4	5	6	7
PCC 6	344	499	400	415	33.43	84.14
PCD 7	343	528	428	439	31.97	84.30
PCD 8	339	517	421	437	23.39	83.68
PCD 9	332	527	416	437	19.67	79.68
PCD 10	338	549	436	453	23.57	81.81
PCD 11	318	522	427	437	29.13	85.13
PCD 12	341	525	420	438	32.83	78.24

TABLE 22

COATS AND REDFERN METHOD (STAGE 3)

Resin code	Parameters					
	Temp. at start, °C	Temp. at end, °C	Temp. at R max, °C	Temp. at 1/e, °C	Analysis from Decomp., %	Analysis to Decomp., %
1	2	3	4	5	6	7
PF (1:0.45)	495	841	662	700	39.89	85.30
PF (1:0.75)	526	772	630	653	32.81	95.53
PCC 1	504	731	592	620	24.93	99.92
PCC 2	511	731	621	632	29.23	99.91
PCC 3	507	729	606	619	34.41	97.92
PCC 4	521	720	620	622	24.14	99.91
PCC 5	515	732	630	634	23.95	99.52

1	2	3	4	5	6	7
PCC 6	499	725	605	610	26.36	99.65
PCD 7	528	767	594	642	32.32	98.50
PCD 8	517	723	620	632	19.46	95.79
PCD 9	527	748	618	634	32.43	99.50
PCD 10	549	758	640	646	27.21	97.26
PCD 11	522	749	623	630	30.23	99.33
PCD 12	525	735	612	624	33.56	98.50

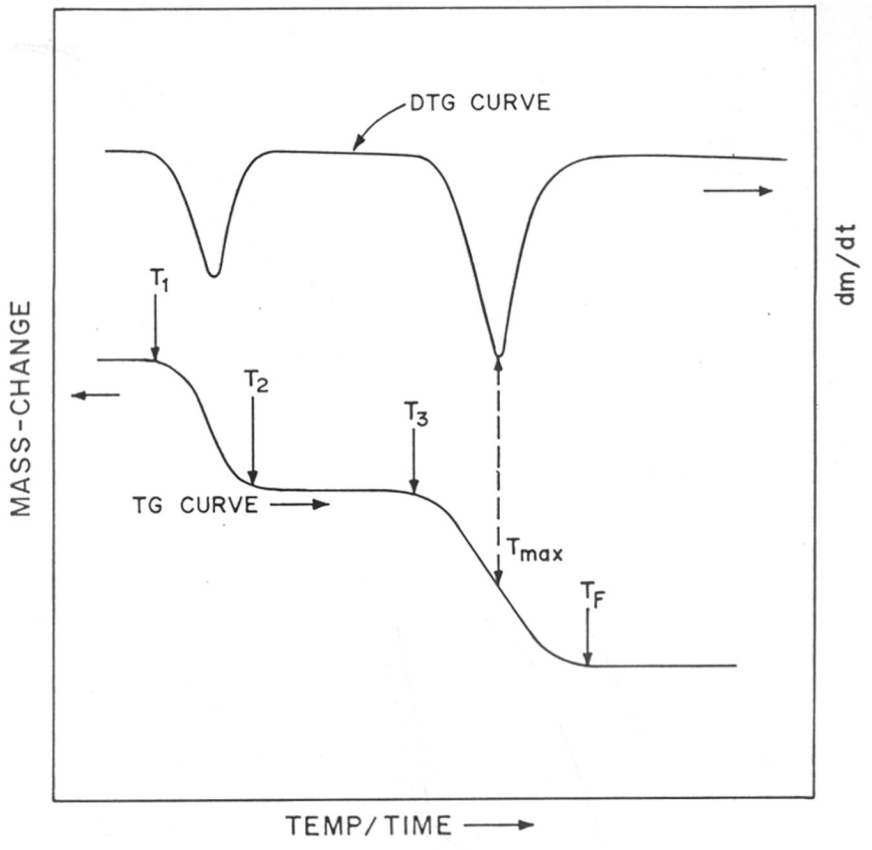


FIGURE.18 : SCHEMATIC REPRESENTATION OF INTEGRAL (TG) AND DERIVATIVE (DTG) MASS-LOSS CURVES

T_1 : STARTING TEMPERATURE OF STAGE 1 DEGRADATION

T_2 : STARTING TEMPERATURE OF STAGE 2 DEGRADATION

T_3 : STARTING TEMPERATURE OF STAGE 3 DEGRADATION

T_F : FINAL TEMPERATURE OF DEGRADATION

T_{max} : TEMPERATURE AT WHICH MASS-CHANGE IS MAXIMUM

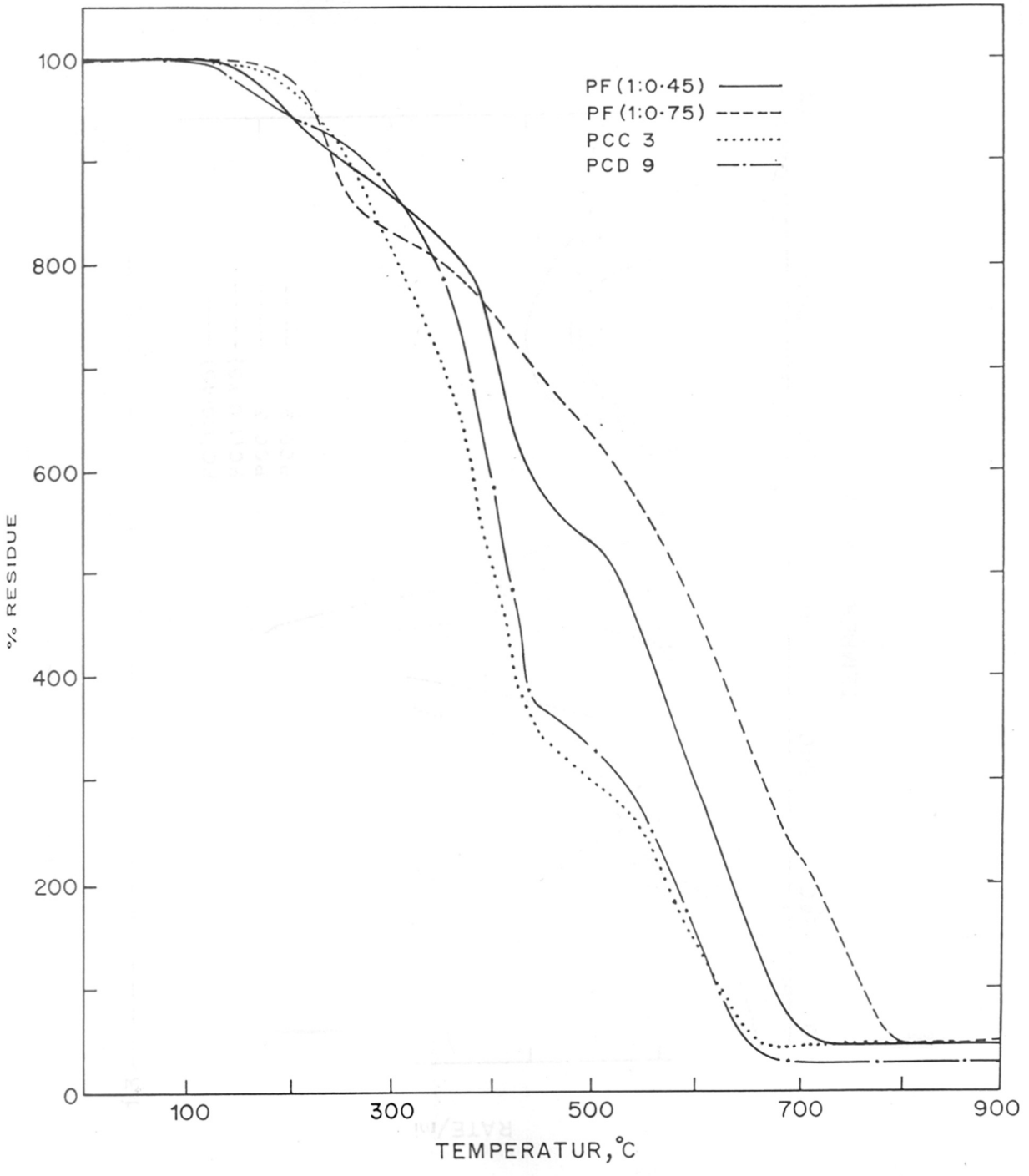


FIGURE 19: THERMOGRAMS OF THE RESINS

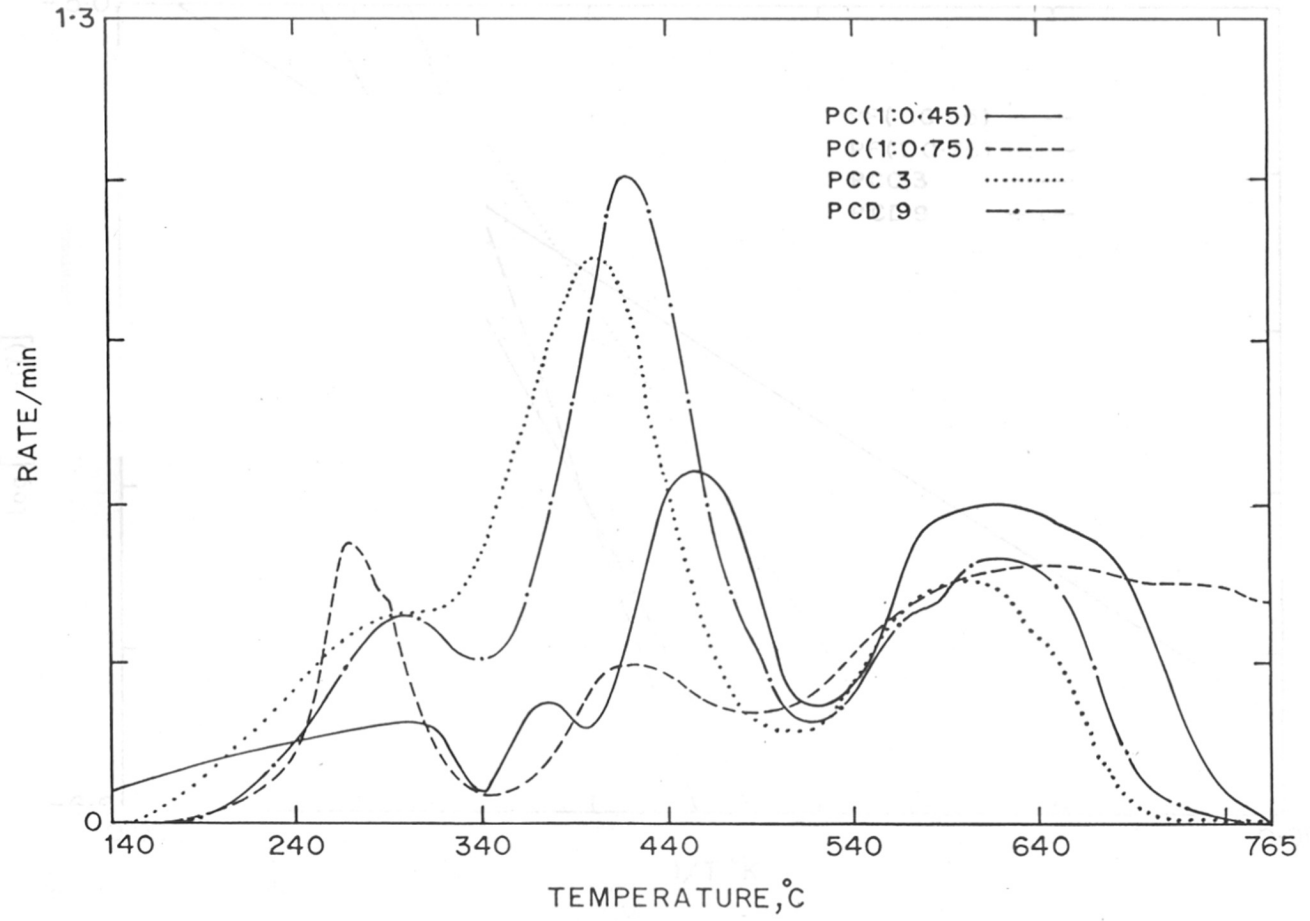


FIGURE 20: DTG OF THE RESINS

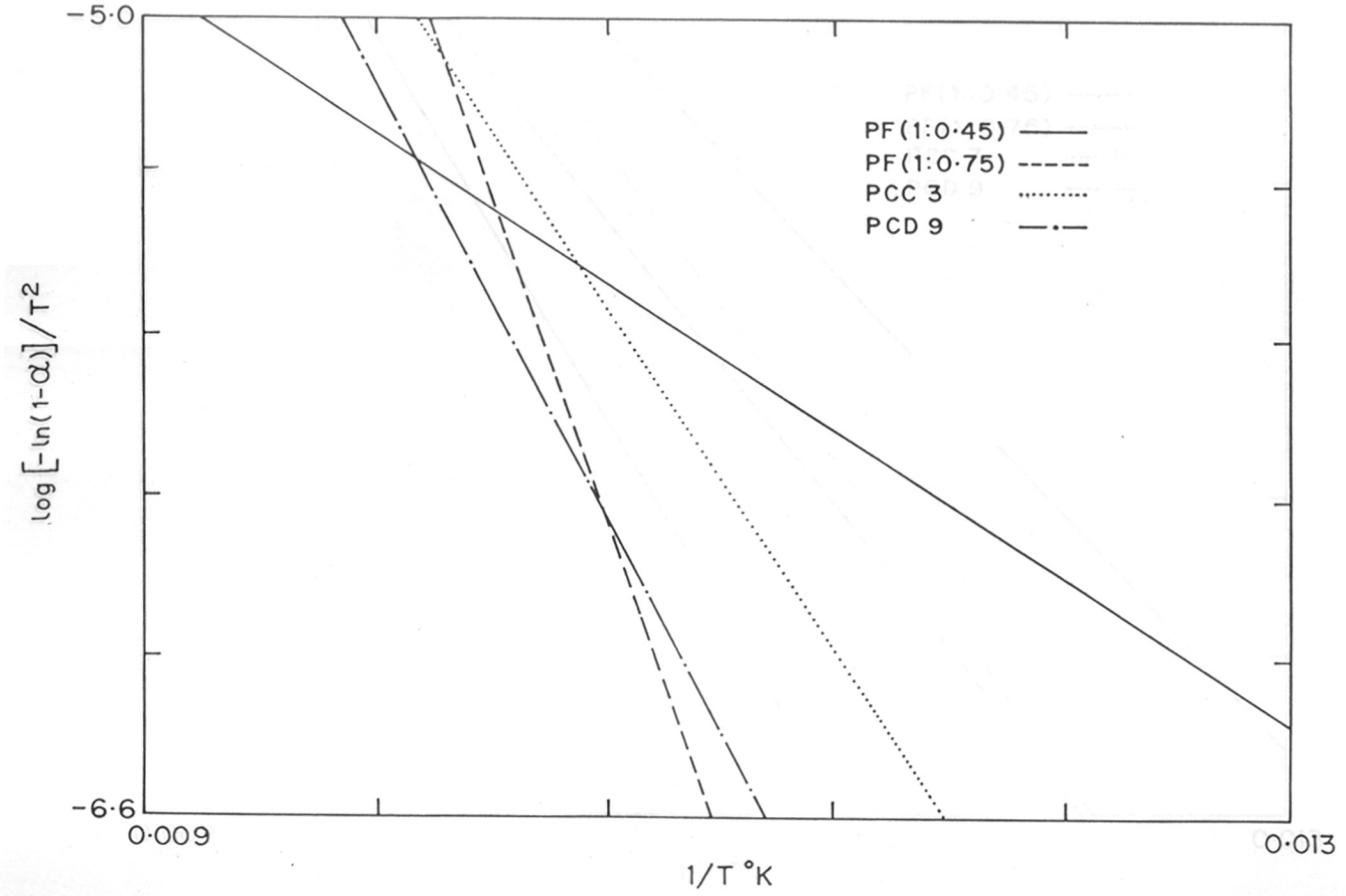


FIGURE 21: COATS AND REDFERN METHOD (ORDER = 1)
STAGE 1

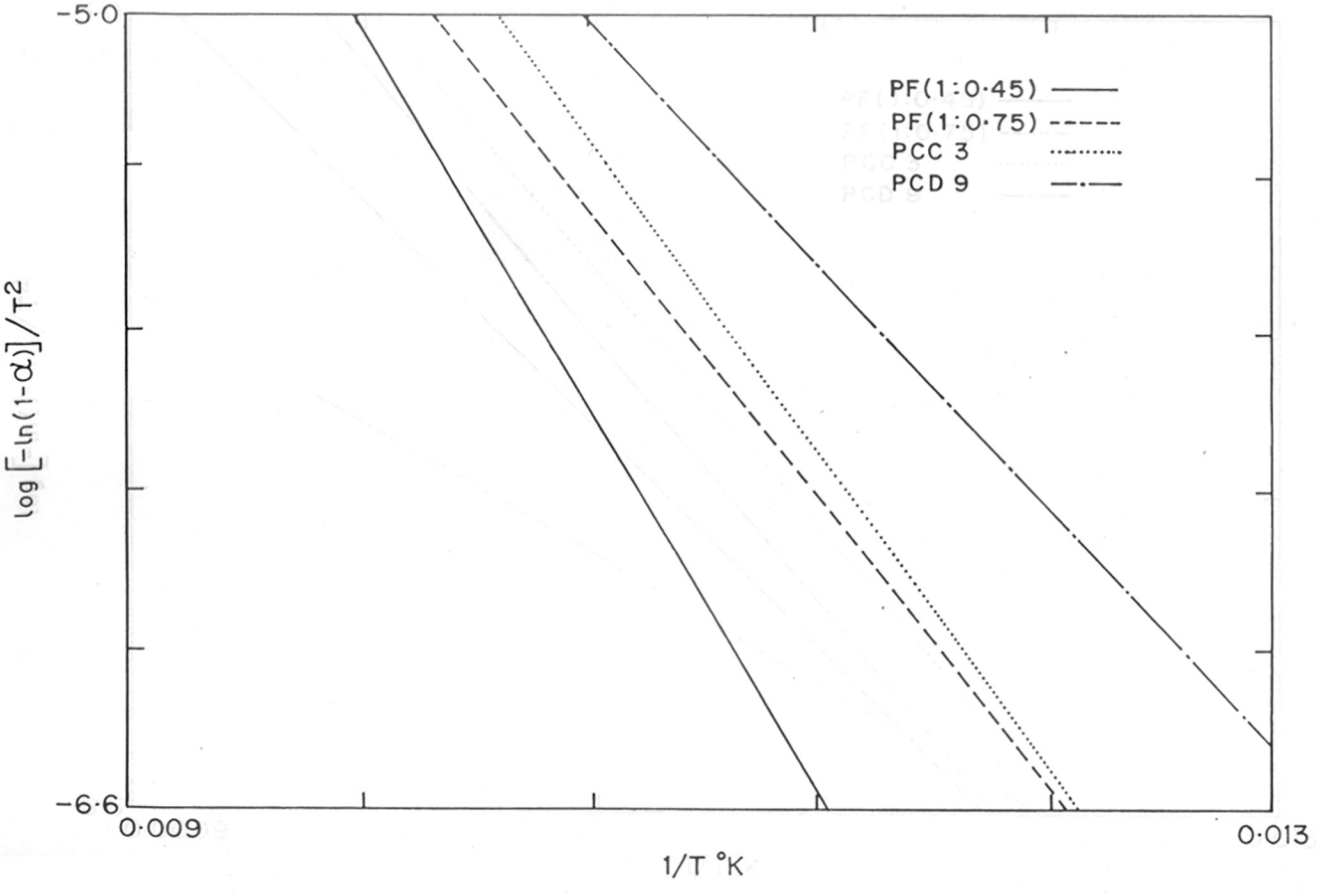


FIGURE 22: COATS AND REDFERN METHOD (ORDER = 1)
STAGE 2

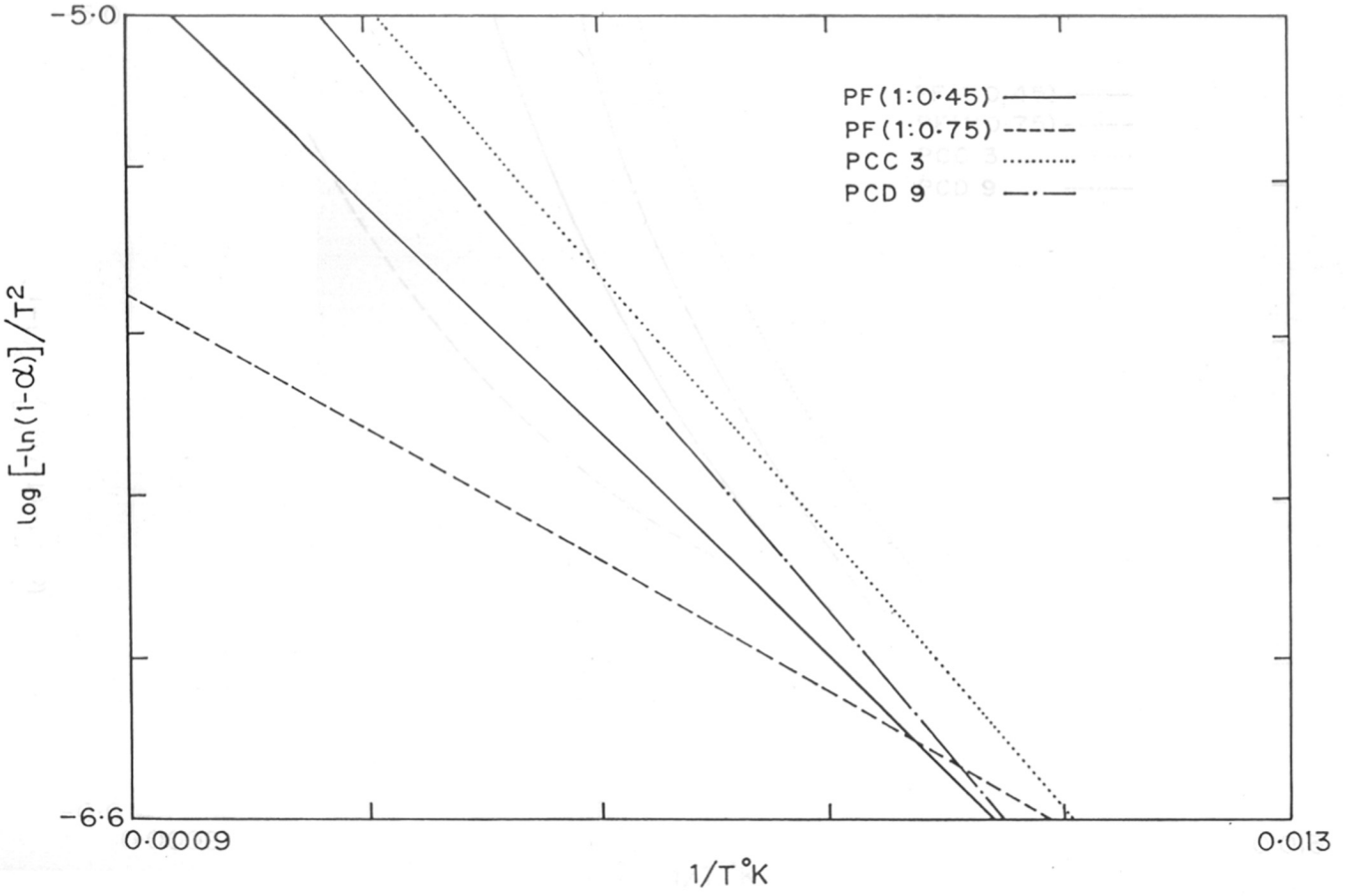


FIGURE 23: COATS AND REDFERN METHOD (ORDER=1)
STAGE 3

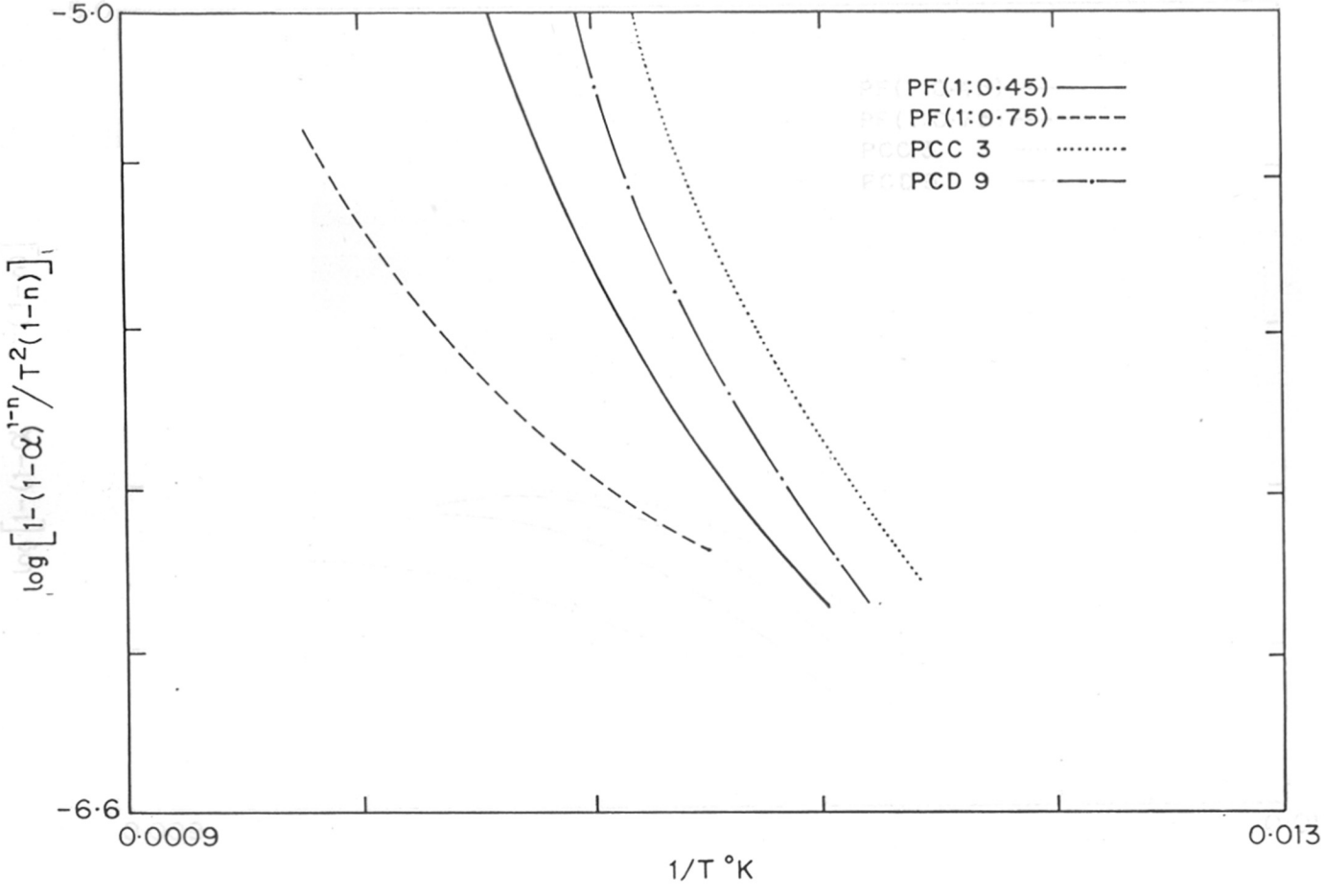


FIGURE 24: COATS AND REDFERN METHOD (ORDER=0)
STAGE 3

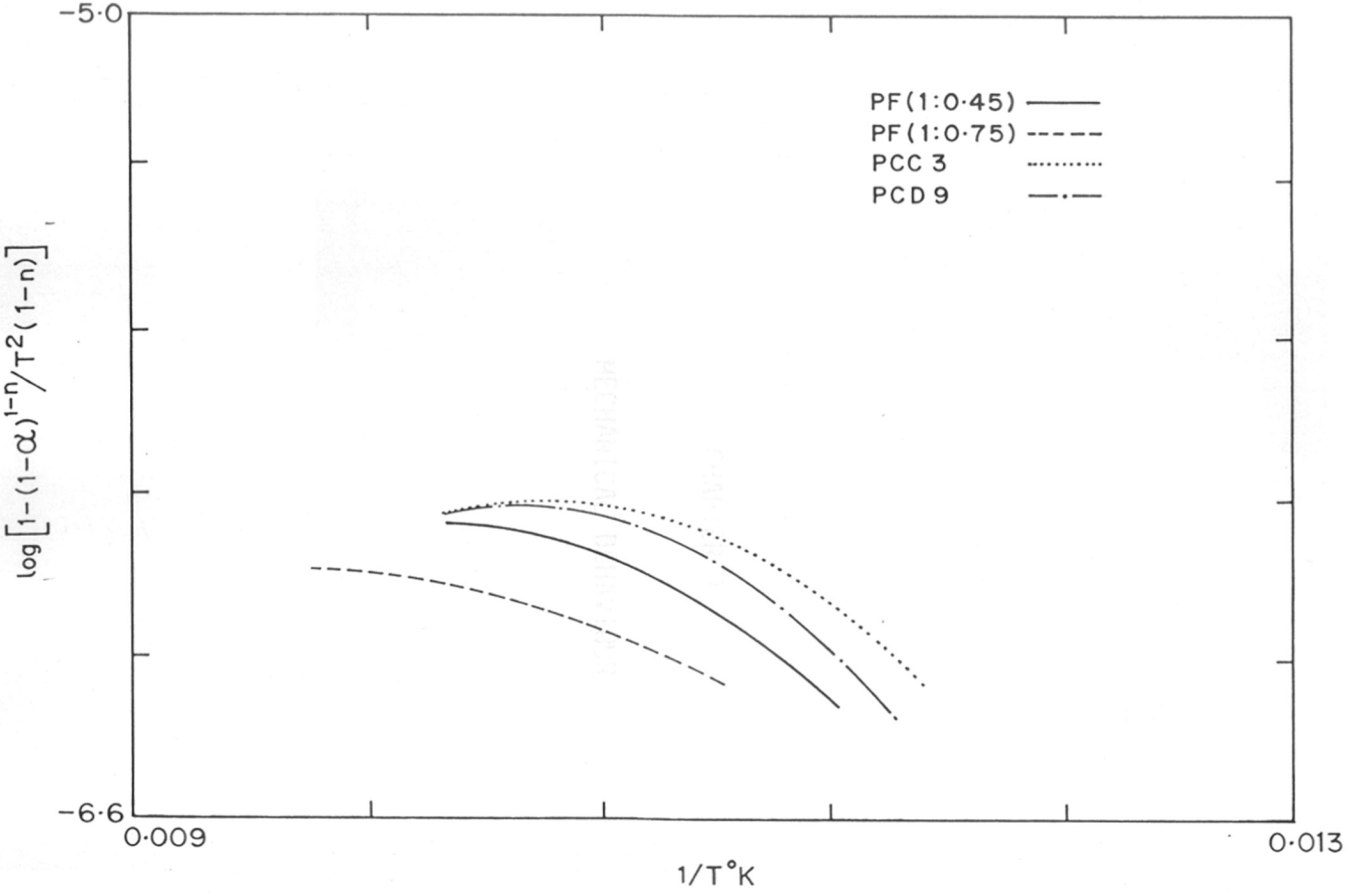


FIGURE 25: COATS AND REDFERN METHOD (ORDER=2)
STAGE 3

CHAPTER 7

MECHANICAL BEHAVIOUR

CHAPTER 7

MECHANICAL BEHAVIOUR

7.1 INTRODUCTION

The performance of a polymer under static service conditions can be well judged by testing its mechanical properties. The static mechanical properties of interest include tensile strength, compressive strength, flexural strength, impact strength, hardness, heat distortion temperature, etc. In the present work, the tensile strength of PC resins prepared from distilled crotonaldehyde were measured and compared with conventional PF novolak resins. The tensile measurements of cured phenolic resins is reported in the literature[177-185] but not much information could be obtained. The variation of modulus of elasticity with different fillers is also reported[186,187].

The load versus elongation data obtained on the Instron mechanical tester were converted into tensile

stress-strain data using the following definitions.

The stress or force per unit area is given by

$$\sigma_1 = F_1/Ao \qquad (1)$$

where F_1 = the tensile load applied at any time, and

Ao = the original cross-sectional area

When a tensile stress is applied to the material, the length of the sample increases. The strain is expressed in terms of the change in length and can be represented as :

$$\epsilon_1 = \frac{L - Lo}{Lo} \qquad (2)$$

where Lo = the original length of the specimen, and

L = the length under stress

The ultimate or breaking strength is obtained by taking the ratio of the load at break to the final cross-sectional area at failure.

$$\sigma_b = F_b/Af \qquad (3)$$

As the material is stretched its cross-sectional area decreases. However, for experimental convenience the calculation of tensile strength is based on the original cross-sectional area, since the elongation at break is low (in the range of 1-2% for thermosetting resins).

Elongation at break is usually expressed as percentage of the original length.

$$\text{Elongation at break, (\%)} = \frac{L-Lo}{Lo} \times 100$$

Since the stress-strain behaviour is time dependent, the speed at which the stress is applied must be fixed. The deformation rate employed in the present work was 0.05 mm/min for a guage length of 2.8 cms. In practice, the specimen is clamped at both ends into the jaws of the testing machine and the sample is pulled by one of the jaws. The area under the stress-strain curve represents the work required to break the test specimen and is a measure of the toughness of the material.

7.2 PREPARATION OF MOLDING POWDER

Phenolic molding powders are heterogeneous compounds. They consist of phenolic resin, cross-linking agent (hexa), fillers, reinforcing fibres, colourants and pigments as well as various lubricants. The molding compounds for compression molding generally have a lower resin content as compared to the injection molding compounds with a resin level upto 50%. In addition, there are different grades based on curing behaviour determined in terms of inclined flow: low, medium and high.

The composition of molding powder used was similar to that used for the conventional phenolic resins[133]. The solid resins were first finely ground and ball milled to a fine powder passing through 300 mesh size. Peanut Shell Flour (PNF), a naturally occuring agrobased cellulosic material passing through 60 mesh size was used as filler. Finely powdered, dry hexa was used as cross-linking agent. Calcium oxide (CaO) and stearic acid were used

as catalyst neutralizer and lubricant respectively[177]. A typical molding powder composition was :

		gms	phr
Resin (300 mesh pass)	:	25.0	100
Filler (60 mesh pass)	:	27.5	110
Hexa (Finely powdered, dry)	:	2.0	8
CaO (Finely powdered)	:	0.5	2
Stearic Acid	:	0.5	2

The above mixture was ball milled in a mild steel jar on a rubber roll mill using ceramic balls at room temperature for 24 hours and used to prepare the tensile test specimens.

7.3 COMPRESSION MOLDING

When heat and pressure are applied to a thermosetting molding material three processes occur : melting, flowing and gelling. The viscosity change during these phases is a complicated function of the temperature, the time or curing rate and the shear rate. The theoretical treatment of the rheology of thermosets[188,189] is consider-

ably more difficult than that of thermoplastic flow because the time is an additional and essential variable due to the curing reaction occuring simultaneously. At first the resin softens under the influence of temperature and viscosity is reduced. Once the cross-linking reaction is initiated with increasing temperature the viscosity increases. The viscosity also depends upon the shear rate that is thermosetting molding compounds exhibit non-Newtonian flow. Constant flow parameters are essential for easy production. Also the flow depends upon the resin content and its reactivity, the type and amount of the fillers, the lubricants, the free phenol content and on the content of humidity. Thus, all these factors reflect in selecting the compression molding temperatures and pressure. After conducting several trial experiments one can finalise the molding cycle to yield a good quality molded specimens. The most important components of the processing economy are the degree of automation and the cycle time[190]. The molding time is composed of the heating time to mold temperature and the time required for the chemical reaction. Since the thermal conductivity of the molding

compounds is relatively low, the heating time is the dominant part. It is therefore reasonable to reduce the molding cycle by preheating the compound outside of the mold upto a temperature just below that of the mold.

The compression molding was carried out in a mild steel three piece strip mold fitted with punch and guiding pins on an electrically heated Carver make hydrolic compression molding press (model C). The dimensions of the molded specimen was 62.5 mm length, 12.5 mm width and 1.5 mm thickness. In actual molding, the empty mold was preheated for 10 min at 140°C. Then the cavity was filled with preweighed quantity of molding powder and the mold was properly closed. The mold was kept at 140°C for 15 min. under 17.1-18.6 kg/cm^2 pressure for the resin to melt and wet the filler. The temperature was then raised to 160°C and kept for 15 mins to let the resin to flow uniformly in the cavity. Finally the temperature was raised quickly to 200°C and kept for varied times of 30 and 90 minutes. After the cycle was completed, the mold was cooled to room temperature

and the molded piece was taken out for testing. Thus, the following curing cycle was followed after preliminary molding trials :

Melting	:	140°C/15 mins
Flow	:	160°C/15 mins
Curing	:	200°C/30 and 90 mins
Molding pressure:		17.1-18.6 kg/cm^2

7.4 TENSILE STRENGTH MEASUREMENTS

The tensile testing was carried out at room temperature on an Instron Tensile Tester, Model 1100 using a 500 kg load cell at 0.05 mm/min. cross-head speed. The distance between the jaws was kept 28 mm and the chart speed was 5 mm/min. The graph of load versus elongation was obtained which was converted into a stress-strain curve using equations (1) and (2).

7.5 RESULTS AND DISCUSSION

The tensile strength of PC resins prepared from distilled crotonaldehyde and PF novolak resins were calculated and compared. As discussed in Chapter 5, the resins both PCD and PF, show softening temperature range in the temperature range of 80° to 120°C wherein the resins change state from amorphous solids to mobile liquid. Secondly the actual molding cycle temperatures were finalised by taking into account Differential Thermal Analysis (DSC) data. The DSC scan gives a measure of the difference in the rate of heat absorption by the sample with respect to an inert reference (maintained at the same temperature) as the temperature is raised at a constant rate. A recorder prints out the data as a trace of dH/dt versus temperature. The integral of this function is the reaction enthalpy. The difference between the heat development H of an uncured sample and a partly cured sample is the measure of the degree of cure[191]. In the absence of a chemical reaction, a second order transition is indicated as a discontinuity in the thermogram caused by change in the specific heat. By assumption of a constant specific heat, further kinetic

data, for instance, cure rate and activation energy can be approximately determined[192-194]. As phenolic resins cure, endothermic processes (evaporation of water, aldehyde and ammonia) superimpose the exothermic chemical reactions, thus complicating the evaluation considerably. However, techniques have been developed for conducting DSC under pressure. We have studied the DSC for finalisation of the molding cycle only. The melting and curing peak temperatures of PCD 9 resin, resin with different amounts of hexa, resin and hexa mixture with CaO and PNF is shown in Table 23. The DSC scans presented in Figure 26 show the melting as well as curing peaks which shift to higher temperature with increasing amount of hexa. The DSC scans of the molding powder are illustrated in Figure 27. It was observed that the melting peak is not clearly seen for molding powder and the curing peak also broadens probably because of the higher amount of fillers in the formulation. Table 23 summarizes the melting peak temperatures for PCD 9 resin compounds. The absence of a curing peak at low temperature means that the resin is thermoplastic and would require additional cross-linking agent for curing. The melting and curing

peak temperatures of the PCD 9 resin with different amounts of hexa, given in Table 23, show an increase in melting point with increasing hexa. The compression molding temperatures were finalised on the basis of the DSC data.

Commercially PF novolak resins are cured by addition of 8-15 weight % hexa. It was observed in the DSC studies that there is little difference in the curing peak temperature at 4, 8 and 12 weight % hexa level. Therefore, the loading of hexa was fixed at 8 weight % for preparation of the molding powder. Also the curing rates of novolak resins with hexa are enhanced by the addition of a base to neutralise the acid catalyst. Two weight % of CaO was added as the neutraliser in the molding powder. Addition of CaO has no effect on the melting as well as curing temperatures. With reference to the TG and DSC data temperature profile for compression molding was defined as written in Section 7.3.

The curing temperature and time employed for compression molding process needs some comments. Commercially, PF novolak resins are cured around 160°-180°C for 30-60 sec. only. In the present work, we have used curing temperature to be 200°C

and curing time to be 30 and 90 minutes. As discussed in Chapter 4, it was observed that PC resins after curing with hexa for 15 minutes give thermoplastic material which can be post-cured at 200°C by heat treatment into a thermoset. So the curing temperature used was 200°C. Secondly, in order to obtain a fully thermoset product after molding, the cycle was prolonged for 30 and 90 minutes. Since the structure of the PC resins includes bulkier groups the reaction with hexa may be decelerated due to steric hindrance. A longer curing cycle would ensure completion of the thermoset network formulation. A number of compression moldings using the above mentioned temperature and time cycle were run at variable pressures from 6.4 to 21.4 kg/cm^2. By observing the finish and physical nature of the molded piece a pressure of 17.1 - 18.6 kg/cm^2 was finalised for the compression molding.

In order to evaluate the tensile strengths, PCD resins (PCD 7, PCD 9, PCD 10 and PCD 12) with varying the molar fraction of crotonaldehyde were used. For comparison purpose, PF resins with varying formaldehyde mole fractions (PF 1:0.45, PF 1:0.60 and PF 1:0.75) were used as 'control'.

In the tensile testing both the PC and PF resins behaved similarly. The specimens exhibited plastic flow and strain hardening for both the resin types except PCD 12 resin. The stress-strain curves for the PCD and PF resin samples cured for 90 minutes are illustrated in Figure 28. All the curves exhibit three regions. In the first region, the deformation is elastic with the stress proportional to the strain upto yield point. Above the yield point the stress remains constant with increasing strain, constituting the 'plastic flow' region signifying stretching of polymer chains in the direction of elongation. Linear stress-strain behaviour is seen again above a certain strain till break point due to the oriented polymer chains. This third region is termed as 'strain hardening' region. Only in the case of PCD 12 resin with the highest amount of aldehyde fraction strain hardening was not observed. The occurance of plastic flow and strain hardening indicates that the resins are not fully cross-linked. The plastic flow stress represents the stress required to uncoil the randomly oriented polymer chains and getting them oriented in the direction of stress. As discussed in Chapter 4,

the molecular structure of PC resins is bulky and the molecular weights are low as compared to PF novolak resins. Due to the bulkiness, the cross-linking reaction is somewhat hindered. The side chain or bridging moiety in the case of PC resins consists of four carbon atoms which would sterically hinder the cross-linking and also lead to plasticizing effect. All these factors influence the strain hardening phenomena and the tensile strength of the polymer.

The stress-strain curves of PCD resins cured for 30 and 90 minutes showed little difference. For comparision purpose, the specimens cured for 90 minutes for both PC and PF resins were tested.

The stress-strain curves are shown in Figure 29 (for PCD 7 resin), Figure 30 (for PCD 9 resin), Figure 31 (for PCD 10 resin), Figure 32 (for PCD 12 resin) and Figure 33 (for PF novolak resins).

The tensile stress at yield and break points are represented in Table 24 (for PCD resins) and Table 26 (for PF resins). For PCD resins the tensile stress

at yield ranges between 250 to 370 kg/cm^2 for specimens cured for 30 as well as 90 minutes. Whereas for PF resins, it ranges from 360-450 kg/cm^2. In case of PCD resins the stress at yield reaches to a maxima at aldehyde mole fraction of 0.43 for samples cured for 30 and 90 minutes while in case of PF resins no specific relation is observed with aldehyde mole fraction (see Figure 34).

In case of PF resins, the tensile stress at break increased linearly with amount of formaldehyde in the polymer while in case of PCD resins it shows a maxima at crotonaldehyde mole fraction of 0.43 (see Figure 35).

In general, no specific dependence of yield stress on mole fraction of aldehyde in the polymer was observed in the case of both PC and PF resins. The yield stress of PF resin is higher than that for corresponding PCD resin, at a fixed phenol to aldehyde mole ratio, by about 25%. The tensile strength at break point for PF resin was quite higher than that of corresponding PCD resin.

The strain data are summerized in Table 25 for PCD resins and Table 26 for PF resins. In all the resins under study, the plastic flow region is almost in the same strain range irrespective of the molar fraction of aldehyde and the curing time. The strain was about 6.0×10^{-3} at yield point, 10.5×10^{-3} at onset of strain hardening and about $16\text{-}17 \times 10^{-3}$ at break.

The effect of mole fraction of aldehyde on the strain for PCD resins cured for 30 minutes is shown in Figure 36. The strain at onset of strain hardening remained almost constant irrespective of the molar fraction of aldehyde whereas at yield and break point the strain depends on the molar fraction of aldehyde. At yield point the strain reaches a minima at crotonaldehyde mole fraction of 0.48 whereas at break point upto a crotonaldehyde mole fraction of 0.43 it remains constant and then further decreases with increasing aldehyde content.

Figure 37 shows the strain of specimens cured for 90 minutes as a function of aldehyde mole fraction. The strain in case of the PF resins show similarity

at all the three stages with respect to formaldehyde content in the resin. Whereas in case of PCD resins, at yield point and onset of strain hardening the strain reaches a minima at crotonaldehyde mole fraction of 0.43, similar to that observed in specimens cured for 30 minutes. But at break point the reverse is observed which is unexplainable.

The percent elongation observed was in the range of 1.5 to 2% for the resins under study. This low percent of elongation is the characteristic of the thermosetting resins.

The non-existance of strain hardening phenomena in the case of PCD 12 resin could be explained on the basis of the chemical structure and the mole ratio of phenol to aldehyde in the resin. For PCD 12 resin, the phenol to crotonaldehyde mole ratio in the polymer is highest which would lead to bulky molecular structure. The number average molecular weight of PCD 12 resin was found to be 562. This means that in PCD 12 resin the number of repeating units in the polymer backbone would be very low as compared to other PCD resins.

Similarly, due to the highly sterically hindered structure, the extent of cross-linking would be low. Thus it may be possible that uncoiling of the randomly oriented polymer chains preceeds the breaking of the specimen at very low applied force.

The moduli were determined for both the elastic deformation before yield point and in the strain hardening region (see Table 27). The initial modulus for specimens curved for 90 minutes for PF resins ranged between 73-80 x 10^3 kg/cm^2 whereas for PCD resins it ranged from 32 to 82 x 10^3 kg/cm^2. The modulus in the strain hardening region was 89 to 112 x 10^3 kg/cm^2 for the PF resins and 42 to 88 x 10^3 kg/cm^2 for PCD resins. The initial modulus for PCD resins cured for 30 minutes was slightly higher than the modulus in the strain hardening region whereas the reverse was observed for samples cured for 90 minutes in the case of both PC and PF resins.

Figure 38 shows the effect of aldehyde mole fraction on the initial modulus. In PCD resins, the initial modulus showed a maxima at a crotonaldehyde mole fraction of 0.43 for samples cured for 30 and 90 minutes whereas

for PF resins it increased linearly with the increase in formaldehyde mole fraction. The modulus in the strain hardening region for PCD resins again showed a maxima at crotonaldehyde mole fraction of 0.43. But in case of PF resins it increased upto a formaldehyde mole fraction of 0.38 and then decreased (see Figure 39).

Thus the initial modulus as well as modulus in the strain hardening region depends on the molar composition of the resin in case of PCD resins irrespective of the curing time, the optimum mole fraction of crotonaldehyde being 0.43.

TABLE 23

DSC TEMPERATURE DATA

Formulations	Melting Peak temperature, °C	Curing peak temperature, °C
PCD 9	78	-
PCD 9 + 4% hexa	84	164
PCD 9 + 8% hexa	86	165
PCD 9 + 12% hexa	89	168
PCD 9 + 8% hexa + 2% CaO	86	165
PCD 9 + 8% hexa + 2% CaO + 50% PNF	Not clear	176

TABLE 24

TENSILE STRESS DATA FOR PCD RESINS

Resin code	Mole fraction of aldehyde	Tensile stress, kg/cm^2			
		At yield point		At break point	
		Curing time, mins.		Curing time, mins.	
		30	90	30	90
PCD 7	0.27	236±10	250±9	520±35	463±29
PCD 9	0.43	400±18	372±10	793±61	952±30
PCD 10	0.48	288±3	288±15	440±57	269±27
PCD 12	0.57	220±0	270± 0	236±2	293±0

TABLE 25

TENSILE STRAIN DATA FOR PCD RESINS

Resin code	Mole fraction of aldehyde	Tensile strain x 10^{-3}					
		At yield point		At onset of strain hardening		At break point	
		Curing time, mins		Curing time, mins		Curing time, mins	
		30	90	30	90	30	90
PCD 7	0.27	6.5±1.1	5.6±1.1	11.1±0.9	10.4±0.7	17.3±1.5	14.7±0.7
PCD 9	0.43	5.9±1.0	4.5±0.7	11.1±1.1	9.5±0.8	17.0±1.2	16.1±0.1
PCD 10	0.48	5.4±0.0	8.5±0.9	10.0±0.0	11.8±1.0	13.0±0.0	16.1±1.7
PCD 12	0.57	7.5±1.6	8.4±0.0	10.7±0.1	-	12.0±0.5	11.4±0.0

TABLE 26

TENSILE STRESS AND STRAIN DATA FOR PF RESINS

Resin code	Mole fraction of aldehyde	Curing time, 90 mins				
		Tensile stress, kg/cm^2		Tensile strain x 10^{-3}		
		At yield point	At break point	At yield point	At onset of strain hardening	At break point
PF (1:0.45)	0.29	387±12	1136±82	5.3±1.2	11.3±0.6	19.7±0.3
PF (1:0.60)	0.38	365±15	1184±75	4.7±1.1	9.9±0.9	17.2±0.6
PF (1:0.75)	0.43	443±21	1277±138	5.5±1.6	9.9±0.1	17.6±2.3

TABLE 27

MODULUS DATA FOR THE RESINS

Resin code	Mole fraction of aldehyde	Curing time, mins.			
		Initial modulus $\times 10^3$, kg/cm^2	Modulus in strain hardening region $\times 10^3$, kg/cm^2	Initial modulus $\times 10^3$, kg/cm^2	Modulus in strain hardening region $\times 10^3$, kg/cm^2
PCD 7	0.27	36.4	45.7	44.6	49.6
PCD 9	0.43	67.8	66.6	82.6	87.9
PCD 10	0.48	53.2	50.8	33.8	42.1
PCD 12	0.57	29.3	12.3	32.1	-
PF (1:0.45)	0.29	-	-	73.0	89.1
PF (1:0.60)	0.38	-	-	77.7	112.1
PF (1:0.75)	0.43	-	-	80.6	108.3

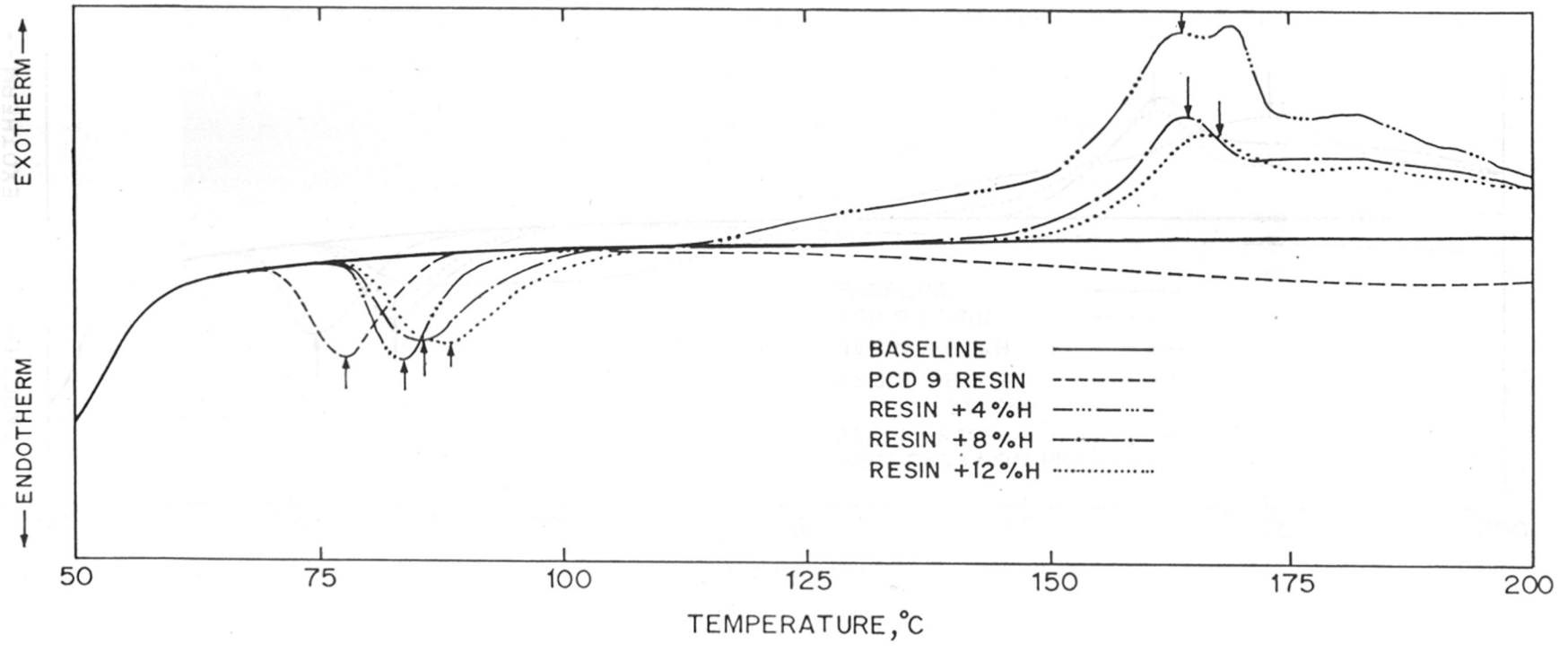


FIGURE 26: DSC SCANS OF RESIN WITH HEXA

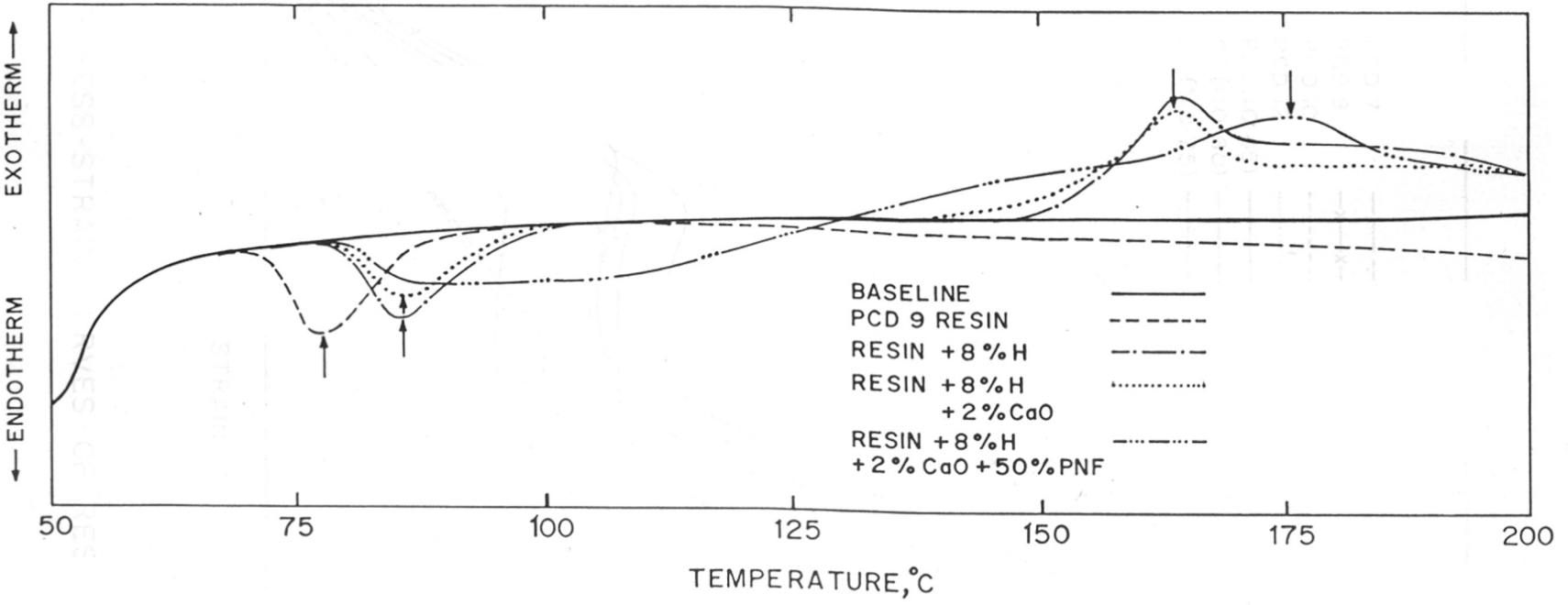


FIGURE 27: DSC SCANS OF RESIN, MOLDING COMPOSITION

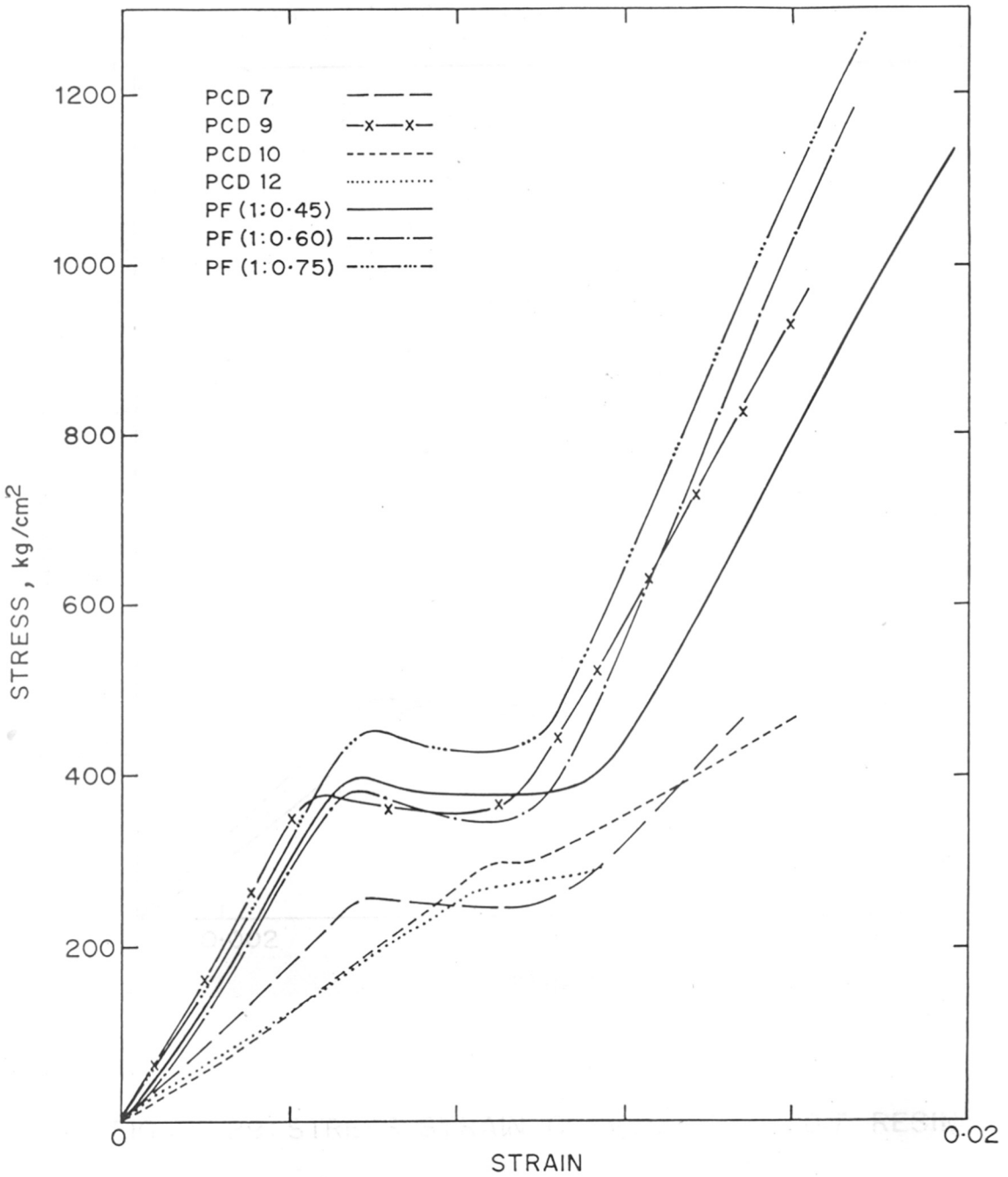


FIGURE 28 : STRESS-STRAIN CURVES OF RESINS CURED FOR 90 MIN

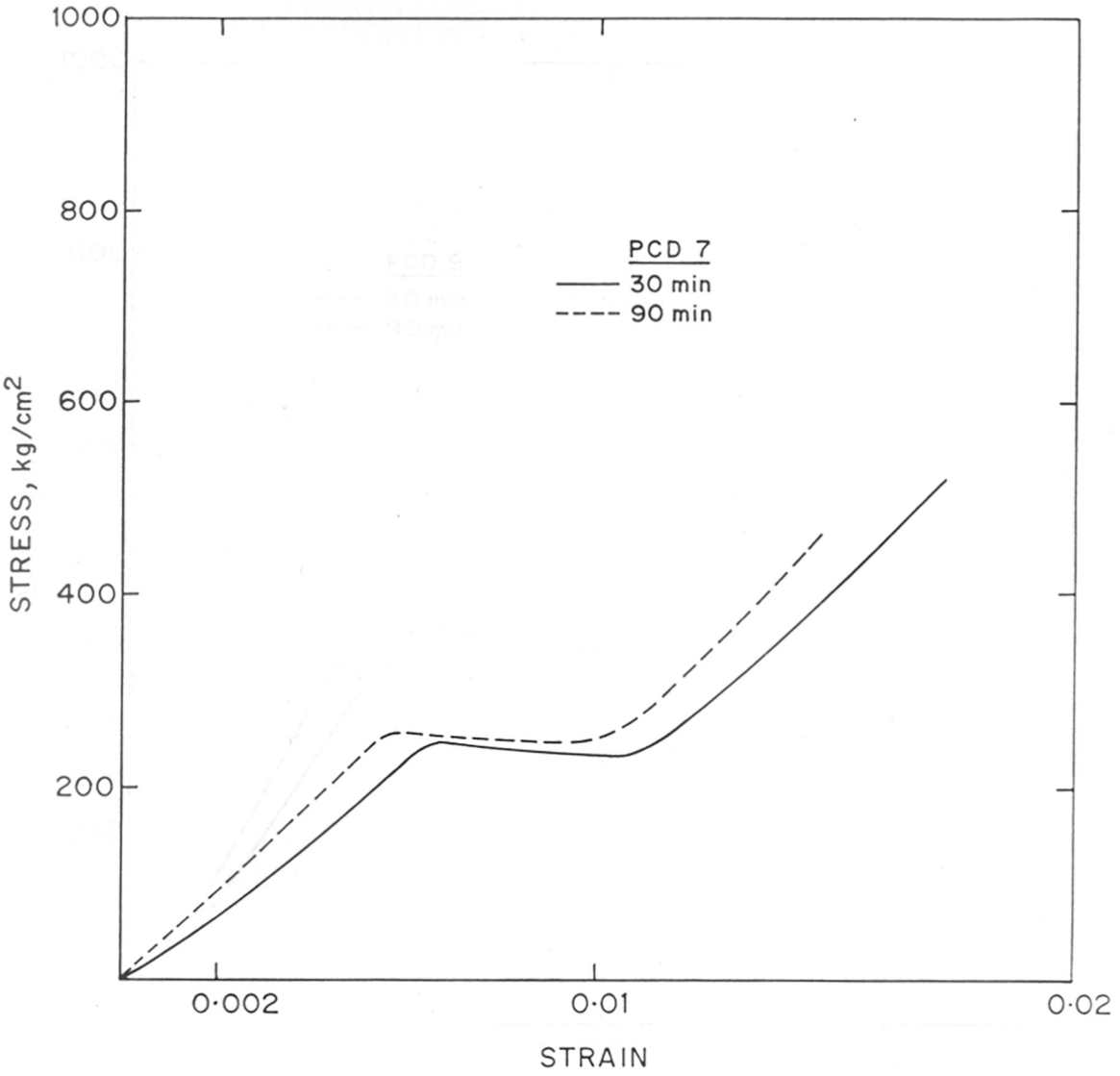


FIGURE 29: STRESS-STRAIN CURVES FOR PCD 7 RESIN

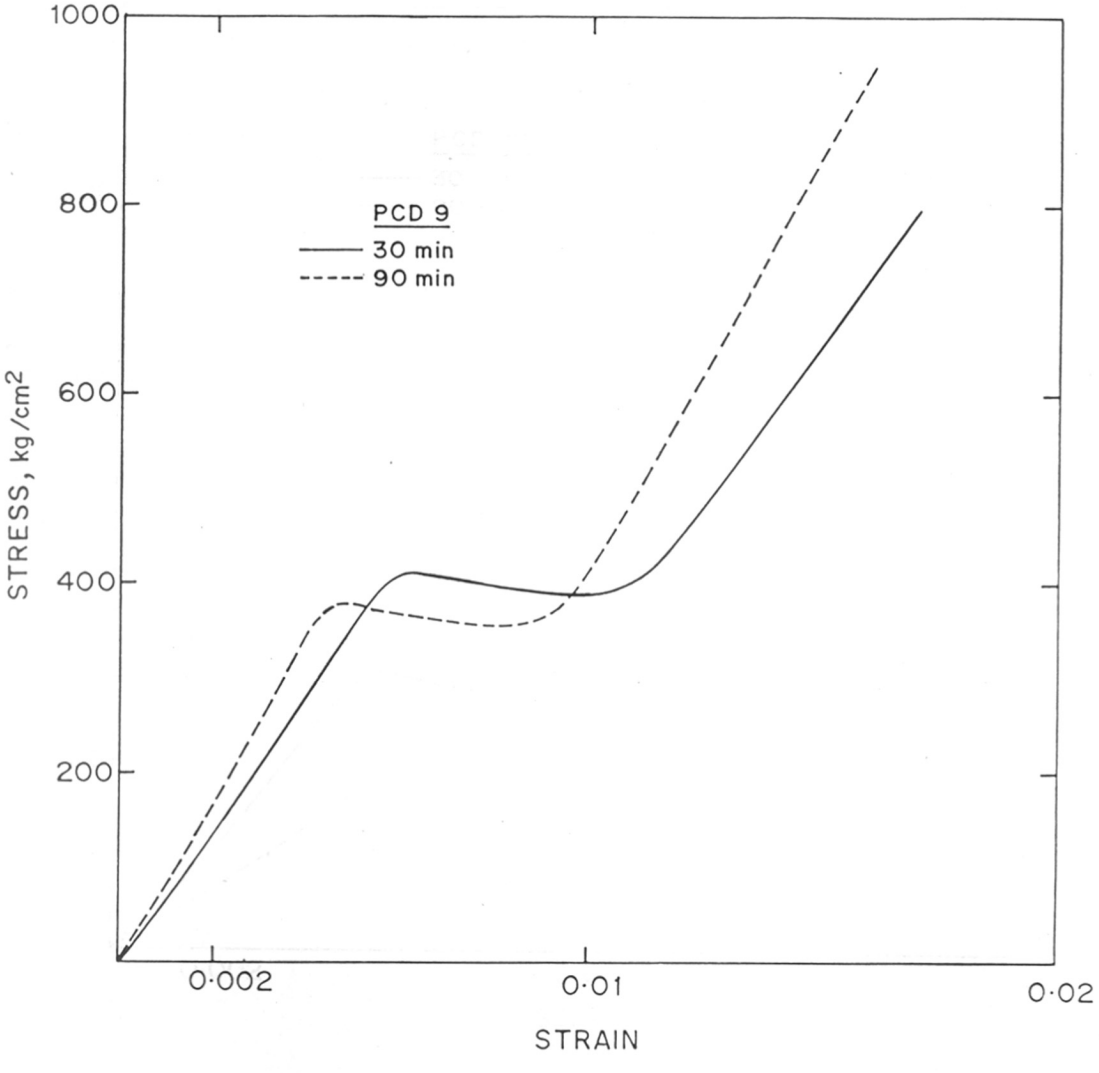


FIGURE 30: STRESS-STRAIN CURVES FOR PCD 9 RESIN

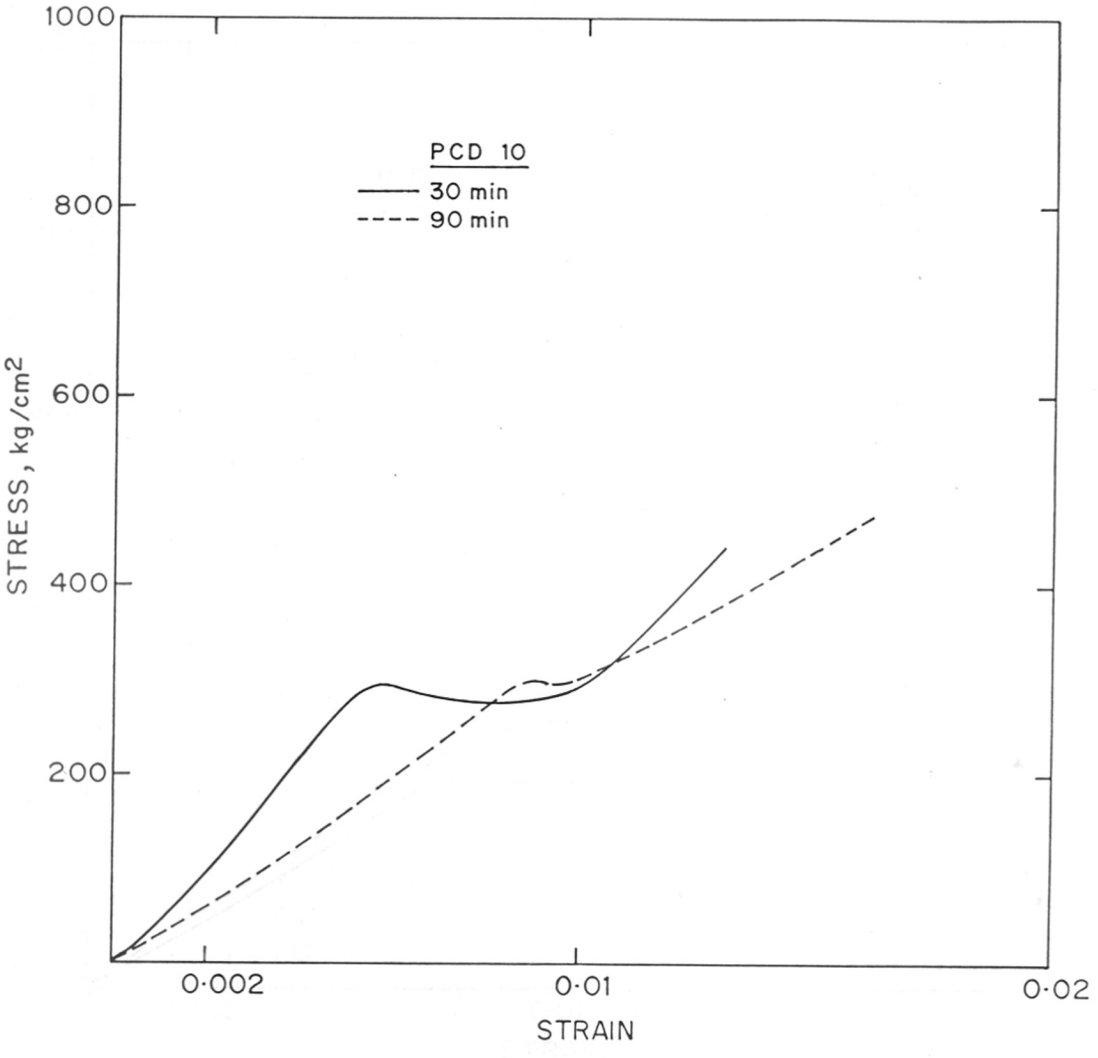


FIGURE 31 : STRESS - STRAIN CURVES FOR PCD 10 RESIN

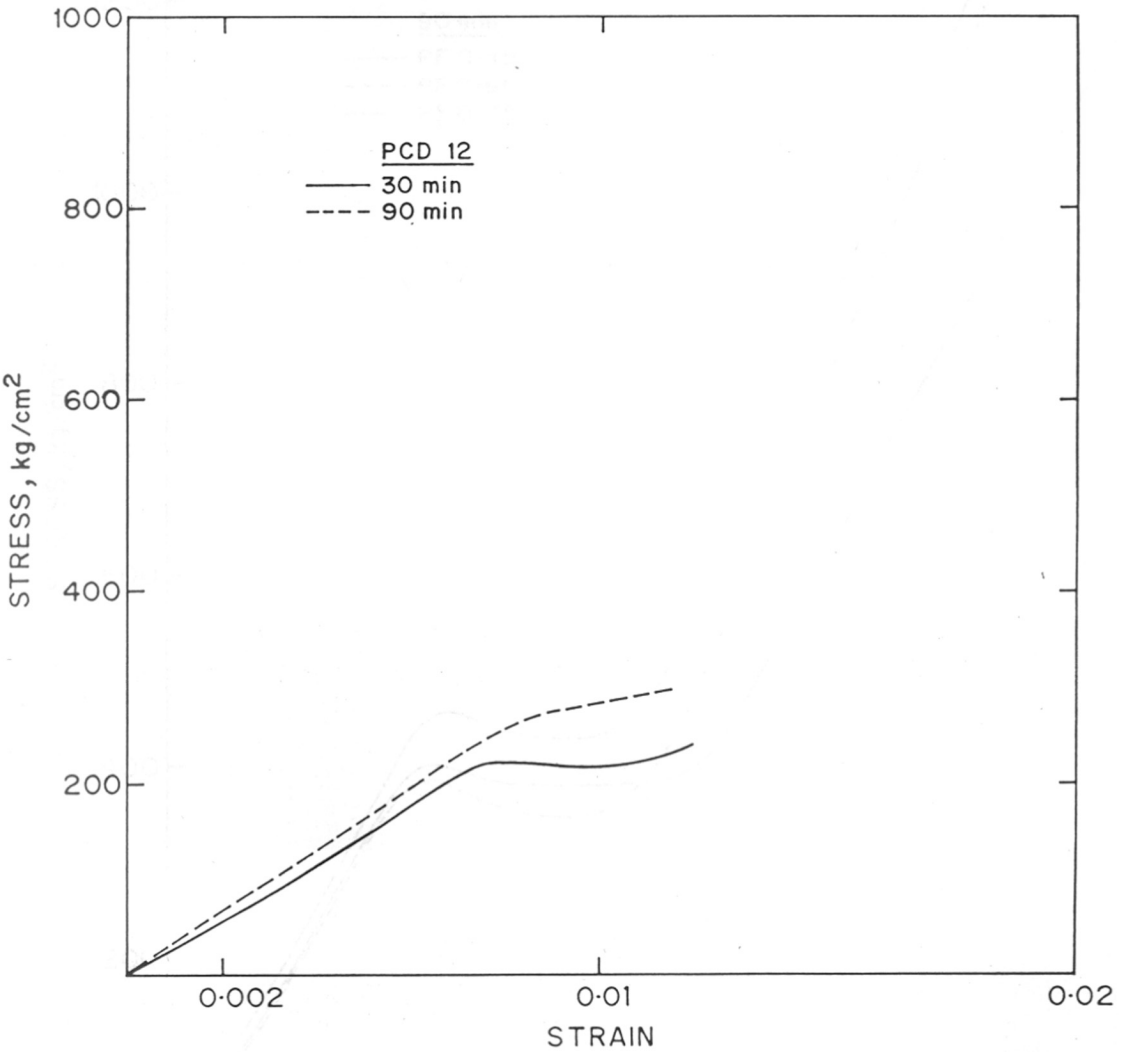


FIGURE 32: STRESS-STRAIN CURVES FOR PCD 12 RESIN

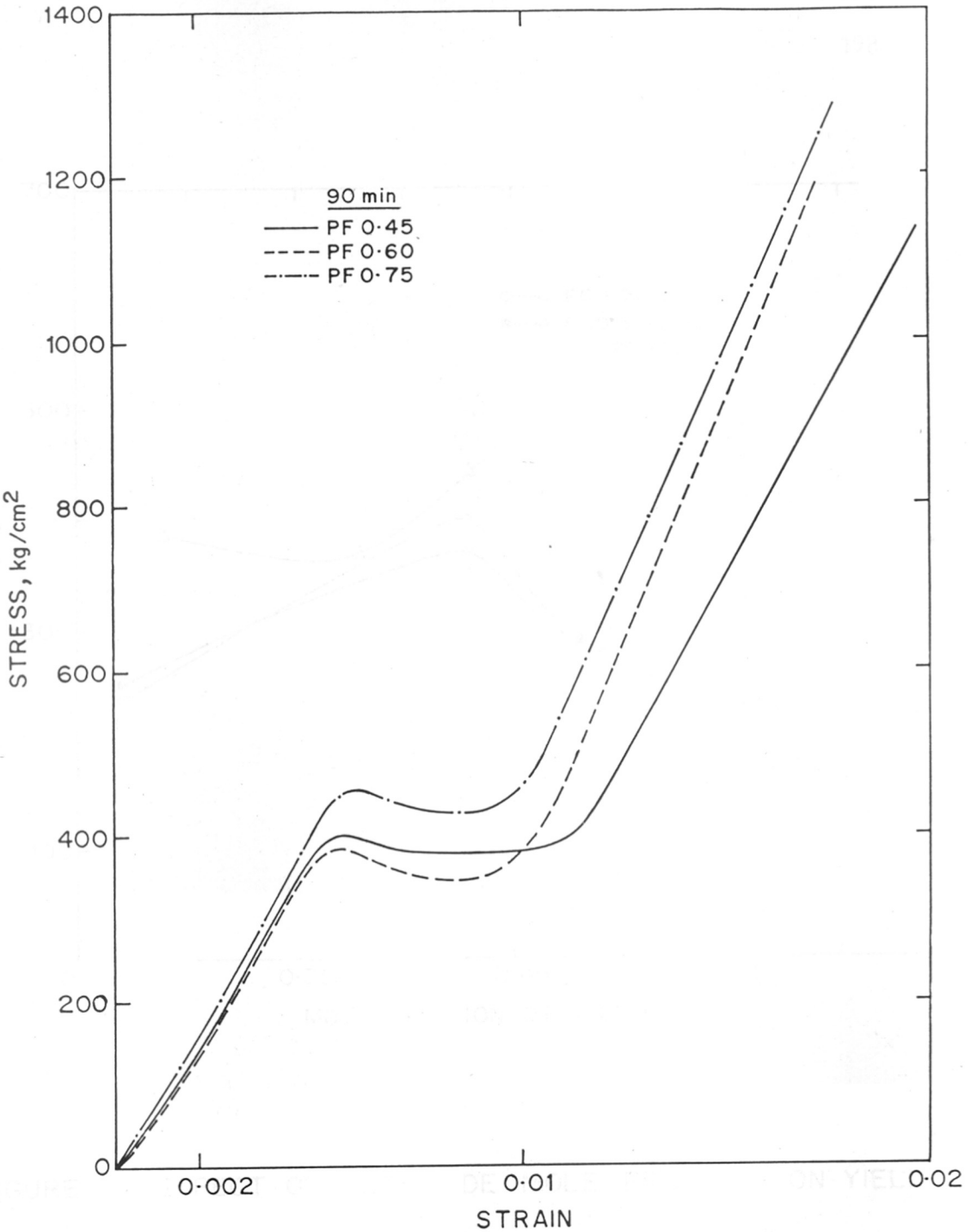


FIGURE 33: STRESS-STRAIN CURVES FOR PF NOVOLAK RESINS

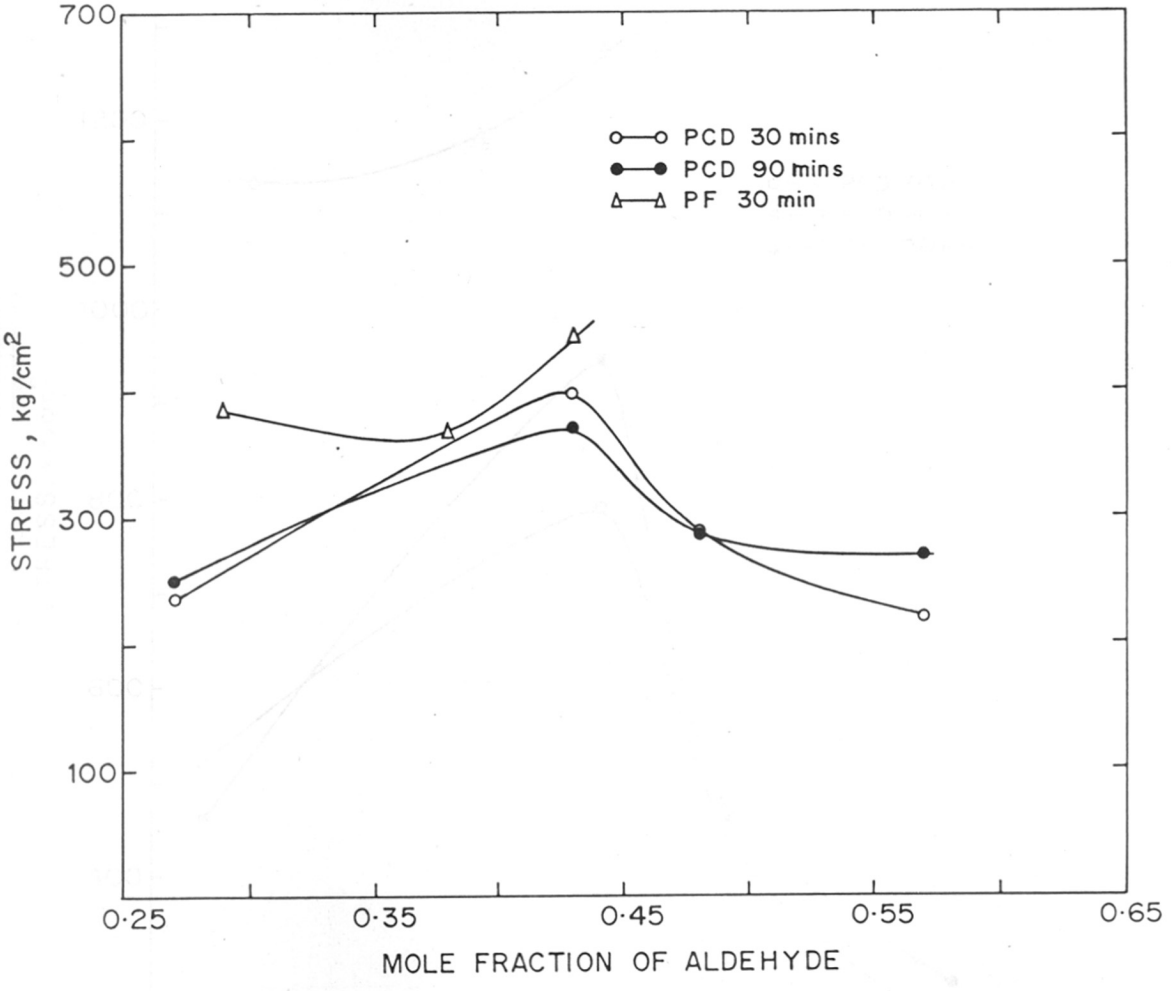


FIGURE 34: EFFECT OF ALDEHYDE MOLE FRACTION ON YIELD STRESS

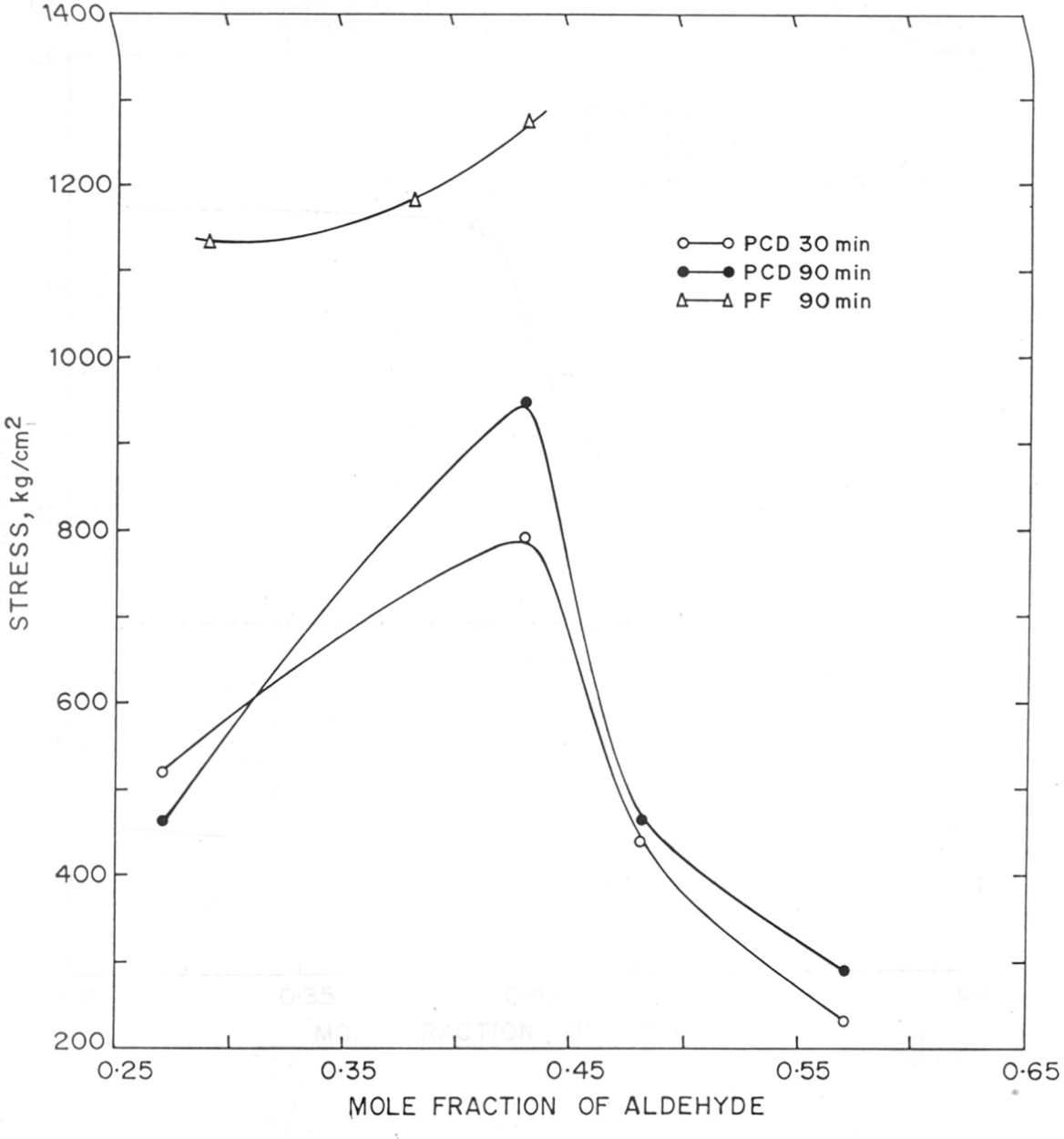


FIGURE 35: EFFECT OF ALDEHYDE MOLE FRACTION ON BREAK STRESS

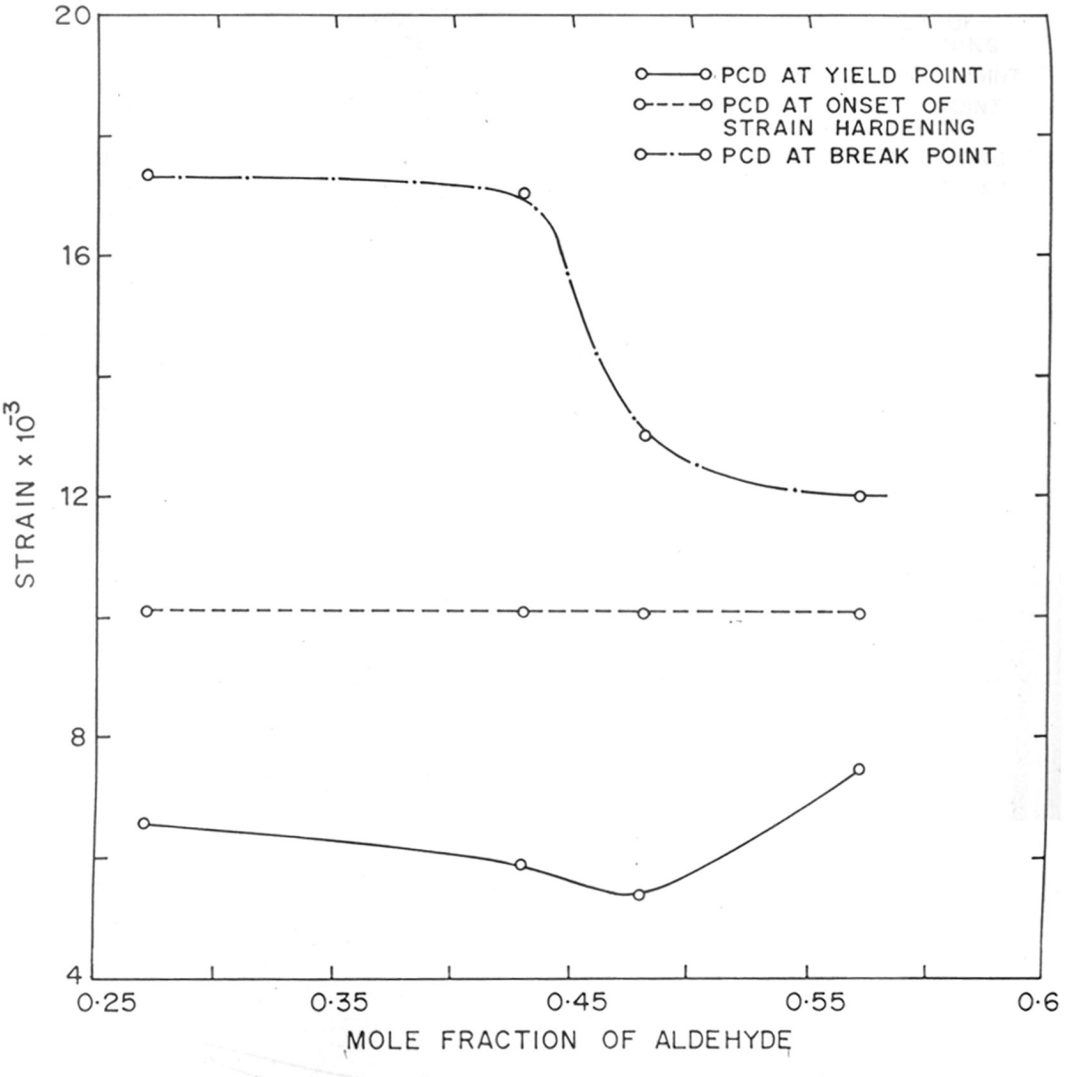


FIGURE 36: EFFECT OF ALDEHYDE MOLE FRACTION ON STRAIN FOR 30 MINUTES CURED SAMPLES

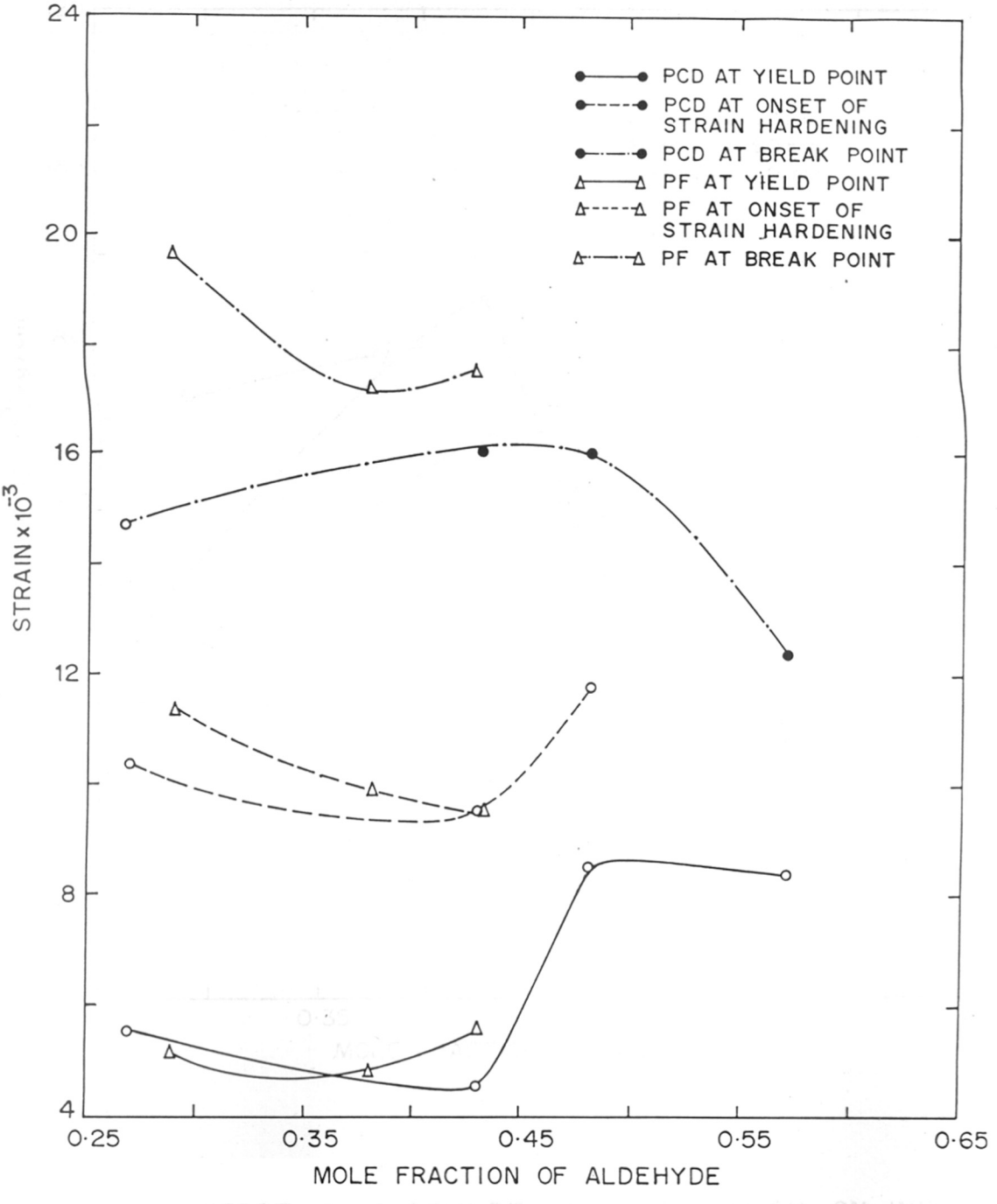


FIGURE 37: EFFECT OF ALDEHYDE MOLE FRACTION ON STRAIN FOR 90 MINUTES CURED SAMPLES

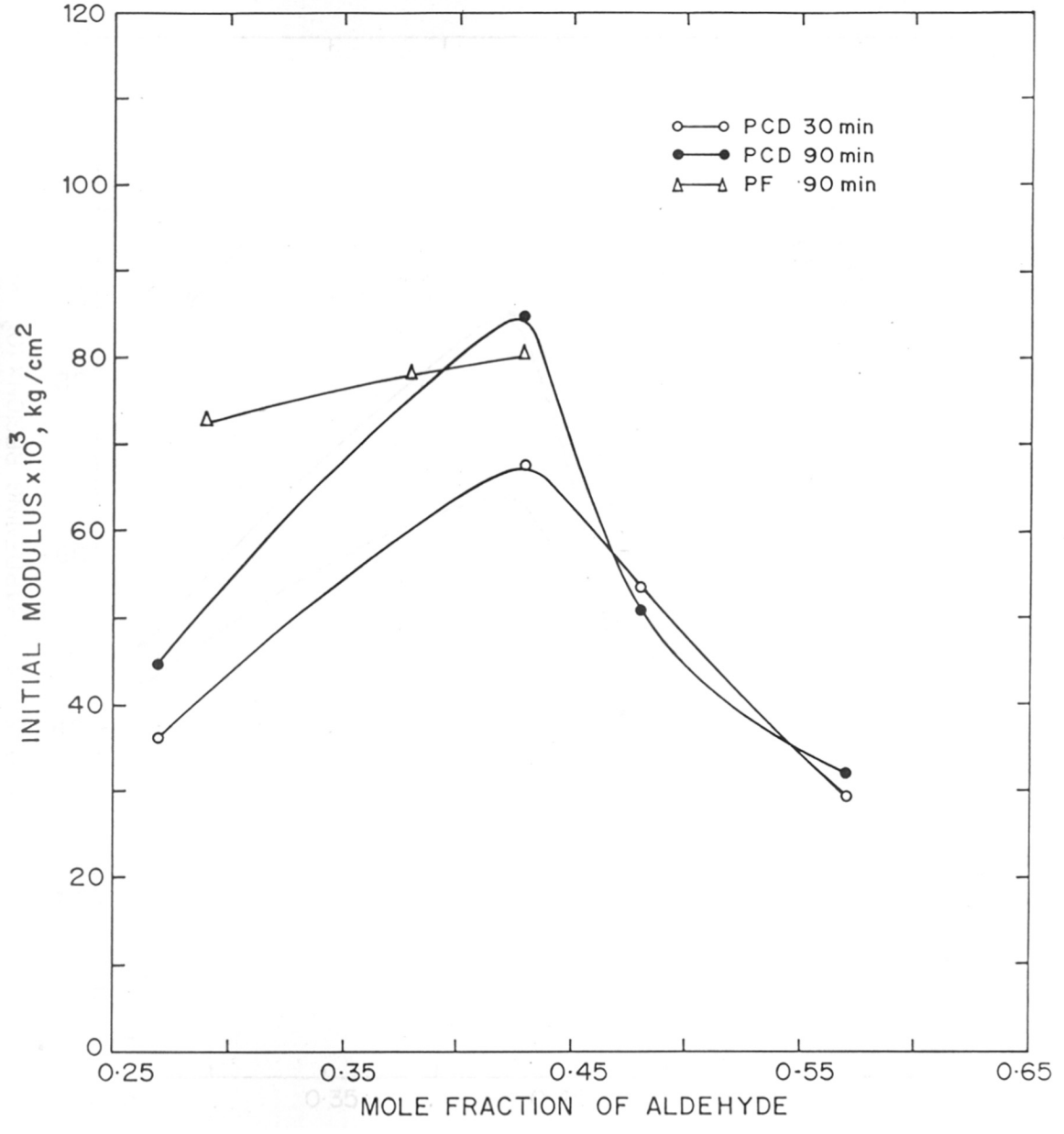


FIGURE 38 : EFFECT OF ALDEHYDE MOLE FRACTION ON INITIAL MODULUS

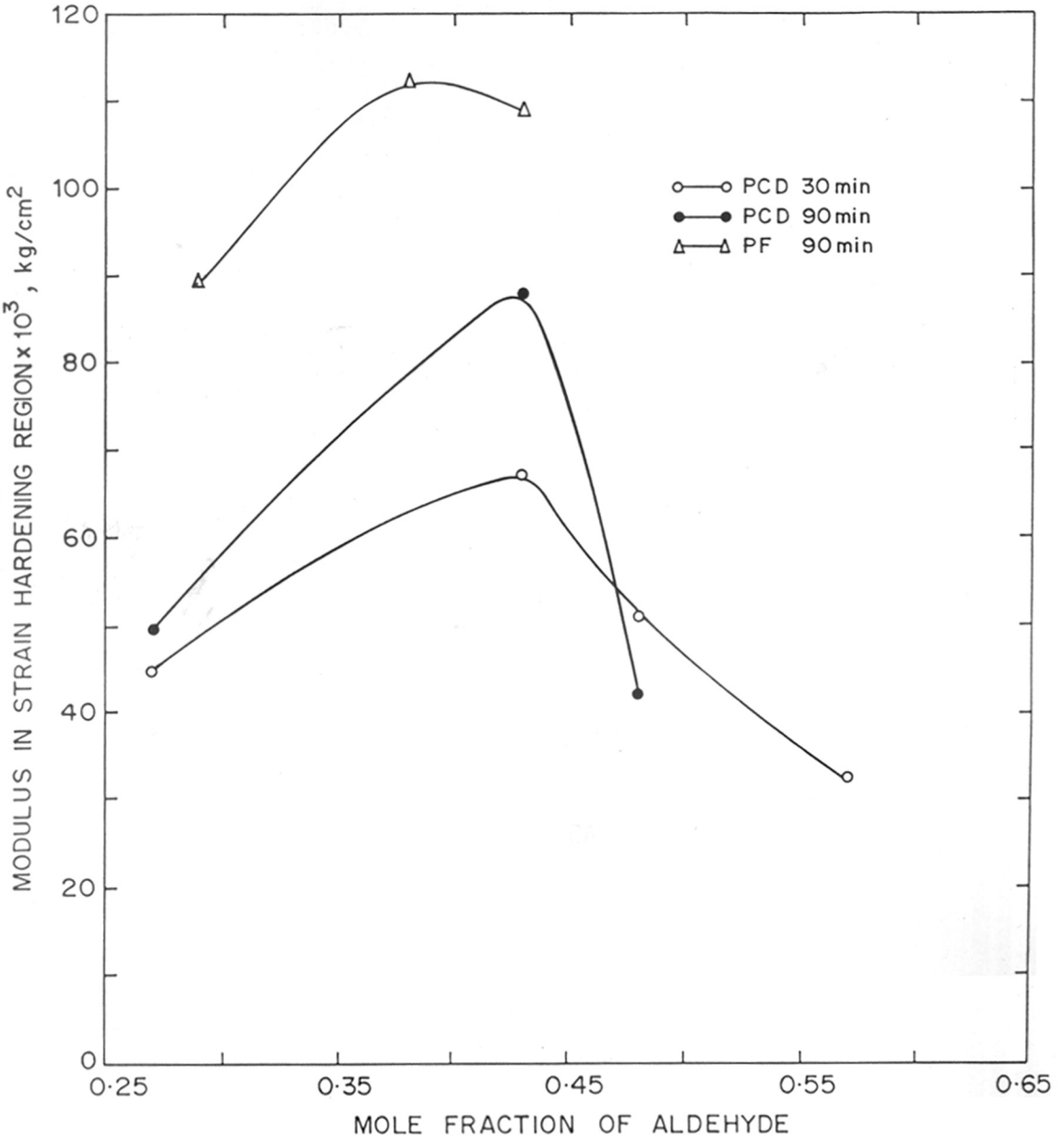


FIGURE 39: EFFECT OF ALDEHYDE MOLE FRACTION ON MODULUS IN STRAIN HARDENING REGION

CHAPTER 8

DYNAMIC MECHANICAL BEHAVIOUR

CHAPTER 8

DYNAMIC MECHANICAL BEHAVIOUR

8.1 INTRODUCTION

Polymeric materials are viscoelastic in nature and their mechanical properties exhibit a pronounced dependence on temperature and time. A number of books[195-198] have discussed both the theoretical and experimental aspects of the dynamic mechanical behaviour of polymers. The general principles as well as useful expirical generalizations of mechanical properties have been established in terms of viscoelasticity. In recent years the technology of investigating the dynamic mechanical properties of materials has advanced considerably.

The commonly used dynamic mechanical instruments measure the deformation of a material in response to a vibrational force. The dynamic modulus, the loss modulus and a mechanical damping or internal friction are determined from the measurements. The modulus indicates stiffness of the material, and it may be shear (torsional)

or tensile modulus depending upon the mode of deformation. The mechanical damping gives the amount of energy dissipated as heat during the deformation.

Polymers exhibit characteristics of both viscous liquids and elastic solids above the glass transition temperature. Elastic materials fully store mechanical energy put in during the deformation, whereas a viscous liquid dissipates the energy fully in flow. When polymeric materials are deformed, part of the energy is stored as potential energy and part of it is dissipated as heat. The energy dissipated as heat manifests itself as mechanical damping or internal friction. The investigation of the dynamic modulus and internal friction over a wide range of temperatures and frequencies has proven to be very useful in studying the structure of high polymers and the variations of properties in relation to end-use performance. Under service conditions, most materials are subjected to dynamic loading and not static stress conditions. Therefore, it is important to study the dynamic mechanical behaviour of engineering materials elucidating the relationship between the dynamic properties

and the structural parameters such as crystallinity, molecular orientation, molecular weight, degree of cross-linking, etc.

The viscoelastic response can be studied either by holding the time factor (frequency) constant and varying the temperture, or by keeping the temperature constant and scanning the frequency range. In usual practice, the viscoelastic response is studied at a fixed frequency over the desired temperature range. The frequency is then changed and the experiment is repeated.

The dynamic mechanical testing may be performed by many methods such as torsion pendulum, resonant rod, forced oscillation procedure, etc. The method used in this work involves torsional deformation type. The sample is held at two ends between clamps, one of which is connected to a stress guage and other to a strain guage. A sinusoidal twisting strain is then applied to the polymer sample at one end and the stress is recorded at the other end continuously[198]. In viscoelastic studies

of polymeric materials the method of sinusoidal excitation and response is very useful[199-201]. In this case the applied force and the resulting deformation both vary sinusoidally with time, the rate usually being specified by frequency 'f' in cycles/sec. or ($\omega = 2\pi f$) in radians/sec. For linear viscoelastic behaviour, the strain will alternate sinusoidally but will be out of phase with the stress[199,200]. This phase lag results from the time necessary for molecular rearrangements and is associated with the relaxation phenomena[202].

In tensile deformation, the dynamic stress, σ, and strain, ϵ, can be expressed as :

$$\sigma = \sigma_0 \sin(\omega t + \delta) \quad (1)$$

$$\epsilon = \epsilon_0 \sin(\omega t) \quad (2)$$

where

σ_0 = the stress amplitude,

ϵ_0 = the strain amplitude,

ω = the angular frequency, and

δ = the phase angle

Then,

$$\sigma = \sigma_0 \sin\omega t. \ \mathrm{Cos}\delta + \sigma_0 \mathrm{Cos}\omega t. \sin\delta \quad (3)$$

The stress can be considered to consist of two components, one in-phase with the strain ($\sigma_o \cos \delta$) and the other 90° out-of-phase ($\sigma_o \sin \delta$). When these are divided by the strain, we can separate the modulus into an in-phase (real) and out-of-phase (imaginary) component. These relationships are :

$$\sigma = \epsilon_o E' \sin \omega t + \epsilon_o E'' \cos \omega t \quad (4)$$

$$E' = \frac{\sigma_o}{\epsilon_o} \cos \delta \quad \text{and} \quad E'' = \frac{\sigma_o}{\epsilon_o} \sin \delta \quad (5)$$

where E' = the real part of the modulus, and

E'' = the imaginary part of the modulus.

The complex representation for the modulus can be expressed as follows :

$$\epsilon = \epsilon_o \, e^{i\omega t} \quad (6)$$

$$\sigma = \sigma_o \, e^{i(\omega t + \delta)} \quad (7)$$

Then,

$$\frac{\sigma}{\epsilon} = E^* = \frac{\sigma_o}{\epsilon_o} e^{i\delta} = \frac{\sigma_o}{\epsilon_o} (\cos \delta + i \sin \delta)$$

$$= E' + i E'' \quad (8)$$

A similar expression for shear modulus involving torsional deformation is :

$$G^* = G' + i G'' \quad (9)$$

where, G^* = the complex shear modulus,

G' = the real part of the modulus, or storage modulus, and

G'' = the imaginary part of the modulus or loss modulus,

and the phase angle 'δ' is given by :

$$\tan \delta = \frac{G''}{G'} \qquad (10)$$

G' is related to the potential energy stored by the material under deformation, whereas G" is associated with the dissipation of energy as heat, when the material is deformed. The tangent, $\tan \delta$, signifying internal friction or damping is referred to as the loss factor. A typical viscoelastic spectrum is shown in Figure 40. All the three parameters defined above are related to the molecular motions and therefore yield useful information about the molecular structure as well as performance of the material.

G' signifies the elastic modulus. Higher the value of G' more rigid is the material. The value of G' is dependent on the temperature. In the temperature sweep, beyond a particular temperature, the value

of G' starts falling rapidly. Above this temperature the material acts as a viscoelastic solid and it is likely to undergo irreversible deformation leading to plastic flow. The temperature at which G' starts falling rapidly, corresponds to the maximum service temperature under dynamic loading. Thus, the variation of G' with the temperature signifies the thermochemical response of the material.

G" signifies the viscous component of the material. The onset of molecular motions leading to energy dissipation is reflected in the form of a peak in the G" value versus temperature. The area under the peak corresponds to the energy dissipated by molecular motions. Thus, greater the area under the peak more would be the impact strength and crack resistance of the material.

The curve showing variation of tan δ with temperature exhibits peaks corresponding to the unlocking of molecular motions. Thus, the transition temperatures at the onset of mobility of pendent groups, amorphous segments, unlocking of Van der Waals forces and glass transition temperature can be determined from the tan δ curve. The tan δ

curve also gives an information about the damping characteristics of the material. Greater the value of tan δ and area under the curve, greater is the damping ability of the material.

8.2 EXPERIMENTAL

The dynamic mechanical characteristics of the resins were investigated on a Rheometrics Dynamic Spectrometer, Model RDS - 7700. The compression molded specimens of the resin compounds were prepared as described in Chapter 7 section 7.3. The dimensions of the molded specimens were 62.5 mm x 12.5 mm x 1.5 mm.

The dynamic mechanical behaviour of PCD resins are compared with conventional PF novolak resins. PCD and PF resins with variable mole fraction of crotonaldehyde (PCD 7, PCD 9, PCD 10 and PCD 12) and formaldehyde (PF 1:0.45, PF 1:0.60 and PF 1:0.75), respectively, in the resin are used for study. The samples were subjected to a frequency sweep between 1 to 1000 radians/sec. at room temperature (25°C) and to a temperature sweep between 30° to 250°C at 100 radians/sec.

8.3 RESULTS AND DISCUSSION

Four PCD and three PF resins, same as those used for tensile measurements, were used for the evaluation of dynamic mechanical behaviour.

The specimens were subjected to a frequency sweep between 1 to 1000 radians/sec. at room temperature (25°C). Figures 41 and 42 depict the dependence of storage modulus on the frequency for the different PCD and PF resins respectively. The storage modulus, G', remains almost unchanged over this frequency range for both the types of phenolic resins. However, the mole ratio of phenol to aldehyde seems to affect the storage modulus. PCD resins with a crotonaldehyde mole fraction of 0.4 to 0.5 in the polymer showed the highest value, whereas in case of PF resins, the highest value of G' was exhibited by a resin with a mole fraction of formaldehyde of 0.38 in the polymer.

The loss modulus, G", however gradually decreases with increasing frequency as shown in Figure 43 for PCD resins and Figure 44 for PF resins. With increasing

frequency of deformation the time available for the polymer molecular motions is reduced, thereby decreasing the extent of energy dissipation. It is noted that the extent of the fall in the G" value is greater for the PCD resins as compared to the PF resins. This indicates that molecular mobility is restricted more in the PCD resins, with increasing frequency. The initial value of the loss modulus is in the range of 1.5 to 2.5 x 10^8 dynes/cm^2 for PCD resins and 0.9 to 2.0 x 10^8 dynes/cm^2 for PF resins.

All the phenolic resin samples were subjected to the temperature sweep between 30° to 250°C at 100 radians/sec. The temperature sweeps of PCD resins were compared with those of PF resins. Figures 45 and 46 show the effect of temperature on the storage modulus and loss modulus of PCD and PF resins respectively.

Table 28 summerizes the storage modulus data. It was noted from the plots and table that the storage moduli for the PCD resins are higher (initial value : 6 to 12.5 x 10^9 dynes/cm^2) than those of the PF resins (initial value : 3.5 to 8.5 x 10^9 dynes/cm^2) irrespective

of the temperature.

Figure 47 represents the effect of mole fraction of aldehyde on the initial value of the storage modulus and on G' value at elevated temperatures. It is observed that the G' values are markedly affected by the mole fraction of aldehyde in the polymer for both PCD and PF resins. Upto a temperature of 150°C, the G' values for PCD resins show a maxima at 0.48 mole fraction of crotonaldehyde in the polymer and 0.38 moles of formaldehyde in the polymer for PF resins. As discussed in previous chapter PCD resins follow different curing behaviour than PF resins, in the sense they remain thermoplastic even after curing with hexa upto 150°C. The semicured PCD resins grow in molecular weight and the softening temperature also increases, which indicate that only linear structural development has occured. The temperature at which G' starts deviating from the initial value corresponds to the upper temperature limit for the material in applications. With reference to table 28, PCD resins show higher temperature (around 185°-195°C) than PF resins (around 168°-172°C) indicating

improved thermochemical properties. It also indicates that the PCD resins are more brittle in nature.

The variation of loss modulus, G", with temperature at 100 radians/sec. in case of both PCD and PF resins can be seen from Figure 45 and 46 respectively. The transition temperatures of PCD resins are about 20°-30°C higher than those of PF resins, indicating that the PCD resins are more brittle than the PF resins. The peaks of both PCD and PF resins are broad.

The tan δ curves for the PCD and PF resins are shown in Figures 48 and 49 respectively. The variation of the tan δ peak temperature with mole fraction of the aldehyde is shown in Figure 50. It is seen that above a mole fraction of 0.43, the tan δ peak decreases with increasing aldehyde amount in the polymer, for the PCD resins. However in case of the PF resins, the tan δ peak temperature does not vary much with the aldehyde mole fraction.

In summary, the PCD resins exhibit improved thermochemical properties in terms of a higher end-use temperature under dynamic loading.

TABLE 28

STORAGE MODULUS DATA

Resin code	Mole fraction of aldehyde	Storage modulus at tempeature, °C					Temperature at deviation, °C
		Initial	100	150	200	250	
PCD 7	0.27	6.26×10^9	5.45×10^9	4.8×10^9	3.8×10^9	2×10^9	195
PCD 9	0.43	9.96×10^9	8.38×10^9	7.38×10^9	5.79×10^9	3×10^9	195
PCD 10	0.48	12.4×10^9	10.2×10^9	9.15×10^9	6.3×10^9	1.6×10^9	194
PCD 12	0.57	6.82×10^9	5.75×10^9	5.06×10^9	3.27×10^9	1×10^9	183
PF (1:0.45)	0.29	3.62×10^9	3.19×10^9	2.92×10^9	2×10^9	1×10^9	169
PF (1:0.6)	0.38	8.29×10^9	7.05×10^9	6.32×10^9	3.51×10^9	2×10^9	171
PF (1:0.75)	0.43	6.93×10^9	6.04×10^9	5.48×10^9	3.11×10^9	2×10^9	170

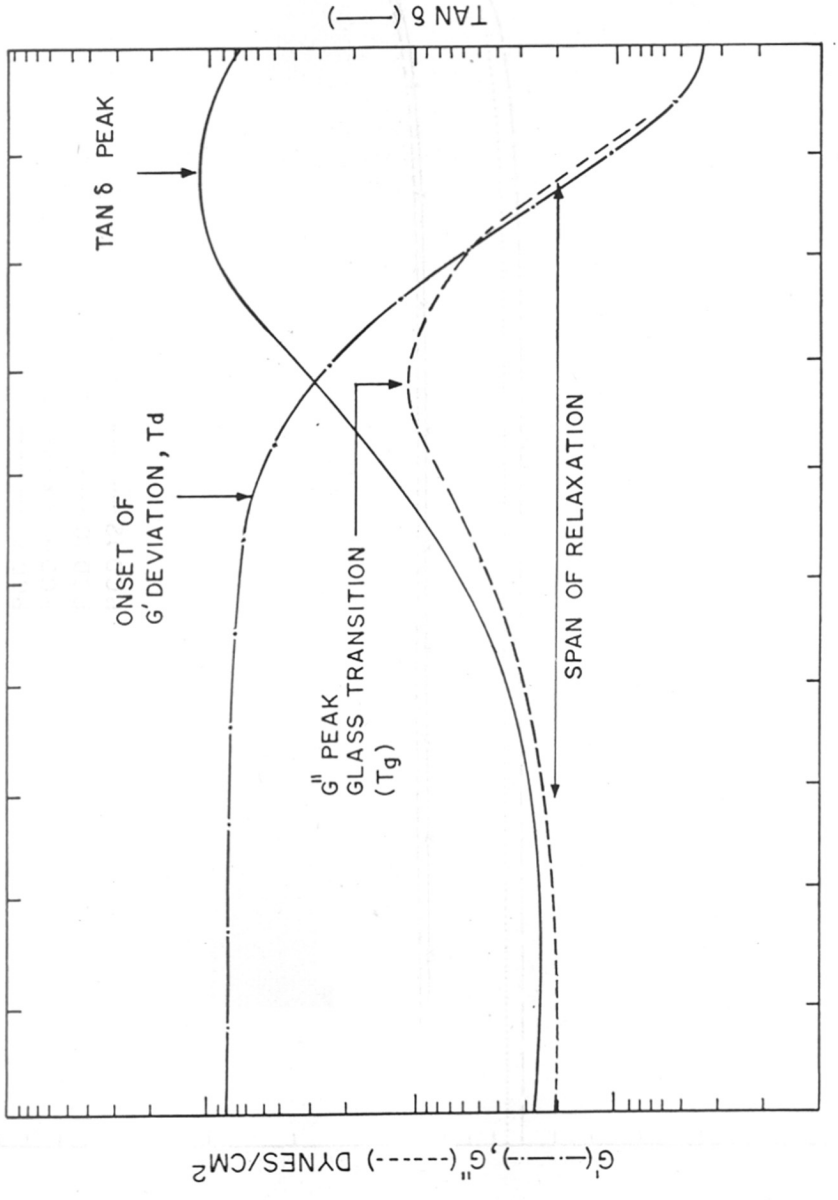


FIGURE 40: TYPICAL VISCOELASTIC SPECTRUM

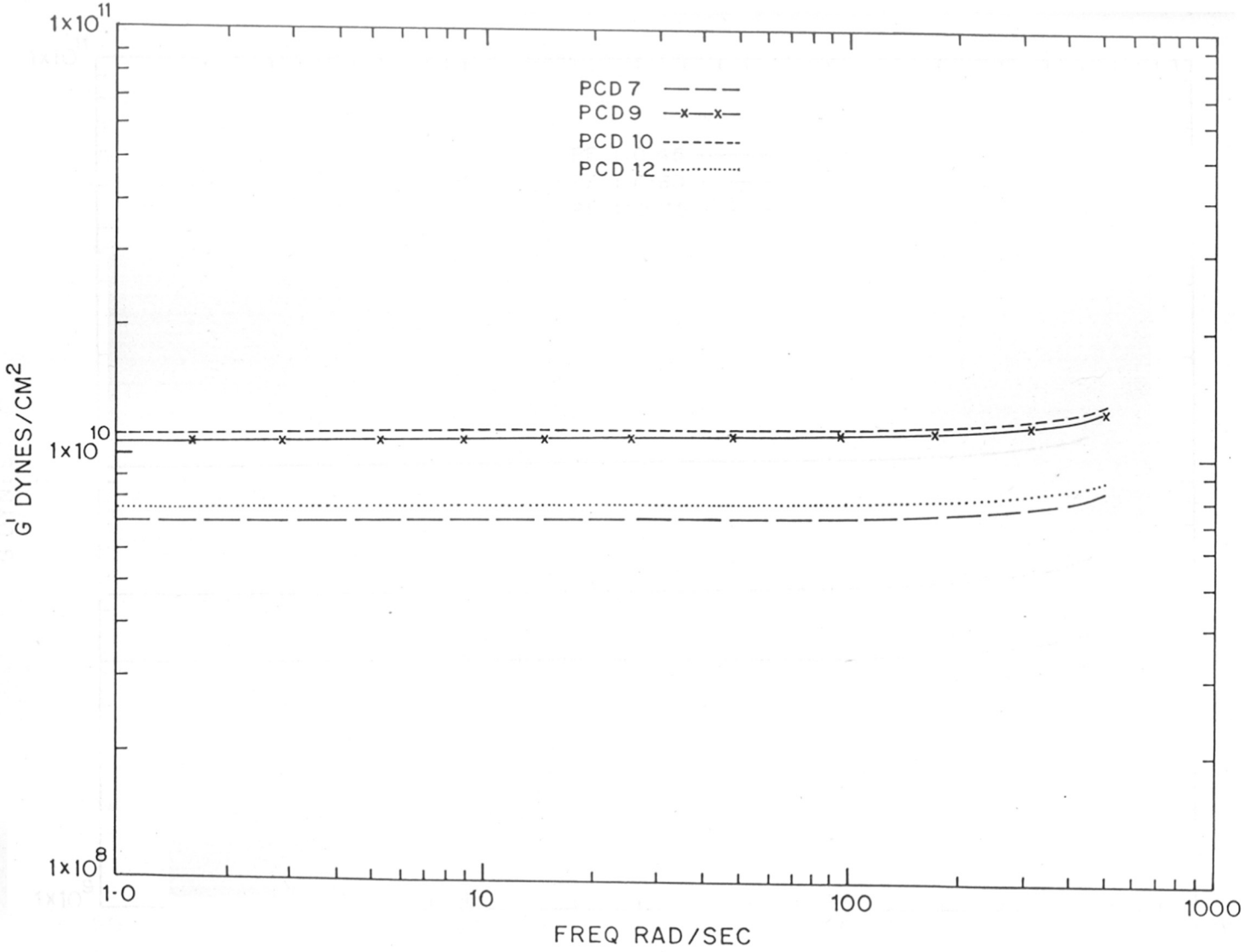


FIGURE 41 : VARIATION OF STORAGE MODULUS WITH FREQUENCY FOR PCD RESINS

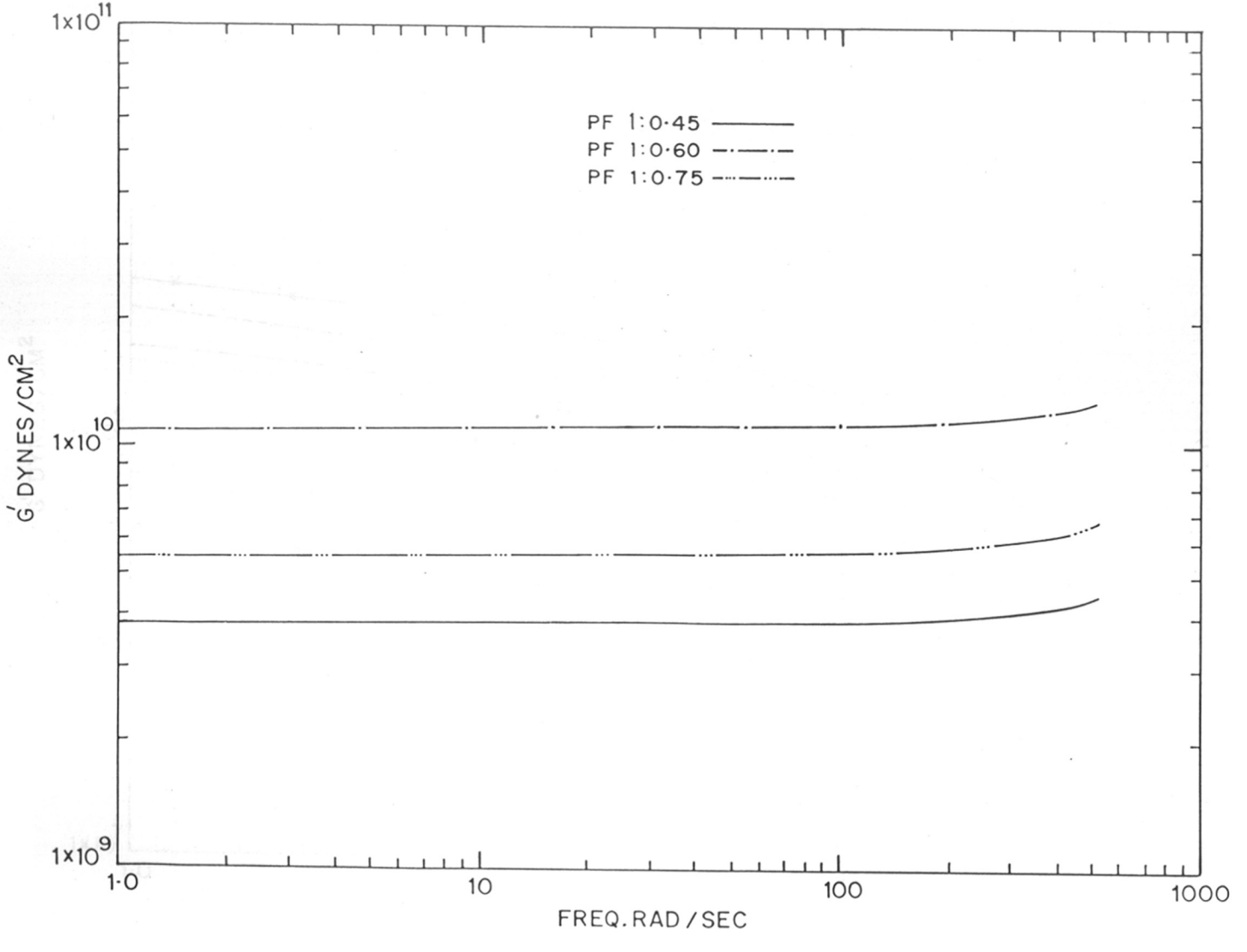


FIGURE 42 : VARIATION OF STORAGE MODULUS WITH FREQUENCY FOR PF RESINS

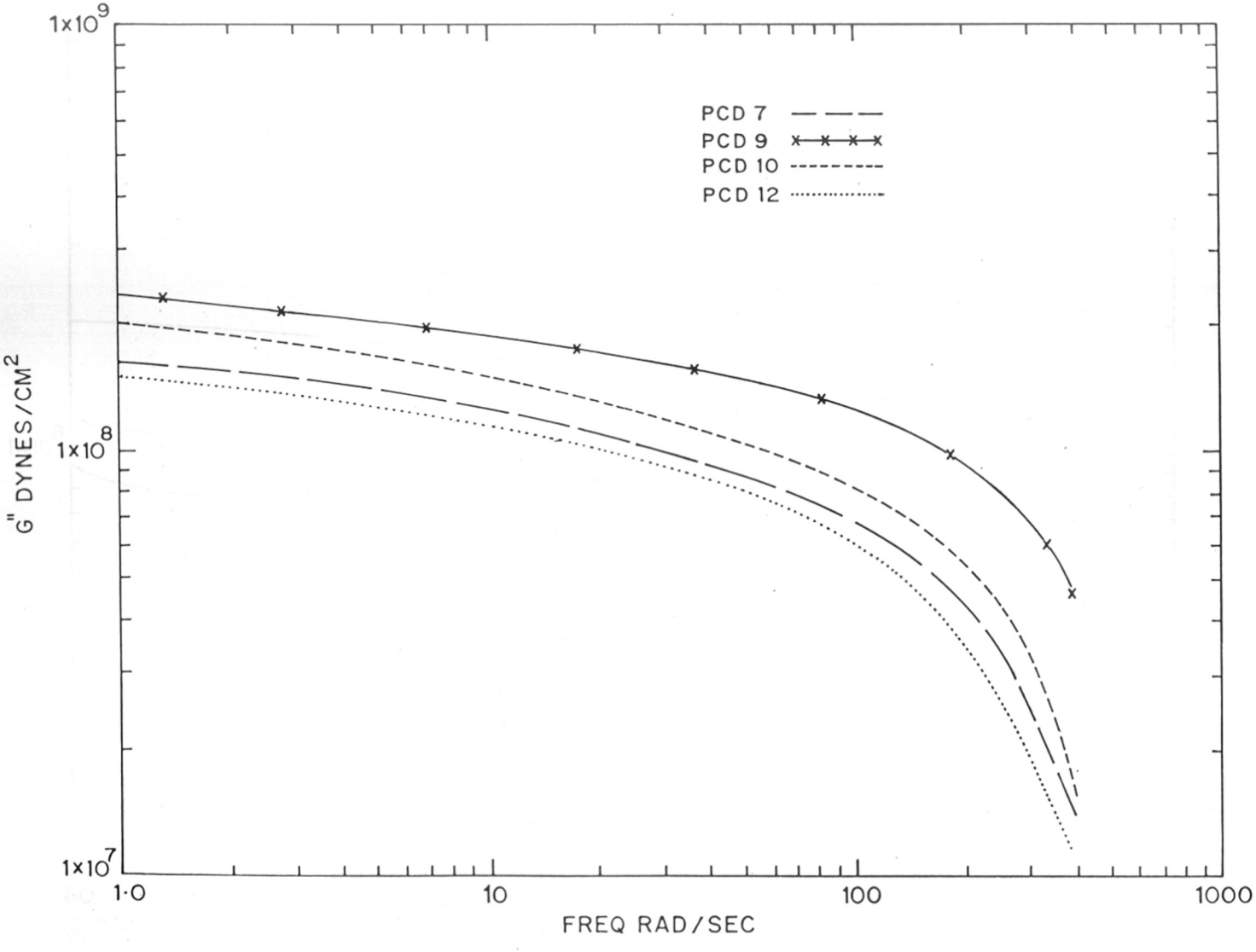


FIGURE 43: VARIATION OF LOSS MODULUS WITH FREQUENCY FOR PCD RESINS

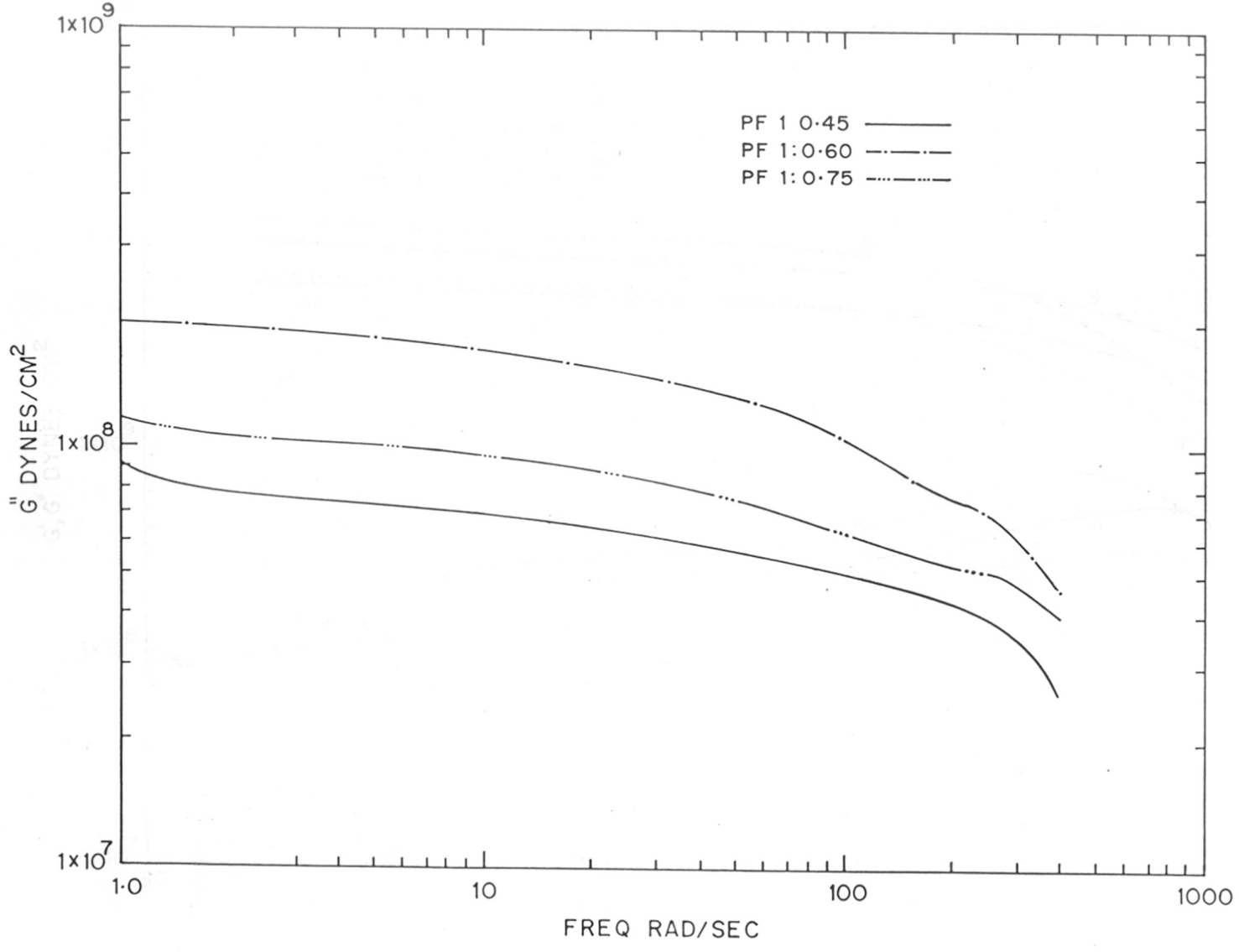


FIGURE 44 : VARIATION OF LOSS MODULUS WITH FREQUENCY FOR PF RESINS

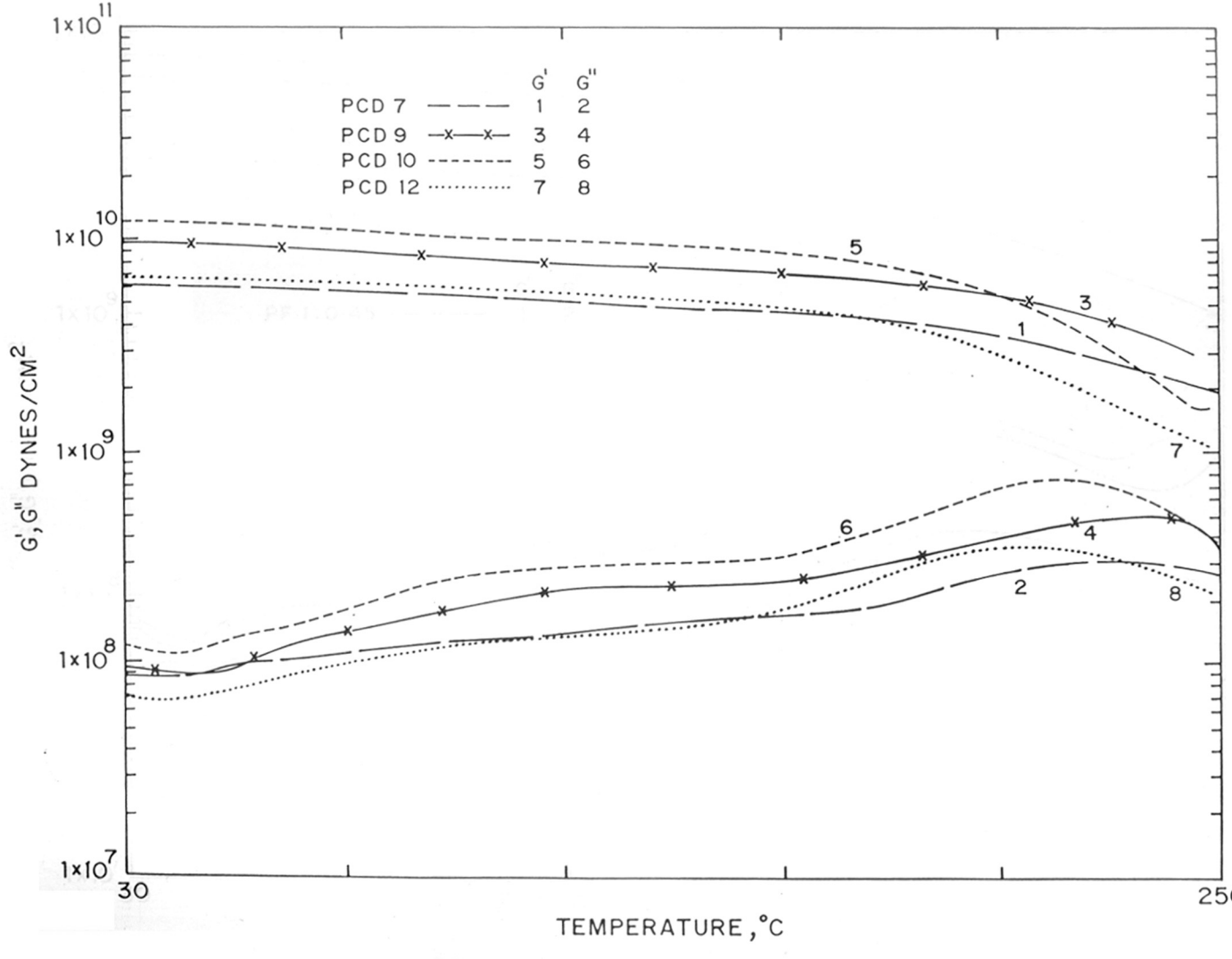


FIGURE 45: VARIATION OF STORAGE MODULUS AND LOSS MODULUS WITH TEMPERATURE FOR PCD RESINS

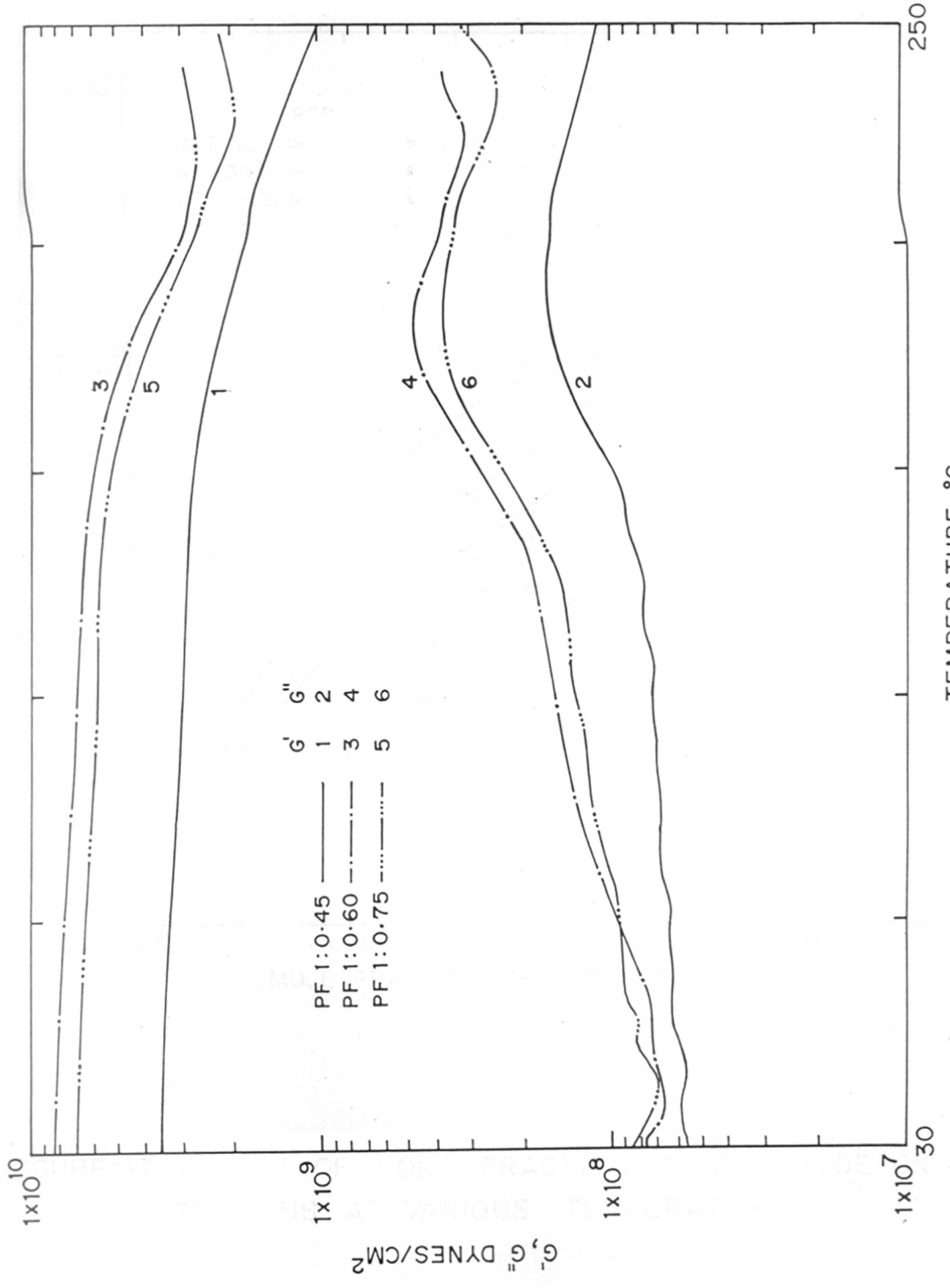


FIGURE 46: VARIATION OF STORAGE MODULUS AND LOSS MODULUS WITH TEMPERATURE FOR PF RESINS

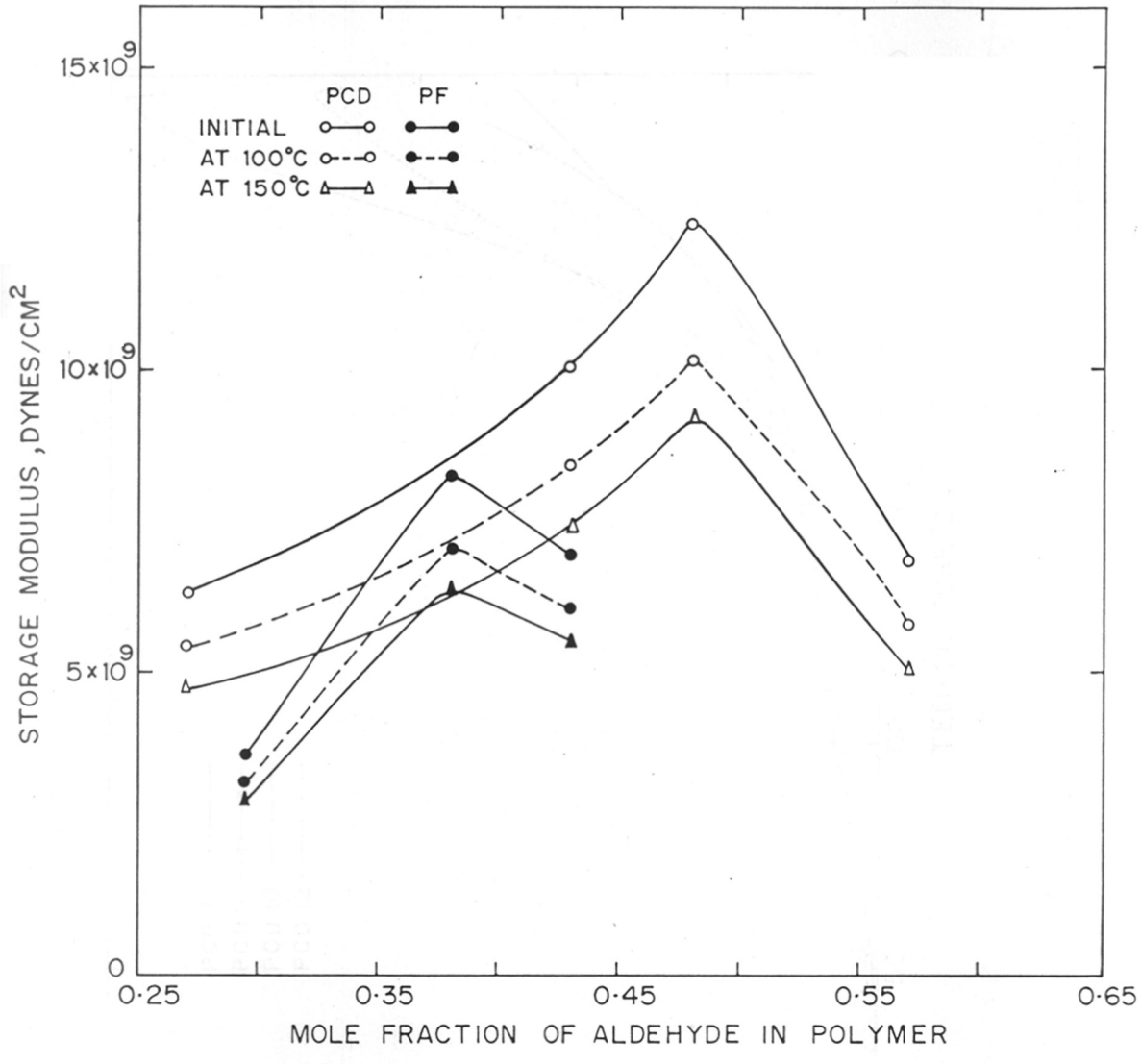


FIGURE 47: EFFECT OF MOLE FRACTION OF ALDEHYDE ON STORAGE MODULUS AT VARIOUS TEMPERATURES

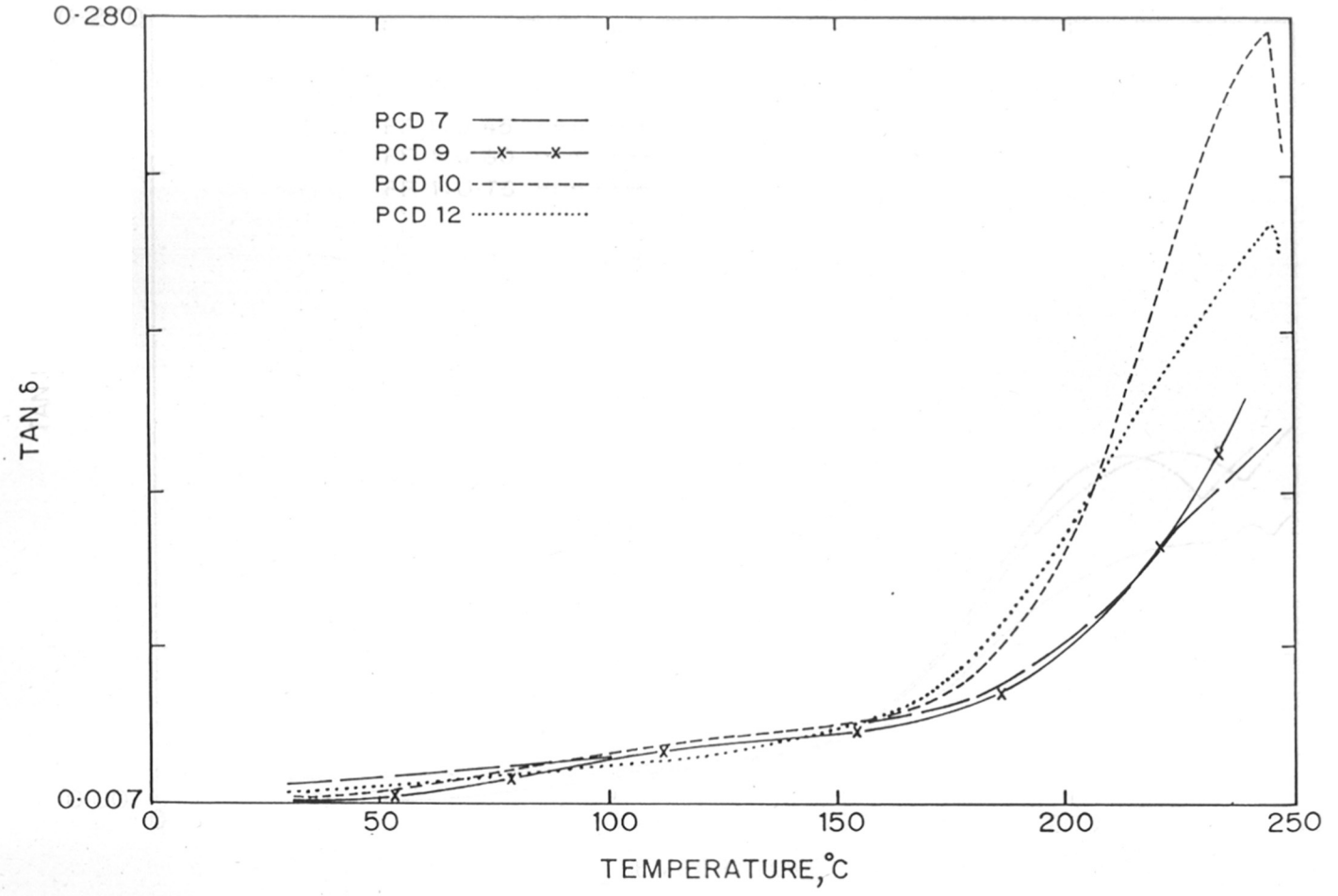


FIGURE 48: VARIATION OF LOSS FACTOR WITH TEMPERATURE FOR PCD RESINS

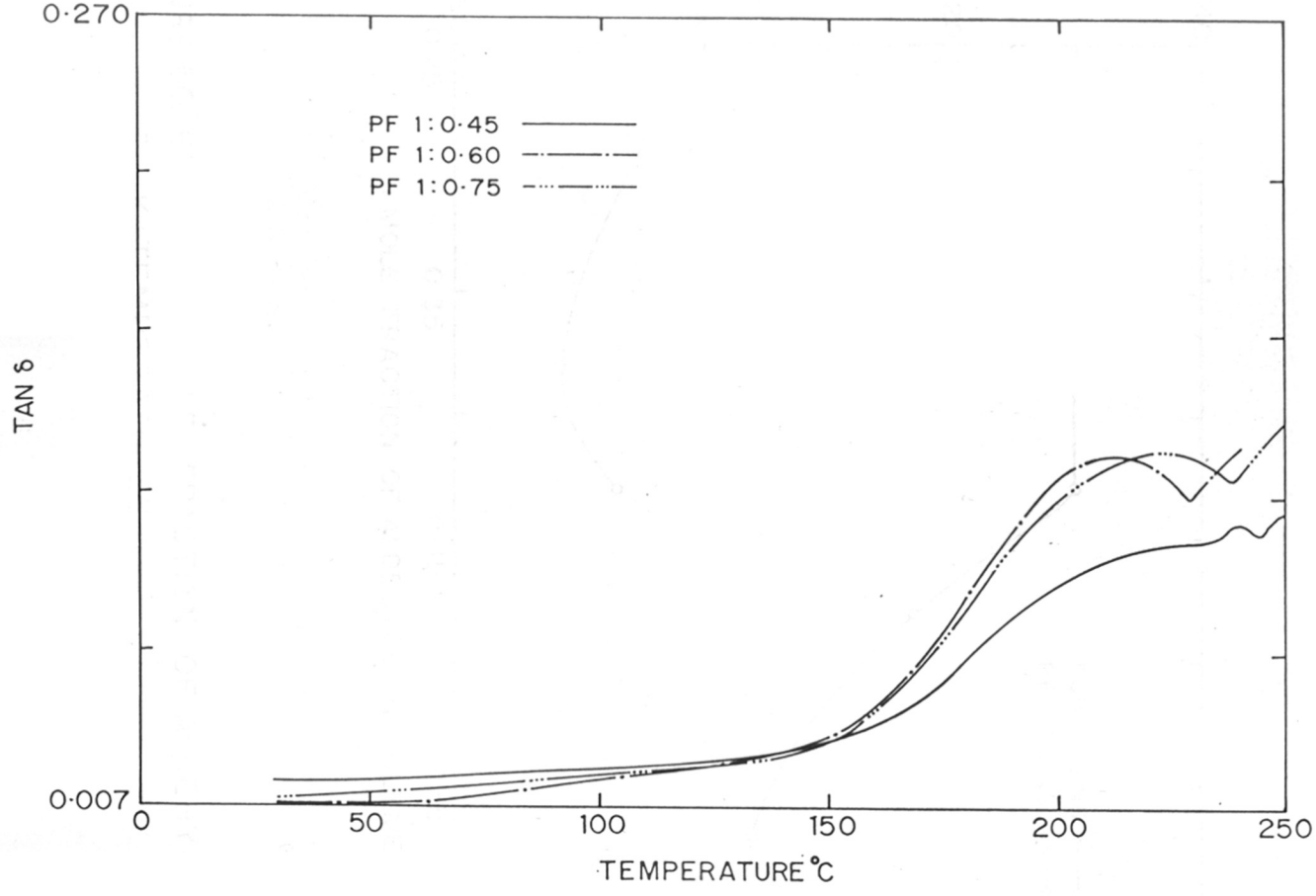


FIGURE 49: VARIATION OF LOSS FACTOR WITH TEMPERATURE FOR PF RESINS

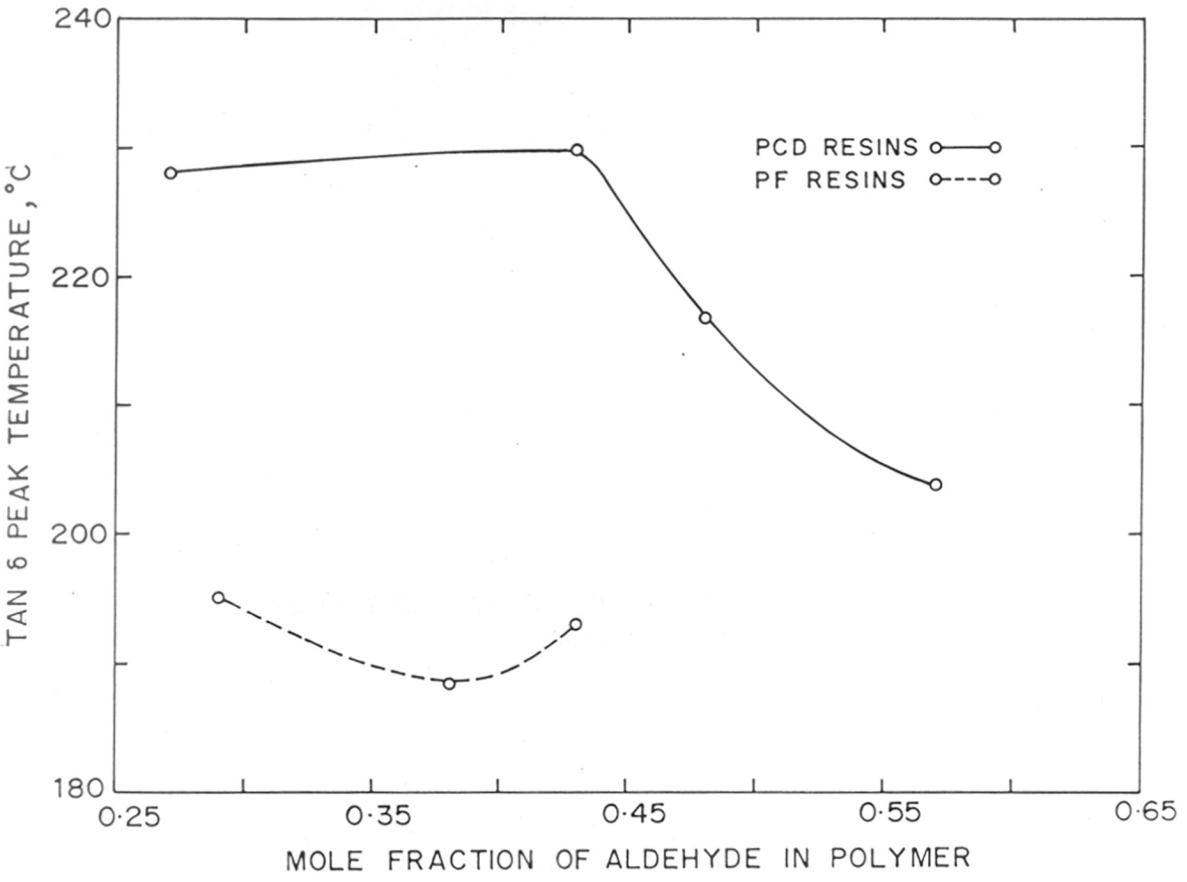


FIGURE 50: EFFECT OF MOLE FRACTION OF ALDEHYDE ON TAN δ PEAK TEMPERATURES

SUMMARY OF CONCLUSIONS AND RECOMMENDATION FOR FURTHER WORK

SUMMARY OF CONCLUSIONS AND RECOMMENDATION FOR FURTHER WORK

SUMMARY OF CONCLUSIONS

Thermoplastic solid resins were prepared by condensing phenol and crotonaldehyde, over a range of mole ratio of phenol to crotonaldehyde (1:0.4 to 1:1.4) using sulfuric acid as catalyst. Two sets of PC resins were synthesised from crude (PCC) and distilled (PCD) crotonaldehyde. Conventional phenol-formaldehyde (PF) novolak resins were prepared over phenol to formaldehyde mole ratio of 1:0.4 to 1:0.75 as reference materials. The PC resins exhibited thermoplasticity over the range of mole fraction of crotonaldehyde (0.27 to 0.58) whereas conventional PF resins exhibitted thermoplasticity over a narrower range of formaldehyde mole fraction (0.28 to 0.45). The polycondensation reaction involves the ortho and para positions of the phenyl ring, the phenolic hydroxyl group and the C=C and C=O groups of crotonaldehyde.

The resins were oligomeric with number-average molecular weights ranging from 400 to 600. The purity of crotonaldehyde was found to influence the extent of conversion of crotonaldehyde, at a fixed ratio of reactants in the feed. It also had a significant effect on the molecular weight, as well as thermal and curing behaviour of the resins. In general, resins from distilled crotonaldehyde were higher in molecular weight and exhibited improved thermal and curing properties than resins from crude crotonaldehyde.

The resins were found to be similar in their chemical structure, independent of the purity of crotonaldehyde and its mole fraction.

PC resins were found to be thermoplastic even after curing with the cross-linking agent hexa up to 160°C. This curing behaviour was observed irrespective of the purity of the crotonaldehyde and the mole fraction of crotonaldehyde in polymer. In comparison, conventional PF novolak resins were transformed into infusible, insoluble thermoset materials. Postcuring of these semicured PC resins at elevated temperatures yielded

insoluble and infusible thermoset products. This unique thermal characteristic could lead to interesting processing possibilities for the PC resins. Thus, it may be possible to use thermoplastic injection molding technique for PC resins followed by heat treatment of the molded part into a thermoset product.

The oxidative thermal degradation of PC resins was found to be in three stages similar to the conventional PF resins. The degradation kinetics was studied using Coats and Redfern method. It was found that all the three stages follow first order kinetics. The PC resins behaved similar to PF resins, except for the onset of degradation which was slightly lower.

The PC and PF resins were compression molded to give tensile test specimens. The temperature conditions of compression molding were defined on the basis of thermal data and differential scanning calorimetric scans. The specimens exhibited plastic flow and strain hardening for both PC and PF resins. The tensile yield stress of PC resins was lower than that of corresponding PF resin, at a fixed mole fraction of aldehyde, by

about 25%. In case of PC resins, both the yield stress and tensile strength at break showed a maxima at a crotonaldehyde mole fraction of 0.43 whereas in case of PF resins it increased linearly with the mole fraction of formaldehyde. The moduli were determined for both the elastic deformation before yield point and in the strain hardening region. Interestingly, the initial modulus, in case of PF resins, remained constant irrespective of formaldehyde mole fraction, whereas the modulus in the strain hardening region increased upto a formaldehyde mole fraction of 0.38. In case of PC resins, moduli in both the region manifested a maxima at crotonaldehyde mole fraction of 0.43.

The dynamic mechanical behaviour of PC and PF resins was investigated on a dynamic spectrometer. The storage moduli for both PC and PF resins were found to be in the range of 3 to 10 x 10^9 dynes/cm^2. PC resin with 0.48 mole fraction of crotonaldehyde exhibited the highest modulus and best high temperture stability. The modulus for PF resins showed a drop in the value in the temperature range of 160° to 170°C whereas for PC resins this temperature range was 180° to 195°C which

indicates that the PC resins have improved thermochemical stability compared to PF resins. The variation of loss modulus with temperature exhibited a peak corresponding to molecular transition. The transition temperature range for PC resins was about 20°-30°C higher than that for the PF resins, indicating that the PC resins are more brittle than the PF resins.

A list of publications in international technical journals based on the Ph.D. research is attached.

RECOMMENDATIONS FOR FURTHER WORK

The synthesis and characterization of PC resins using a mild catalyst, such as oxalic acid which is commercially used for preparation of novolak resins, should be investigated. The reaction kinetics and the chemical structure development of the PC resins in the condensation reaction be studied extensively. The possibility of synthesis by basic catalysis may be explored. PC resins using alkyl-phenol, resorcinol, polyhydric phenols may be synthesised per specific end applications.

The possibility of using thermoplastic injection molding technique may be explored after evaluating the parameters for injection molding and a detailed study in this field is recommended.

The blending of PC resins with other thermosetting resins such as UF, MF and PF resins, may change the characteristics of the thermosetting resins. This could improve processibility of the base resins. It is also suggested that the changes in the characteristics of thermosetting resins may be investigated and the data may be used for thermoplastic injection molding.

The mechanical and electrical properties should be investigated in details. The effect of different fillers on the resin characteristics should also be explored.

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