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PHENOL-CROTONALDEHYDE RESINS. III. CURING BEHAVIOR WITH HEXAMETHYLENETETRAMINE *

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ABSTRACT

Solid thermoplastic resins were prepared by acid-catalyzed condensation of phenol and crotonaldehyde (both crude and distilled). The thermal and curing properties were compared with the conventional phenol-formaldehyde (PF) novolak resins. Phenol-crotonaldehyde (PC) resins were found to be thermoplastic even after curing with the crosslinking agent hexamethylenetetramine up to 160°C. This curing behavior was observed irrespective of the purity of the crotonaldehyde or the phenol-to-crotonaldehyde mole ratio in the resin. Postcuring of these resins at elevated temperatures yielded insoluble and infusible thermoset products. This unique thermal characteristic could lead to interesting processing possibilities for the resins. The technical feasibility of thermoplastic processing of the PC resins followed by postcure heat treatment for transforming the molded part into a thermoset has been demonstrated.

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INTRODUCTION

The acid-catalyzed condensation of phenol and crotonaldehyde results in solid thermoplastic resins similar to the conventional phenol-formaldehyde (PF) novolak resins [1]. Although the softening temperature range of the phenol-crotonaldehyde (PC) powder resins is comparable to that of the PF resins, the curing behavior of the PC resins has been found to be different [2]. Conventional PF resins, when cured with 8-15 wt% hexamethylene-tetramine (hexa) at elevated temperatures, set into insoluble, infusible solids [3].

However, PC resins, on curing with hexa under identical conditions, did not form a thermoset but gave soluble, higher melting thermoplastic products [2]. This peculiar behavior offers interesting processing possibilities. It may be possible to process the PC resins containing hexa (8-12%) on thermoplastic injection molding equipment into intricate product shapes, followed by post-curing of the molded parts in ovens to impart to them the desirable thermoset characteristics. This was the driving force for the present investigation, which reports the effect of the amount of hexa, curing temperature, and postcuring heat treatment on the thermal and solubility characteristics of PC resins in comparison with the PF resins.

EXPERIMENTAL

Phenol (L. R. Grade) was obtained from S. D. Chemicals, India, and used as received.

The PC resins were prepared from crude and distilled crotonaldehyde. Crude crotonaldehyde obtained from Deccan Sugar Institute, Pune, India, was dried repeatedly over anhydrous calcium chloride and then used to prepare the PC resins. The dried crotonaldehyde was distilled. The fraction boiling at 102°C was collected, redistilled, and then used for the preparation of PC resins.

Gas chromatographic (GC) analysis of crude and distilled crotonaldehyde was done on a Nucon (Model 5500) gas chromatograph. An SE-30 column and a thermal conductivity detector (TCD) were used. GC analysis of crude crotonaldehyde indicated the following composition: crotonaldehyde \approx 80%, water \approx 15%, lower-boiling fractions (two) \approx 2.5%, and higher-boiling fractions (two) \approx 2.5%. Similarly, GC analysis of distilled crotonaldehyde indicated a purity greater than 99.5%. TLC of the crude crotonaldehyde showed five components; after distillation only one major component and a very slight impurity remained [2].

Sulfuric acid (A. R. Grade) was obtained from Ranboxy Laboratories, India, and used as received.

The polycondensation of phenol with crotonaldehyde was conducted at the reflux temperature of the crotonaldehyde-water azeotrope (84°C) in a 1-L three-necked flask fitted with a mechanical stirrer, a thermowell, and a reflux condenser. The catalyst, sulfuric acid (1 wt% referred to phenol), was used as a 9.4 wt% aqueous solution. After completion of the reaction, unreacted monomers and water of condensation were distilled out under reduced pressure. The distillate was analyzed for unreacted phenol and crotonaldehyde.

The phenol-to-crotonaldehyde (P:C) mole ratios in the PC resins used were 1:0.66 for PC(crude) and 1:0.89 for PC(distilled). For comparative evaluation, the conventional PF resin with phenol-to-formaldehyde mole ratio of 1:0.75 was prepared and used. Also, the effect of the P:C ratio on the curing behavior was investigated by studying PC(distilled) resins at three P:C mole ratios, 1:0.47, 1:0.89, and 1:1.37.

The softening temperatures of the resins and the resin-hexa mixtures were determined by the capillary method. The temperature range over which the opaque particles transform into a clear, mobile liquid was recorded as the softening temperature range. The temperature at which the cured resin starts to soften was recorded.

The curing behavior was studied by evaluating the "flow length" of the resin pellet at different temperatures. Finely powdered resin was mixed with a predetermined quantity of hexa. Exactly 0.5 g of the mixture was pelletized at room temperature with 3.5 tons force. The pellet was placed on the horizontal plate of the flow-length apparatus, kept in an air circulating oven at a fixed temperature. After 5 min the horizontal plate was tilted 30° toward the vertical and the molten resin was allowed to flow for 10 min. The length of the flow in millimeters was recorded as the "flow length."

The number-average molecular weights were determined by vapor-pressure osmometry at 50°C with ethyl acetate as the solvent. Benzil was used as the standard.

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 PC(crude) resins and at 140°C for the PC(distilled) resins. The curing time was 15 min 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% hexa and cured for 15 min. The results of this set would have a bearing on the temperature of injection molding and also on the conditions of postcuring 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% hexa cured at 140 and 160°C. The postcuring treatment was 160, 180, and 200°C for 15 min.

RESULTS AND DISCUSSION

The use of hexa as a crosslinking agent is necessary for curing PC resins. When the PC resins were heated at elevated temperature (120°C for 15 min) 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 PC-(crude) resins (at 120°C) is illustrated in Fig. 1. 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 PC(crude) resin. Also, the curing of the PF resin is more sensitive to the amount of hexa than the PC(crude) resin, as illustrated by the slopes of the lines in Fig. 1.

The curing behavior of the PC resins is markedly different from that of the PF resins (Table 1). The thermoplastic PF resin turned into infusible, insoluble thermoset on curing at 120°C for 15 min even at low loading (4%) of hexa, whereas the cured PC resins remained 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 ethyl acetate, whereas the cured PF resins were insoluble.

The difference in the curing of the PC(crude) and PC(distilled) resins 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) [2]. The only difference between crude and distilled crotonaldehyde was found to be the presence of 5% impurities, such as ethanol, acetaldehyde, acetic acid, acetaldo, as well as the dimer and trimer of crotonaldehyde [2]. These could take part in the polycondensation reaction and thereby influence the resin properties.

It is interesting to note that the softening points of the PC resins increased substantially on curing with hexa at 120°C. This indicates that the PC resins

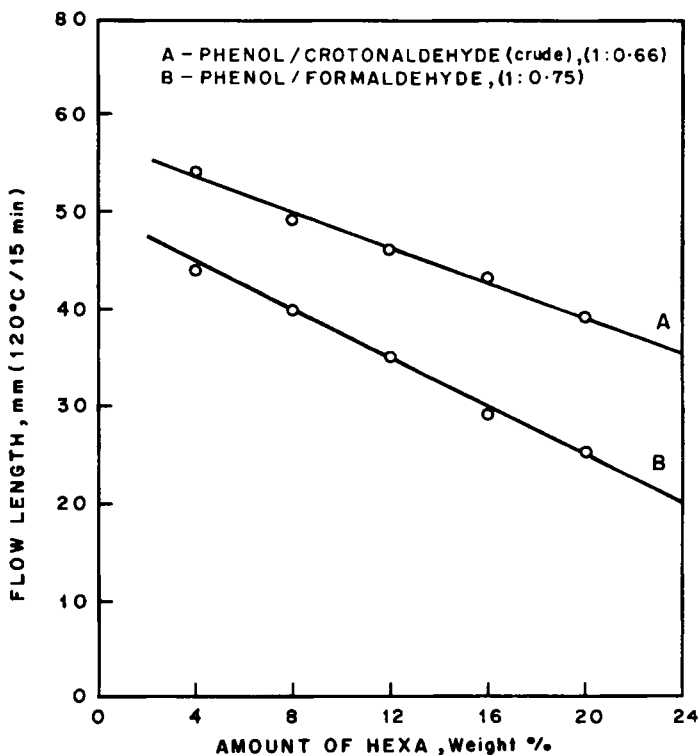


FIG. 1. Dependence of the curing behavior on amount of hexa.

do react with hexa to form only linear linkages. The increase in the softening temperature is associated with an increase in the \bar{M}_n as shown in Table 2.

This unique curing behavior of the PC resins was confirmed over a broad range of P:C ratios (Table 3). The softening point of the base resin and its reactivity increase (as indicated by shorter flow lengths) with increasing amount of crotonaldehyde in the resin. However, the cured resins were all soluble and their softening points were comparable, independent of the P:C ratio.

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 [4-6]. One of the proposed reactions involved hydrolysis of hexa by trace amounts (0.1-0.5 wt%)

TABLE 1. Effect of the Amount of Hexa on the Fusion Characteristics of Phenolic Resins

Hexa, wt%	Softening temperature range, °C							
	PF resin (1:0.75)		PC(crude) resin (1:0.66)		PC(distilled) resin ^a (1:0.89)			
	Before curing	After curing (120°C/15 min)	Before curing	After curing (120°C/15 min)	Before curing	After curing (140°C/15 min)	Before curing	After curing (140°C/15 min)
0	72-76	—	80-84	80-84	100-103	100-103	100-103	100-103
4	80-84	Infusible	90-94	112-116	104-108	104-108	134-139	134-139
8	86-89	Infusible	93-97	120-123	109-113	109-113	149-153	149-153
12	90-94	Infusible	95-98	125-128	114-118	114-118	153-157	153-157
16	93-97	Infusible	99-101	130-133	120-124	120-124	156-160	156-160
20	98-102	Infusible	100-103	139-142	123-127	123-127	161-165	161-165

^aCuring was carried out at 140°C because of the high softening temperatures of the resin.

TABLE 2. Molecular Weight Data for Cured PC(crude) Resins (P:C = 1:0.66)

Hexa, wt%	Softening temperature range with hexa (before curing), °C	Characterization after curing (120°C/15 min)		
		Softening temperature range, °C	Increase in the softening temperature range, °C	\bar{M}_n
0	80-84	80-84	—	285
4	90-94	112-116	22 ± 2	400
8	97-97	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

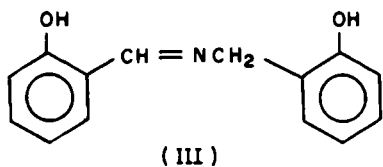
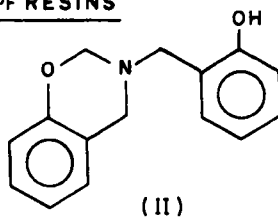
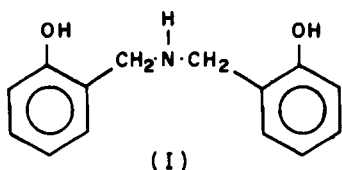
of moisture in the resin, generating formaldehyde. The acidic nature of phenol may also lead to the generation of α -amino alcohols [7, 8]. It is known that the predominant moiety bridging the benzene rings in novolak resins is the methylene group, although the presence of other bridging structures, such as dibenzylamines, benzoxazines, and azomethines, has also been reported [9-11] (Fig. 2, Structures I, II, and 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-catalyzed reaction between alkylphenol and crotonaldehyde contains three or four carbon atoms [12, 13] (Fig. 2, Structures IV, V, VI, and VII). The presence of such bulky groups on the benzene rings 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 Structures I, II, and III (Fig. 2) which crosslink on curing at elevated temperatures.

The observation that the materials are thermosetting under these conditions deserves comment. Crotonaldehyde, both crude and distilled, absorbs at IR frequencies corresponding to C=C double bond (at 1 640, 1 310, and 970 cm^{-1} , for *trans* isomer) and C=O (at 1 680 cm^{-1}), whereas the resins prepared from both crude and distilled crotonaldehyde do not absorb in these regions [2], indicating that there is a very little or no unsaturation. Therefore, the crosslinking

TABLE 3. Curing Characteristics of PC(distilled) Resins

Phenol-crotonaldehyde (distilled) mole ratio	Softening temperature range, °C	Softening temperature range with 8 wt% hexa, °C	Flow length (140°C/15 min), mm	After curing (140°C/15 min)	
				Softening temperature range, °C	Solubility in acetone
1:0.47	94-97	102-106	27	152-155	Soluble
1:0.89	100-103	109-113	25	149-153	Soluble
1:1.37	105-109	116-120	18	143-146	Soluble

(A) REPORTED STRUCTURES IN CURED PF RESINS



(B) REPORTED STRUCTURES OF ALKYL PHENOL-CROTONALDEHYDE CONDENSATES

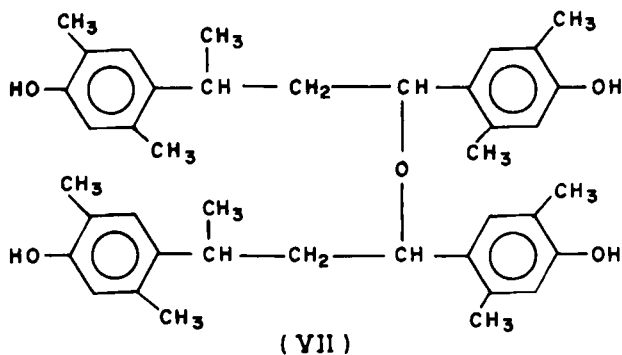
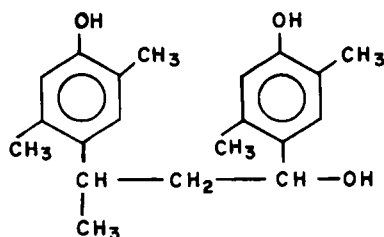
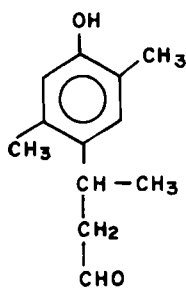
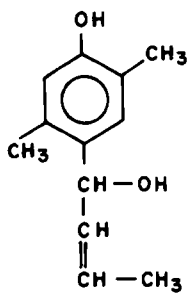


FIG. 2. Reported structures.

TABLE 4. Effect of Temperature on Curing of PC Resins

Resin type	Curing temperature, °C	Flow length (15 min), mm	Cured resin characteristics	
			Softening temperature range, °C	Solubility in acetone
PC(crude) ^a	120	49	120-123	Soluble
	140	38	138-142	Soluble
	160	22	220-224 ^c	Slightly soluble
	180	20	235-239 ^c	Slightly soluble
PC(distilled) ^b	120	—	—	—
	140	25	149-153	Soluble
	160	22	228-232 ^c	Slightly soluble
	180	19	250-254 ^c	Slightly soluble

^aResin from crude crotonaldehyde; softening temperature with 8% hexa (before curing), 93-97°C; P:C = 1:0.66; soluble in acetone.

^bResin from distilled crotonaldehyde; softening temperature with 8% hexa (before curing), 109-113°C; P:C = 1:0.89; soluble in acetone.

^cResin softens but does not melt into clear liquid.

reaction with hexa may be taking place by the conventional route, as in PF resins.

The effect of the curing temperature on the fusion characteristics of the cured PC resins was investigated to determine the upper limit on the temperature of thermoplastic processing (Table 4). It is evident that the extent of cross-linking increases with rising curing temperature. Also, the reduction in the flow length indicates that the reactivity of the resin increases with rising temperatures. Thus, the upper limit on temperature for thermoplastic processing of PC resins appears to be 140-160°C at hexa loading of 8 wt%.

The results of postcuring heat treatment experiments are given in Table 5.

TABLE 5. Postcuring Heat Treatment of PC Resins

Resin type ^a	Cured at 140°C/15 min with 8 wt% hexa			Cured at 160°C/15 min with 8 wt% hexa		
	Postcuring temperature, °C	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	Solubility in acetone
PC(crude)	160	171-175	Soluble	220-223 ^b	Soluble	Soluble
	180	205 ^b	Insoluble	225 ^b	Insoluble	Insoluble
	200	Infusible	Insoluble	Infusible	Insoluble	Insoluble
PC(distilled)	160	190-194	Soluble	228-230 ^b	Soluble	Soluble
	180	215 ^b	Insoluble	235 ^b	Insoluble	Insoluble
	200	Infusible	Insoluble	Infusible	Insoluble	Insoluble

^aResin characteristics as in Table 4.

^bResin softens but does not melt into clear liquid.

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.

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