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THERMAL CHARACTERIZATION OF CARDANOL–FORMALDEHYDE RESINS AND CARDANOL–FORMALDEHYDE/POLY(METHYL METHACRYLATE) SEMI-INTERPENETRATING POLYMER NETWORKS

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ABSTRACT

Thermal characteristics of cardanol–formaldehyde (CF) (both novolac and resol) polymers and cardanol–formaldehyde/poly(methyl methacrylate) (PMMA) resin interpenetrating network (IPN) polymers have been investigated. Cardanol–formaldehyde resins were synthesized, and thermal degradation data are compared with those of phenolics. Cardanol–formaldehyde products decompose at a faster rate and hence have lower thermal stability. Between cardanol–formaldehyde (resol) and cardanol–formaldehyde (novolac) products, the former decomposes at a faster rate. The TG of semi-IPNs indicates that thermal degradation of PMMA is slowed down by formation of IPNs. PMMA is known to degrade to show 50% weight loss at 350 °C, whereas cardanol–formaldehyde (resol) based semi-IPNs show only 15% weight loss at this temperature. The PMMA stabilization is greater in the case of novolac resin based semi-IPN systems. Coats–Redfern plots are drawn for both homopolymers and semi-IPNs, and good fits are obtained for the reaction parameter $n = 1$. Two distinct stages of decomposition are indicated in both cases, and activation energies are deduced from the slopes of the plots.

The activation energies for the first stage of decomposition for the CF(resol)/PMMA semi-IPNs range from 40–55 kJ mol^{-1}, whereas the corresponding values for semi-IPNs based on the novolac system are between 44 and 65 kJ mol^{-1}. The second stage of decomposition, which is between 400 °C and 500 °C, has an activation energy between 90 and 110 kJ mol^{-1} for the semi-IPNs, whereas it is 139 kJ mol^{-1} for the CF resin. The differences in the values are interpreted on the basis of the structure of the polymer.

INTRODUCTION

Cardanol (C.A. Registry No. 37330-39-5) based polymers have been the subject of investigation in many patents and reviews [1–7]. Although these

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resins have been used in friction materials [7,8], flame retardants [9] etc., studies on their thermal characterization have been limited. Recently, Daniel O'Connor and Frank D. Blum reported the thermogravimetric behaviour in air of cardanol–formaldehyde systems in a comparative work on substituted phenols [10]. They showed that the thermal stability of substituted phenols increases as the length of the side chain decreases. A detailed study, however, on the thermal stability, thermal decomposition and kinetic parameter of decomposition is required to understand the thermal behaviour of a polymer. The present communication reports results of TG experiments on two materials: (1) cardanol–formaldehyde (novolac and resol) resin and (2) cardanol–formaldehyde (novolac and resol) polymethyl methacrylate (PMMA) semi-interpenetrating networks (semi-IPNs). The semi-IPNs were synthesized [11,12] in the laboratory with a view to improve the mechanical properties of cardanol–formaldehyde polymers.

EXPERIMENTAL

Materials

Methyl methacrylate (MMA)

The following procedure was used for the purification of MMA (from Koch-Light Laboratories, Haverhill, UK). MMA was washed with 10% aqueous sodium hydroxide to remove the inhibitor. The monomer was washed with distilled water till all the base had been removed, and it was then dried over anhydrous Na_2SO_4.

α,α'-Azobisisobutyronitrile (AIBN)

AIBN (Merck, for synthesis) was purified by crystallization from methanol.

Cardanol

Cardanol was obtained by vacuum distillation of cashew nut shell liquid (CNSL) at 3.4 mmHg; the fraction distilling at 228–235 °C had a refractive index of 1.509, as reported for pure cardanol [13]. CNSL conformed to the Indian Standard specification IS:840 (1964).

Synthesis

Cardanol–formaldehyde (resol) prepolymer (I)

250 g (0.825 mol) of cardanol, 101.9 ml (1.249 mol) of 37% aqueous formaldehyde and 3.9 g (0.01 mol) of barium hydroxide octahydrate were mixed thoroughly in a reaction kettle fitted with a mechanical stirrer and reflux condenser. The reaction mixture was heated at 70 °C for 3.5 h. The resulting resin was freed from unreacted formaldehyde (if any) and barium

hydroxide by washing with water. The product was dried at 70 °C and powdered. This product (**I**) served as the prepolymer for the synthesis of cardanol–formaldehyde (resol) as well as cardanol–formaldehyde (resol)/PMMA semi-IPNs.

Cardanol–formaldehyde (resol)

A 6 g portion of the cardanol–formaldehyde (resol) prepolymer **I** was cured by hot pressing using a hydraulic press at 140 °C for 1.5 h at 33.3 kg cm^{-2} and then subjected to post-curing at 170 °C for 1 h.

*Cardanol–formaldehyde (novolac) prepolymer (**II**)*

250 g (0.825 mol) of cardanol, 37% aqueous formaldehyde and 20 ml of 4N sodium hydroxide were taken in a reaction kettle fitted with a mechanical stirrer and reflux condenser. The reaction mixture was heated under constant stirring at 100 °C for 4 h. The product was washed with 10% hydrochloric acid and then with water and dried at 70 °C. The product was powdered. This powder served as the starting material for cardanol–formaldehyde (novolac) and its semi-IPN with PMMA.

Cardanol–formaldehyde (novolac)

A 160 g sample (0.201 mol) of cardanol–formaldehyde (novolac) prepolymer **II** was mixed thoroughly with 4.8 g (0.034 mol) (3%) of hexamethylenetetramine (HMTA) and kept in an oven at 120 °C for 1.5 h. The partially cured product was powdered and passed through an ASTM 34 sieve.

A 6.2 g portion of this material was mixed with 0.104 g (0.0007 mol) (2%) of HMTA. The samples were hot pressed at 120 °C for 30 min at ca. 33.3 kg cm^{-2} using a hydraulic press. The samples were then subjected to post-curing at 170 °C for 1 h.

Cardanol–formaldehyde (resol)/PMMA semi-IPN

The cardanol–formaldehyde (resol) prepolymer (**I**) powder (10 g) was mixed with varying amounts of MMA and AIBN (1% by weight relative to MMA) and stirred thoroughly in a reaction kettle under nitrogen. The temperature was maintained at 70 °C for 1.5 h. The product was powdered and the particle size was adjusted to allow it to pass through an ASTM 34 sieve. The powder was hot pressed using a hydraulic press at 140 °C for 1.5 h and post-cured at 170 °C for 1 h.

Cardanol–formaldehyde (novolac)/PMMA semi-IPN

The cardanol–formaldehyde (novolac) prepolymer (**II**) powder (10 g; 0.0128 mol) was mixed with 0.5 g (0.0035 mol) (5% w/w) of HMTA, 90 g (0.9 mol) of MMA and 0.9 g (0.0055 mol) of AIBN and stirred thoroughly in a reaction vessel under nitrogen. The temperature was maintained at 70 °C for 1.5 h. The product was powdered, its particle size being adjusted to pass through an ASTM 34 sieve. The powder was hot pressed at 120 °C for 1.5 h using a hydraulic press and post-cured at 170 °C for 1 h.

Methods of measurement

A Dupont 990 Modular Thermal Analysis system consisting of 951 TGA and 905 DSC modules was used for thermal analysis. All TG and DSC curves were recorded under a N_2 atmosphere at a flow rate of 50 ml min^{-1} and the heating rate was 10° min^{-1}; for TG the sample weight was 10 ± 0.2 mg and for DSC it was 10 ± 0.2 mg. Experimental conditions were identical for all samples.

RESULTS AND DISCUSSION

Figure 1 gives the TG curves for phenol–formaldehyde (PF) (resol), phenol–formaldehyde (novolac, 5% HMTA), cardanol–formaldehyde (resol) and cardanol–formaldehyde (novolac, 5% HMTA). Comparison of the curves shows that phenolics have an increased thermal stability compared to cardanol based resins. This is in agreement with findings reported by O'Connor and Blum [10]. The thermal degradation pattern of phenol–formaldehyde resins has been thoroughly studied, and degradation takes place in two stages [14] (500–600 °C and > 600 °C). The reaction is reported to take place through a thermo-oxidation process. The thermal degradation of phenol–formaldehyde and cardanol–formaldehyde is compared in Table 1, which indicates the reported decomposition temperatures for 10% and 50% weight loss for the two systems in air [15]. Cardanol–formaldehyde has poor

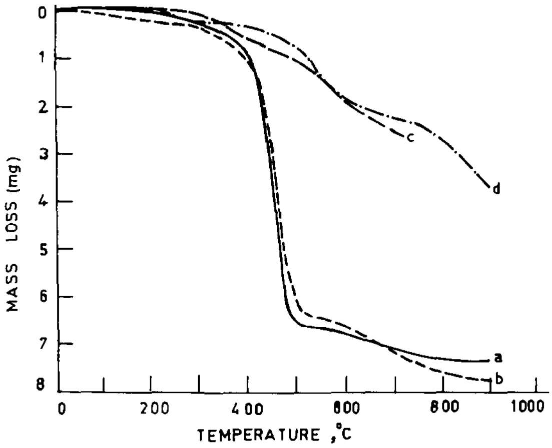


Fig. 1. TG curves for (a) CF (resol), (b) CF (novolac), (c) PF (resol) and (d) PF (novolac).

TABLE 1

Thermal degradation data of cardanol–formaldehyde and phenol–formaldehyde. DT = decomposition temperature

System	10% DT (°C)	50% DT (°C)
Cardanol–formaldehyde	340	485
Phenol–formaldehyde	430	830

thermal stability and loses 50% of its weight at 485 °C, whereas phenol–formaldehyde requires 830 °C for the same weight loss. The difference in thermal stability is attributed to the structural features of cardanol–formaldehyde. The structures of cardanol–formaldehyde and phenol–formaldehyde are given in Fig. 2.

In the case of cardanol the long side chain does not form part of the network. The degradation of the side chain is expected to occur at a relatively low temperature due to the facile *β*-cleavage at the double bonds. The major component of cardanol is the monomer with the double bond at the 8-position, and *β*-cleavage at the sixth or tenth carbon atom would lead to a weight loss of approximately 40% or 22% respectively. A loss of the whole side chain would result in a weight loss of around 65% (Scheme 1).

As is the case with the reported samples, cardanol–formaldehyde products decompose at a much faster rate. Phenol–formaldehyde had a weight loss of ca. 10–13% in comparison with 74–80% weight loss for cardanol–formaldehyde. The increased weight loss approximately accounts for the loss of the C_{15} side chain. Comparison between the degradation patterns of cardanol–formaldehyde resol and novolac products suggests an almost identical pattern up to ca. 50% weight loss (460 °C). Above this temperature, resol decomposes at a faster rate than novolac. This decreased rate in thermal decomposition above 460 °C for novolac in comparison with resol could be due to the increased crosslinking brought about by HMTA. The

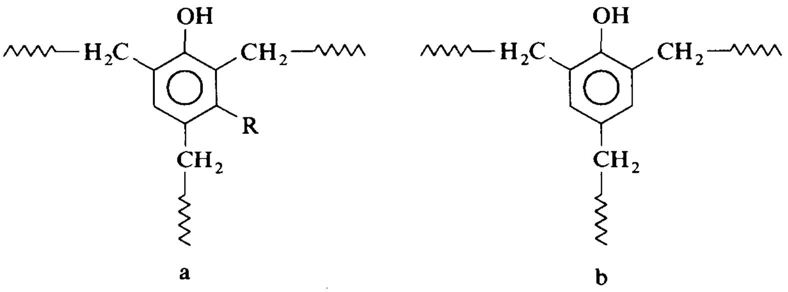
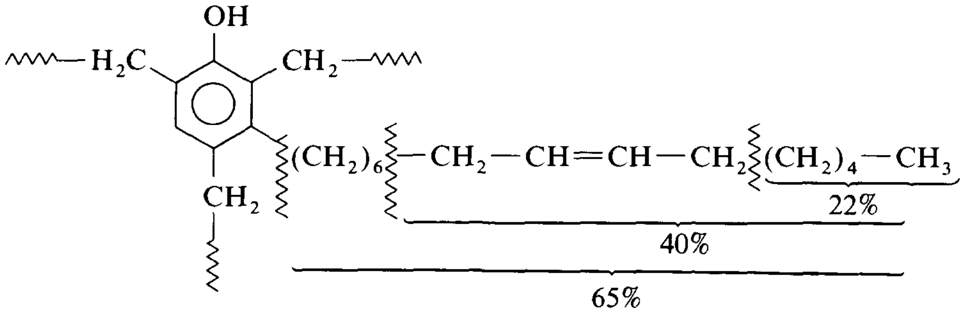


Fig. 2. Structures of CF and PF resins. a, Cardanol–formaldehyde: $R = -(CH_2)_6-CH_2-(CH_2)_7-CH_3$, $-(CH_2)_6-CH_2-CH{=}CH-(CH_2)_5-CH_3$ (major component), $-(CH_2)_6-CH_2-CH{=}CH-CH_2-CH{=}CH-(CH_2)_2-CH_3$ or $-(CH_2)_6-CH_2-CH{=}CH-CH_2-CH{=}CH-CH_2-CH{=}CH_2$. b, Phenol–formaldehyde.



Scheme 1.

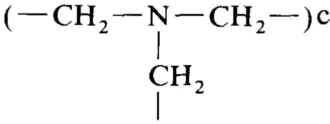
tertiary amine  $(-CH_2-\underset{\underset{|}{CH_2}}{\underset{|}{N}}-CH_2-)$ crosslinkage points in novolac could also be expected to play a role in scavenging the radicals formed during the decomposition, thereby increasing the thermal stability.

Figure 3 gives the TG curves for cardanol-formaldehyde (resol)/PMMA semi-IPNs containing various proportions of PMMA. Thermal degradation of PMMA has been extensively investigated [16]. PMMA is known to degrade to around 25%, 50% and 90% weight loss at 300 °C, 350 °C and 400 °C, respectively, via a stepwise unzipping process. The polymer chains break at random vulnerable points and the depolymerization occurs through a chain mechanism. The unzipping of PMMA by thermal degradation could be represented as follows (Scheme 2).

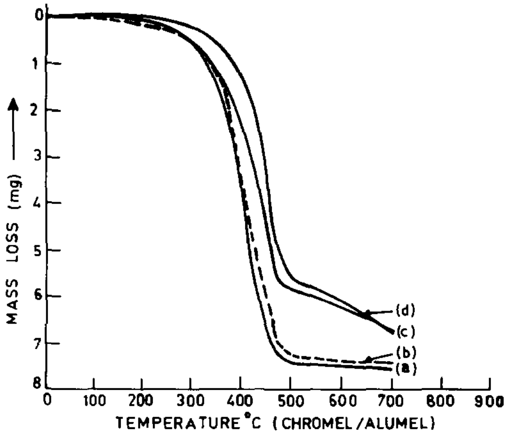
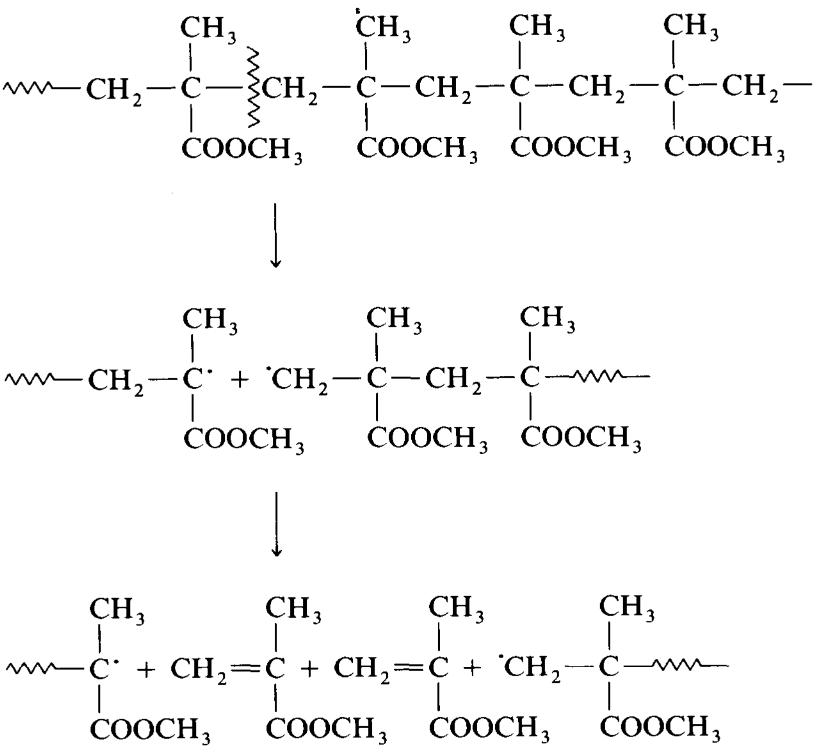


Fig. 3. TG curves for CF (resol)/PMMA semi-IPNs containing PMMA: (a) 90%, (b) 83.3%, (c) 75% and (d) 40%.



Scheme 2.

Figure 3 indicates only a low weight loss, of the order of less than 15% even at 350 °C, for the products under study. This is quite low, considering the fact that some of the samples contain high proportions of PMMA, varying from 40–90%. This suggests the influence of cardanol–formaldehyde (resol) on the mechanism of PMMA degradation. The likely mechanism for this improvement in thermal stability could be the interaction of cardanol–formaldehyde phenolic units with the PMMA free radicals generated by PMMA decomposition, thereby slowing down or preventing the chain depolymerization of PMMA, the phenols acting as a free radical trap. Substituted phenols are known to interact efficiently with free radicals. Similar stabilization of polymer networks during thermal degradation to that observed here has,in fact, been reported in the case of polyurethane/PMMA IPNs, where PMMA acted as a radical scavenger, stabilizing the polyurethane against degradation [17]. Kem et al. have also reported thermal stabilization effects due to interpenetration in polyurethane/polystyrene systems [18].

Comparison of the thermal degradation pattern of cardanol–formaldehyde (resol) based semi-IPNs with that of cardanol–formaldehyde (resol) homopolymer also indicates a char content of around 12% for the homo-

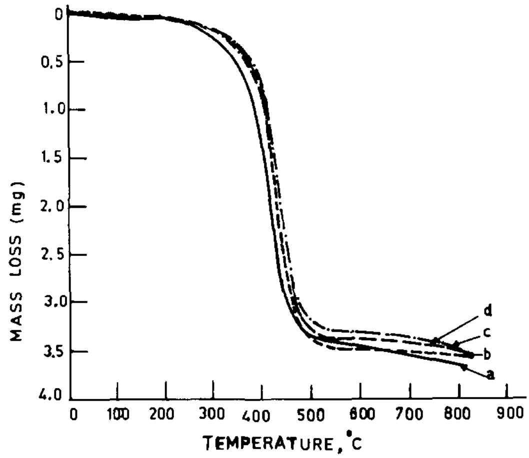


Fig. 4. TG curves for CF (novolac)/PMMA semi-IPNs containing PMMA: (a) 87.5%, (b) 83.3%, (c) 75.0% and (d) 50.0%.

polymer, in comparison with almost no char content for the semi-IPNs at 500 ° C.

Figure 4 gives TG curves for cardanol–formaldehyde (novolac)/PMMA semi-IPNs. The data indicate greater stabilization of PMMA towards decomposition in comparison with that in the resol system. For a 75% PMMA semi-IPN, ca. 50% weight loss was observed in the case of resol semi-IPNs, whereas only 37% weight loss was indicated in the case of novolac semi-IPNs. The increased thermal stability of PMMA in the case of novolac semi-IPNs could be attributed to the presence of tertiary amino cross-linkage points, in

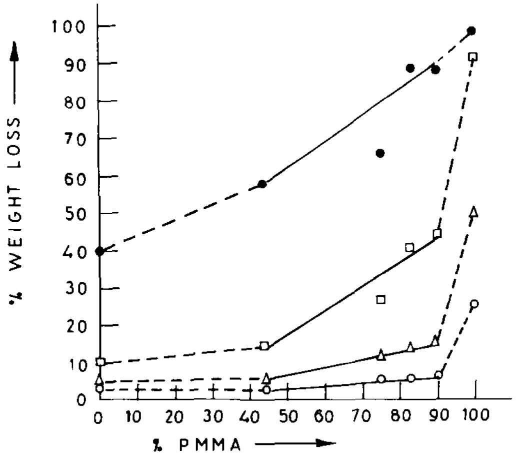


Fig. 5. Plots of weight loss (TG) vs. PMMA content for CF (resol)/PMMA semi-IPNs at 300 ° C, 350 ° C, 400 ° C and 450 ° C.

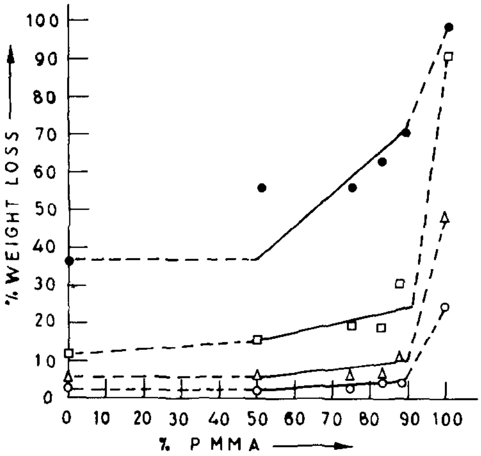


Fig. 6. Plots of weight loss (TG) vs. PMMA content for CF (novolac)/PMMA semi-IPNs at 300 ° C, 350 ° C, 400 ° C and 450 ° C.

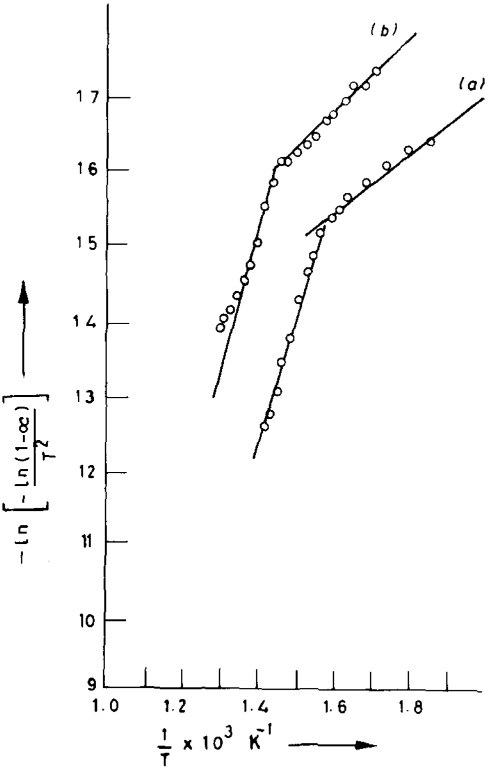


Fig. 7. Coats-Redfern plot for (a) cardanol-formaldehyde (resol) and (b) cardanol-formaldehyde (novolac).

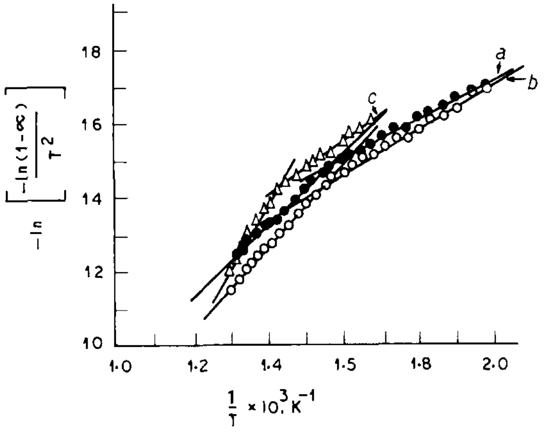


Fig. 8. Coats–Redfern plot for cardanol-formaldehyde (resol)/PMMA semi-IPNs containing (a) 10.0% PMMA, (b) 83.3% PMMA and (c) 44.0% PMMA.

addition to the phenolic groups, both of which could act as scavenger for the radicals of thermal degradation of PMMA.

The percentage weight losses at 300 °C, 350 °C, 400 °C and 450 °C are plotted vs. percentage PMMA content for resol and novolac semi-IPNs in Figs. 5 and 6 respectively. The plots show a linear trend for different semi-IPNs, whereas the homopolymers (0 and 100% PMMA) give rise to distinct discontinuities in the graph. This result could also be indicative of

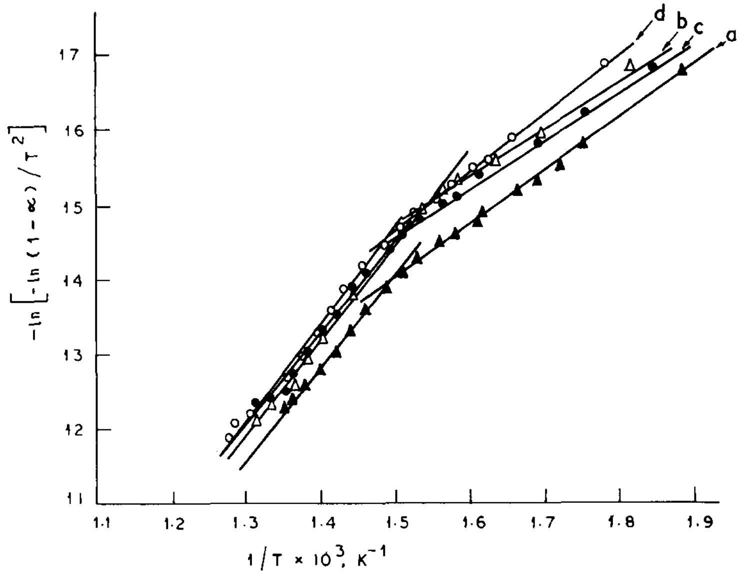


Fig. 9. Coats–Redfern plot for cardanol-formaldehyde (novolac)/PMMA semi-IPNs containing (a) 87.5% PMMA, (b) 83.3% PMMA, (c) 75.0% PMMA and (d) 50.0% PMMA.

TABLE 2

Activation energy (E) for the thermal decomposition of cardanol–formaldehyde/PMMA semi-IPNs

Semi-IPN composition		E (kJ mol^{-1}) for first stage (200–400 °C)	E (kJ mol^{-1}) for second stage (400–500 °C)
Cardanol–formaldehyde (%)	PMMA (%)		
Resol			
10.0	90.0	48.55	88.30
16.7	83.3	44.90	90.14
25.0	75.0	43.05	92.09
62.5	37.5	55.16	111.81
100.0	0.0	32.38	138.0
Novolac			
12.5	87.5	55.70	92.29
16.7	83.3	55.95	101.43
25.0	75.0	59.03	106.43
50.0	50.0	65.90	107.75
100.0	0.0	44.41	138.0

mechanistic involvement of cardanol–formaldehyde in the thermal degradation of PMMA, and vice versa.

Figures 7, 8 and 9 give the Coats–Redfern plots for cardanol–formaldehyde polymers (resol and novolac) and for their respective semi-IPNs. Good fits are obtained for the reaction order parameter $n = 1$. Two distinct stages of decomposition are indicated in both cases, the first stage between 200 °C and 400 °C and the second stage between 400 °C and 500 °C.

Activation energies for these two stages of decomposition for the different samples are deduced from the slopes of Coats–Redfern plots (Table 2). Activation energies for the first stage of decomposition for the cardanol–formaldehyde (resol)/PMMA semi-IPNs range between 40 and 55 kJ mol^{-1}, whereas corresponding values for novolac based semi-IPNs range between 44 and 65 kJ mol^{-1}. This higher activation energy for the novolac system is also in accordance with the increased thermal stability of novolac based semi-IPNs deduced from the weight loss calculation. The activation energy for the second stage of decomposition is between 90 and 110 kJ mol^{-1} for semi-IPNs, whereas for the cardanol–formaldehyde homopolymers the value is higher (138 kJ mol^{-1}).

Comparison indicates a large difference in activation energies between the first and second stages. The activation energy, for the first stage of decomposition has a value around 40–50 kJ mol^{-1}, the magnitude of which is low for a possible free radical type of decomposition. The cardanol side chain decomposition could, in fact, follow an ionic mechanism by the attack of double bonds by acid protons (available from the phenolic groups) and subsequent β-cleavage of the carbonium ions formed.

The second stage of decomposition, having an activation energy around 140 kJ mol^{-1}, may in all probability follow a radical decomposition mechanism.

ACKNOWLEDGEMENT

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