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Synthesis and mechanical properties of cardanol-formaldehyde (CF) resins and CF-poly(methylmethacrylate) semi-interpenetrating polymer networks

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Cardanol-formaldehyde (CF) resins (both novolac and resol) and CF–poly(methylmethacrylate) (PMMA) semi-interpenetrating polymer networks were synthesized and their mechanical properties and thermal transitions were evaluated. The lower tensile strength of CF resins compared to phenol-formaldehyde (PF) resins may be understood on the basis of the structure of the C_{15} side chain imparting steric hindrance and reduction in intermolecular interactions. Interpenetration of CF with PMMA increased the mechanical properties only marginally. Scanning electron micrographs of the semi-IPNs showed two distinct phases. Thermomechanical analysis gave two glass transition temperatures, T_g, for the IPNs, the lower T_g corresponding to the PMMA phase and the higher T_g to the CF phase. However, the unusual increase in T_g of the CF from 128 °C to 144 °C suggests restrictions in the segmental motion of the CF phase brought about by mixing with another rigid polymer such as PMMA.

1. Introduction

Cosynthesis and interpenetration of two different polymer networks present a convenient technique for achieving desirable properties in polymer materials. According to Sperling [1] an interpenetrating polymer network (IPN) can be defined as a combination of two different polymers in network forms, at least one of which is synthesized/cross-linked in the immediate presence of the other [2–4]. The factors that contribute to improving the ultimate properties include the nature and compatibility of the interpenetrating networks, the method of synthesis, cross-linking reactions, etc. [4–7]. Most of the IPNs that are synthesized phase separate to varying extends [8], but natural entanglements prevent the further phase separation [6] resulting in prevention of creep and flow [1] which are desirable in many applications. Moreover, interpenetration provides synergistic effects and proper selection of components can give rise to improved mechanical properties [9–13]. Many researchers have utilized this opportunity to develop IPNs from polymers based on renewable resources, such as castor oil, by blending with synthetics [9, 10, 14–17]. Such studies may give rise to improved methods for utilization of these abundant alternate resources. This paper reports results on studies on the synthesis and evaluation of mechanical properties and thermal transitions of semi-IPNs of cardanol-formaldehyde (CF) resins and poly(methylmethacrylate).

Cardanol (37300-39-5) belongs to the family of long-chain hydrocarbon phenols extracted from plant species such as *Anacardium occidentale* L. found in many parts of the world [18]. There are innumerable patents and reports [19–23] citing development of polymers from cardanol and cashew nut shell liquid (from which cardanol was obtained by vacuum distillation). Recent studies point to possibilities for development of cardanol-based speciality polymers [24–27]. Cardanol condenses with formaldehyde [28–30] to give polymers similar to phenol-formaldehyde resins, but their mechanical properties were not reported. Cardanol differs from phenol in having a C_{15} hydrocarbon side chain at the meta position and so it may be worthwhile to investigate the system.

2. Experimental procedure

2.1. Materials

Methylmethacrylate (MMA) was washed with 10% aqueous sodium hydroxide to remove the inhibitor. The monomer was then washed with distilled water until all the base had been removed. It was then dried over anhydrous Na_2SO_4 and then vacuum distilled. α-α′, Azoisobutyronitrite (AIBN) (for synthesis) was purified by crystallization from methanol.

Cardanol was purified by distillation under vacuum at 0.0034 m Hg and the fraction distilled at 228–235 °C was collected.

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2.2. Methods

2.2.1. Synthesis

2.2.1.1. Cardanol-formaldehyde (resol) prepolymer (I) [31]. 250 g (0.825 mol) cardanol, 101.9 ml (1.249 mol) 37% aqueous formaldehyde and 3.9 g (0.012 mol) 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 3½ h. The resulting resin was freed from formaldehyde (if any) and catalyst 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.

2.2.1.2. Cardanol-formaldehyde (resol). 6 g cardanol-formaldehyde (resol) prepolymer (I) was compressed in an MS closed mould into rectangular bars of 0.1 m × 0.013 m × 0.002 m using a hydraulic press at 140 °C for 1½ h at 3.33 MN m^{-2} and then subjected to post curing at 170 °C for 1 h.

2.2.1.3. Cardanol-formaldehyde (resol)–PMMA semi-IPNs. The cardanol-formaldehyde (resol) prepolymer (I) powder (10 g) was mixed with varying amounts of MMA and AIBN (1% by weight MMA) and stirred thoroughly in a reaction kettle under nitrogen. The temperature was maintained at 70 °C for 1¼ h. The product was powdered and the particle size was adjusted to pass through an ASTM 34 sieve. The powder was compressed into rectangular bars using a hydraulic press at 140 °C for 1½ h and post cured at 170 °C for 1 h.

2.2.1.4. Cardanol-formaldehyde (novolac) prepolymer (II) [30]. 250 g (0.825 mol) cardanol, 54 ml (0.66 mol) 37% aqueous formaldehyde and 20 ml 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.

2.2.1.5. Cardanol-formaldehyde (novolac). 160 g (0.201 mol) cardanol-formaldehyde (novolac) prepolymer (II) was mixed thoroughly with 4.8 g (0.034 mol) (3%) hexamethylenetetramine (HMTA) and kept in an oven at 120 °C for 1½ h. The partially cured product was powdered and passed through ASTM 34 sieve.

5.2 g of this material was mixed with 0.104 g (0.0007 mol) (2%) HMTA and cold pressed in an MS closed mould into rectangular bars of 0.1 m × 0.013 m × 0.004 m size using a hydraulic press. The cold pressed samples were again compressed after placing them in the mould at 120 °C for ½ h at 3.33 MN m^{-2}. The samples were then subjected to post curing at 170 °C for 1 h.

2.2.1.6. Cardanol-formaldehyde (novolac)–PMMA semi-IPN. The cardanol-formaldehyde (novolac) prepolymer (II) powder (10 g, 0.0125 mol) was mixed with 0.5 g (0.0035 mol) (5%) HMTA, 90 g (0.9 mol) MMA and 0.9 g (0.0055 mol) AIBN and stirred thoroughly in a reaction vessel under nitrogen. The temperature was maintained at 70 °C for 1½ h. The product was powdered and the particle size was adjusted to pass through an ASTM 34 sieve. The powder was compressed into rectangular bars using a hydraulic press at 120 °C for 1½ h and post cured at 170 °C for 1 h.

2.2.2. Characterization

Scanning electron microscopic photographs were taken using a Jeol 35C microscope.

The tensile strength was measured using a Universal testing machine (Instron Model 1195) at an extension rate of 2.5 cm min^{-1}. Shore A and Shore D hardness were measured using a hardness tester of Model – SHR-A-Gold and SHR-D-Gold, respectively. A dupont 990 Modular thermal analysis system consisting of 942 TMA was used for thermal analysis.

3. Results and discussion

3.1. Mechanical studies

Formaldehyde condensation polymers of cardanol were synthesized in the novolac and resol forms. In the case of novolac, the polymer was synthesized in the presence of varying percentages of HMTA as cross-linking agent, whereas resol was a simple condensation product of cardanol and formaldehyde. The mechanical properties of the samples are compared in Table I. Phenol-formaldehyde has a much higher reported tensile strength (34–68.9 MN m^{-2}) [32] and although the comparison of the mechanical properties with that of phenol-formaldehyde has to consider the difference in synthetic condition and procedures, the values for cardanol-formaldehyde novolacs and resols appear to have much poorer mechanical properties. The structure of cardanol-formaldehyde (novolac and resol) is represented in Fig. 1.

The presence of $C_{15}H_{25}$, $C_{15}H_{27}$, $C_{15}H_{29}$ or $C_{15}H_{31}$ side chains in the aromatic nucleus in the case of cardanol (1) could be expected to provide steric hindrance for the aromatic nucleus to come specially close together to condense with formaldehyde and thus, would lead to lower build up of molecular weight in comparison with phenol-formaldehyde, (2) the presence of such a long substitution could also impart strain on the CH_2 bridge linkages between the aromatic nuclei leading to weakening of bonds, and (3) the long side chain could reduce the intermolecular interaction and thereby bring down the strength of the polymer. The poor mechanical properties of cardanol-formaldehyde in comparison to phenol-formaldehyde could thus be explained. Table I suggests that the tensile strength of cardanol-formaldehyde novolac is

TABLE I Mechanical properties of cardanol-formaldehyde polymers (novolac and resol)

System	Total % HMTA added	UTS ($MN m^{-2}$)	Elongation (%)	Hardness	
				Shore A	Shore D
Cardanol-formaldehyde (novolac)	3.5	4.4	19.4	87.5	45.0
	4.0	5.26	10.8	91.5	44.5
	5.0	3.34	9.9	91.5	44.5
	6.0	3.314	5.2	92.0	38.0
	7.0	1.87	4.0	92.0	46.5
Cardanol-formaldehyde (resol)	–	2.63	2.9	92.0	57.5

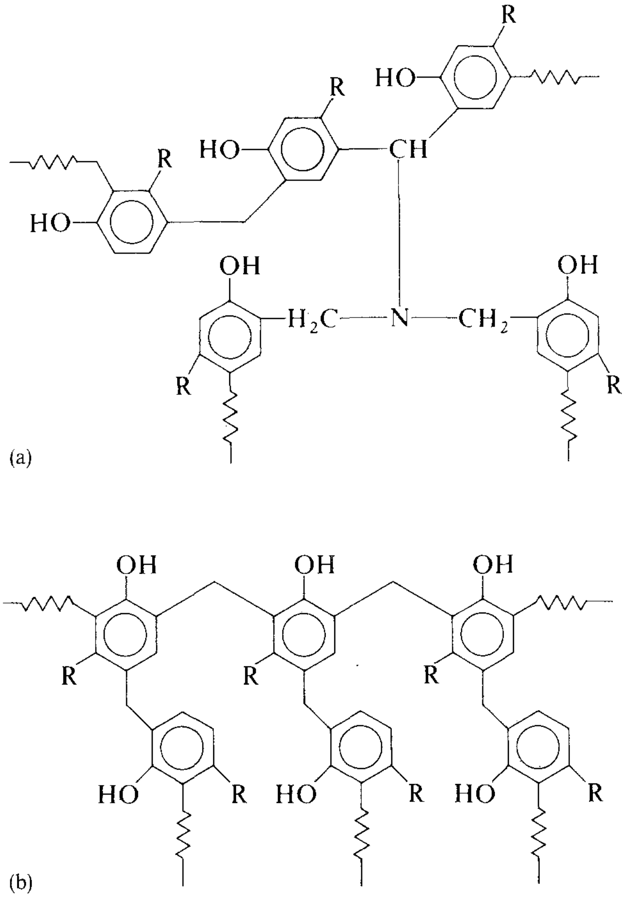

Figure 1 Structure of (a) cardanol-formaldehyde (novolac) and (b) cardanol-formaldehyde (resol). R = $C_{15}H_{25}$, $C_{15}H_{27}$, $C_{15}H_{29}$.

higher than that of the resol system. The tensile strength of novolacs reach a maximum when it is cured with 4% HMTA. Further addition of HMTA results in a decrease of the tensile strength. At high HMTA composition, the polymer becomes brittle and hence results in lower strength.

3.1.1. Cardanol-formaldehyde (novolac and resol)-poly(methylmethacrylate) semi-IPNs

The IPNs of PMMA and cardanol-formaldehyde (novolac and resol) were synthesized by preparing cardanol-formaldehyde prepolymer and further polymerizing and cross-linking it after mixing with MMA and its initiator. MMA polymerization progresses along with the polymerization and cross-linking of cardanol-formaldehyde prepolymer. This is expected to give the semi-IPNs of cardanol-formaldehyde and PMMA.

Tables II and III indicate the mechanical properties at varying compositions of semi-IPNs of PMMA with novolac and resol resins, respectively. In the cases of both novolac and resol based semi-IPNs, the values indicate that incorporation of a considerable amount of PMMA (as high as 50% for novolac and 75% for resol) does not have any marked effect on the tensile strength. The per cent elongation of these products has reduced marginally. Incorporation of PMMA at higher percentages, however, helps in increasing the tensile strength. The variation in tensile strength with the percentage of cardanol-formaldehyde resin is given in Fig. 2. From the plot, it is observed that in the case of novolac based semi-IPN systems, the tensile strength passes through a maximum at 87.5% PMMA and then decreases on further addition of PMMA. The per cent elongation also indicates a decrease. In the case of semi-IPNs based on the resol system, tensile strength decreases when the PMMA content is reduced from 90%. Compared to the reported property improvement effected by semi-IPN formation of two polymeric networks [1], the changes in mechanical properties of cardanol-formaldehyde on interpenetration with PMMA appear to be marginal. Incorporation of PMMA up to 87.5% into the novolac system has increased strength from 3.34 MN m^{-2} to 6.131 MN m^{-2} and the trend of marginal improvement on the tensile strength is observed to reverse on further incorporation in the case of PMMA, whereas semi-IPNs based on the resol system, containing 90% PMMA shows a tensile strength of 7.17 MN m^{-2} and the strength decreases with the decrease in PMMA content. This is in comparison with the tensile strength of more than 50.0 MN m^{-2} [33] for PMMA homopolymer. Improvement in strength properties of cardanol-formaldehyde interpenetrated with PMMA is quite marginal when compared with the reported high and synergistic improvements in mechanical properties brought about by IPN formation.

The behaviour in cardanol formaldehyde–PMMA semi-IPNs can be attributed to the variation in the method of synthesis and to the rigidity of the system concerned. Interpenetration of the rigid system is

TABLE II Mechanical properties of cardanol-formaldehyde (novolac)–PMMA semi-IPNs

Composition of semi-IPNs				Hardness	
Novolac, resin (%)	PMMA (%)	UTS ($MN\,m^{-2}$)	Elongation (%)	Shore A	Shore D
10	90.0	5.18	1.08	90	54
12.5	87.5	6.13	0.5	88	50
25.0	75.0	4.73	3.4	94	46
50	50.0	3.61	2.4	84	43
62.5	37.5	3.18	4.1	84	38
71.4	28.6	3.04	4.1	58	39
100	0	3.34	9.9	92	38

TABLE III Mechanical properties of cardanol-formaldehyde (resol)–PMMA semi-IPNs

Composition of semi-IPNs				Hardness	
Resol, resin (%)	PMMA (%)	UTS ($MN\,m^{-2}$)	Elongation (%)	Shore A	Shore D
10	90	7.17	3.3	83	55
12.5	87.5	4.13	2.0	Out of scale	66
16.6	83.3	3.7	1.8	Out of scale	58
25	75	2.67	1.8	85	56
50	50.0	2.43	1.4	90	65
100	0	2.63	2.9	92	57.5

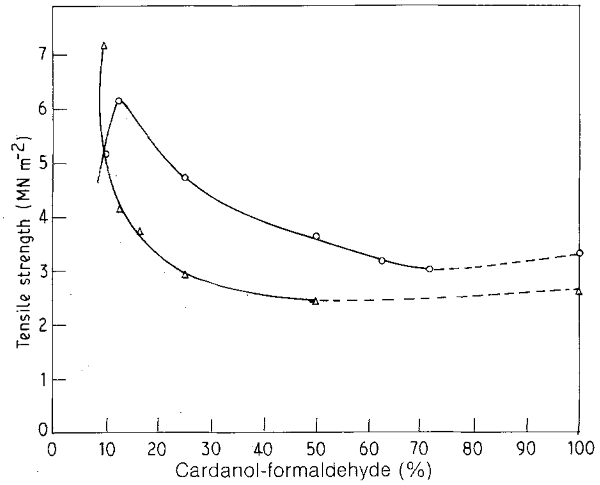

Figure 2 Plot of tensile strength ($MN\,m^{-2}$) versus cardanol-formaldehyde (%) for IPN system. (○–○) IPN from cardanol-formaldehyde (novolac) and PMMA (△–△) IPN from cardanol-formaldehyde (resol) and PMMA.

known to give rise to products of drastically poorer mechanical properties. The drastic decrease in mechanical properties of PMMA incorporation of low percentages of cardanol-formaldehyde and vice versa could thus be attributed to the rigidity in both the homopolymer systems.

Mixing of two different polymers is not expected to impart any mutual strain. But placing of two polymers in juxta position and restricting their mobilities by cross-linking them independently at different points could lead to strain of the chain segments between cross-links and subsequent bending and uncoiling of the chain segments [9]. This will be pronounced when both the polymeric networks involved are rigid in value.

The basic discrepancy in strength properties can also be attributed to the inability of PMMA chains to interpenetrate freely with the sterically restricted cardanol-formaldehyde system. And it is notable that most of the IPNs reported so far involve heterogeneous systems usually constituting one rubbery phase and one glassy phase. The cardanol-formaldehyde–PMMA semi-IPNs studied in this case do not fall under the elastomer–plastic IPN system. Both networks in the semi-IPN are plastic materials and this will also result in restricting the property improvements. The plastic ingredients lack the ability to interpenetrate mutually and hence could have resulted in individual domains which are interpenetrated to a very low level. Hence, the expected synergistic behaviour is not reflected in the observed mechanical properties. The property improvement also depends on various factors such as the nature of the two chains, the method of their synthesis, relative ratio of formation of each network and their compatibility.

3.2. SEM studies

The surface structure of cardanol formaldehyde–PMMA semi-IPNs was studied using scanning electron microscopy. Micrographs of the surface test specimens of cardanol-formaldehyde novolac, cardanol-formaldehyde (novolac)–PMMA semi-IPNs for two magnifications are shown in Figs 3 and 4. Distinct changes can be observed from the comparison of the cardanol-formaldehyde (novolac) (100%), 50 cardanol-formaldehyde (novolac)–50 PMMA and 12.5 cardanol-formaldehyde (novolac)–87.5 PMMA semi-IPNs. Discontinuous cardanol-formaldehyde (novolac) phase is observed in the case of both IPNs.

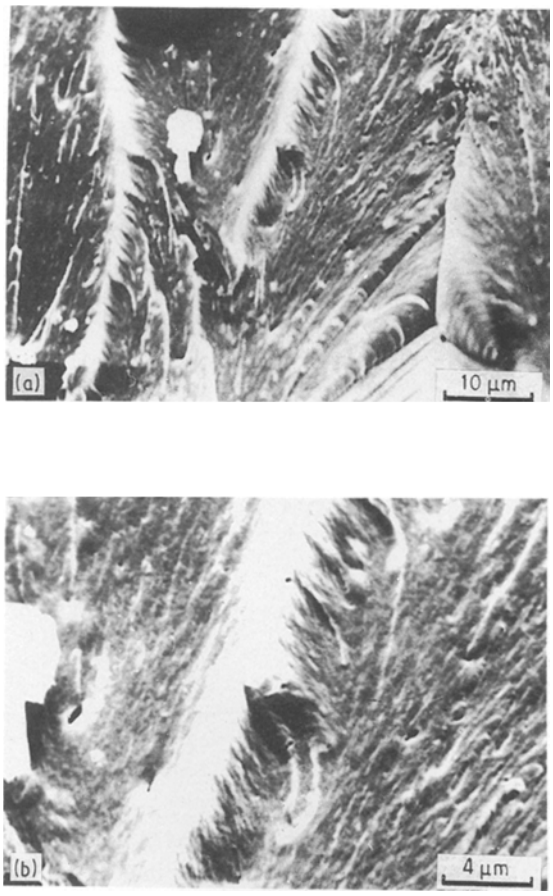

Figure 3 Scanning electron micrographs of cardanol-formaldehyde (novolac) PMMA semi-IPNs containing 0% PMMA.

Electron micrographs of 71.4 cardanol formaldehyde (resol)–28.6 PMMA and 16.7 cardanol-formaldehyde (resol)–83.3 PMMA SEMI IPNs are shown in Figs 5 and 6. Comparison of these micrographs with those of the novolac semi-IPNs suggests a different structure for resol. 71.4 cardanol-formaldehyde (resol)–28.6 PMMA has a more or less layered structure and cardanol-formaldehyde (resol) phase for both the semi-IPM compositions appear to be more continuous in comparison with the novolac phase in the novolac-based IPNs.

3.3. Thermo-mechanical analysis

The measurement of the strength at the glass transition temperature, T_g, can be used to prove the existence of interpenetration. Figs 7 and 8 show the TMA plots for resol- and novolac-based semi-IPNs, respectively. The T_gs deducted from the TMA plots are tabulated in Tables IV and V.

Two T_gs are shown for all the semi-IPNs samples studied. The lower T_g (T_{g_1}) corresponds to the PMMA phase and the higher one (T_{g_2}) corresponds to the cardanol-formaldehyde phase. The increase in T_{g_1} with increasing PMMA content for the novolac-based semi-IPN indicate improved interaction between the phases on increasing PMMA content. However, the increasing T_g for the cardanol-formaldehyde (novolac) phase (from 128 °C to 144 °C) is an unusual phenomenon. The reported trend in T_gs suggests the T_g to lie between the individual T_gs of homopolymers. The cardanol-formaldehyde (novolac) has a T_g of only

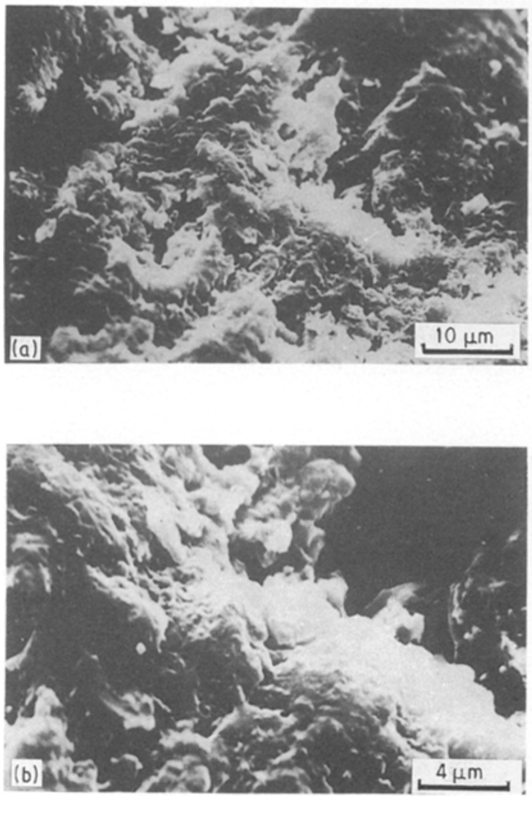

Figure 4 Scanning electron micrographs cardanol-formaldehyde (novolac)–PMMA semi-IPNs containing 50% PMMA.

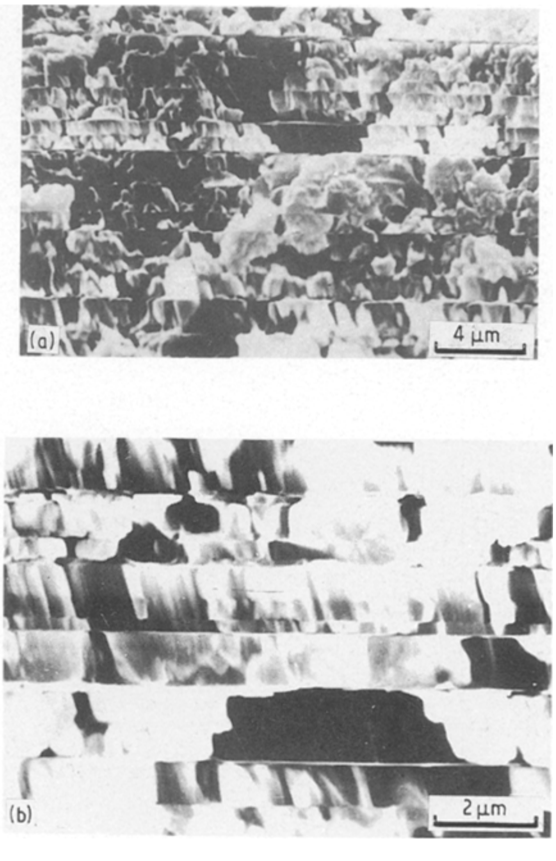

Figure 5 Scanning electron micrographs of cardanol-formaldehyde (resol)–PMMA semi-IPNs containing 28.5% PMMA.

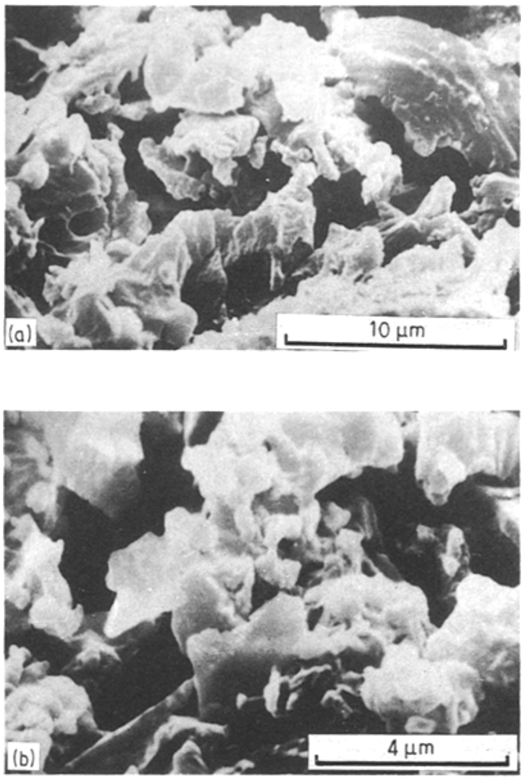

Figure 6 Scanning electron micrographs of cardanol-formaldehyde (resol)–PMMA semi-IPNs containing 83.3% PMMA.

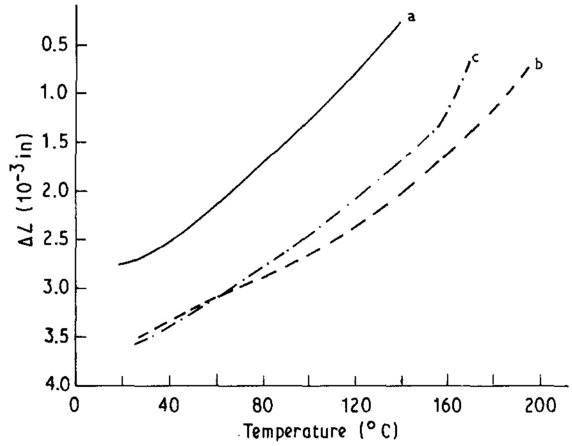

Figure 7 TMA plot for cardanol-formaldehyde (resol)–PMMA semi-IPN. (a) 0% PMMA, (b) 50% PMMA, (c) 75% PMMA.

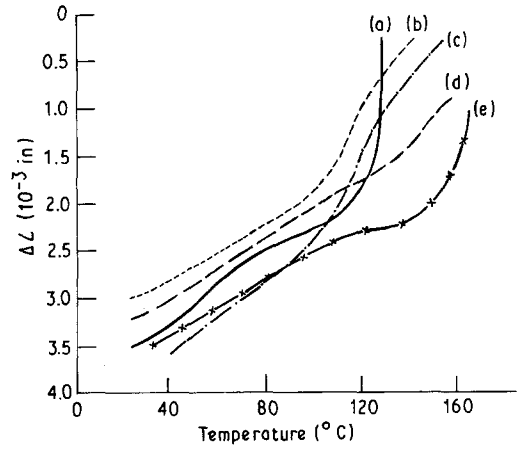

Figure 8 TMA plot for cardanol-formaldehyde (novolac)–PMMA semi-IPN. (a) 0% PMMA, (b) 50% PMMA, (c) 75% PMMA, (d) 83.3% PMMA, (e) 87.5% PMMA.

TABLE IV Glass transition temperature of cardanol-formaldehyde (resol)–PMMA semi-IPNs

Semi IPN composition			
Resol, resin (%)	PMMA (%)	T_{g_1} (°C)	T_{g_2} (°C)
0	100	105	–
25	75	106	152
50	50	106	156
100	0	–	126

TABLE V Glass transition temperature of cardanol-formaldehyde (novolac)–PMMA semi-IPNs

Semi IPN composition			
novolac, resin (%)	PMMA (%)	T_{g_1} (°C)	T_{g_2} (°C)
0	100	105	–
12.5	87.5	110	144
16.7	83.3	110	136
25.0	75.0	108	132
50.0	50.0	106	128
100	0	–	128

128 °C, which increases to 144 °C for 12.5 cardanol-formaldehyde (novolac)–87.5 PMMA semi-IPNs. This suggests possible restrictions in the segmental motion of the cardanol-formaldehyde (novolac) chains brought about by mixing with another rigid polymer system such as PMMA.

A similar trend is also observed for resol-based semi-IPNs as far as the T_{g_2} is concerned. There appears to be little change in the T_g of PMMA in this case.

4. Conclusions

The mechanical properties of cardanol-formaldehyde polymers are found to be lower than those of phenol-formaldehyde systems. The synthesis of interpenetrating networks with cardanol-formaldehyde polymer and PMMA does not give any marked improvement in the strength property of cardanol-formaldehyde homopolymers. This is attributed to the inability of the PMMA chains to interpenetrate freely with the sterically restricted CF system.

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