Studies on the Effect of Curing Agent Concentration and Type of Phenol on Various Physico-Chemical Properties of Resole and Epoxy Blends

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ABSTRACT: Resoles were prepared with different phenols, separately, with formaldehyde having phenol-to-formaldehyde molar ratio of 1:2 in basic medium at 70°C. These resoles were physically blended with different weight percentages of diglycidyl ether bisphenol-A (DGEBA)-epoxy resin. The blends were cured with 40, 50, and 60 wt % polyamide based on the total weight of the blend resin at 100°C. It was found that the blend system containing equal weight ratio of resole, prepared from *p*-cresol, and epoxy resins

showed the least cure time with 40 wt % polyamide among all other blend systems. Also, the cured films of such blend systems showed the best chemical resistance, thermal stability, and hardness as compared to their other blend systems and blend counterparts. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 110: 3812–3819, 2008

Key words: resole; DGEBA-epoxy resin; blend; polyamide; chemical resistance; thermal stability; chemical resistance

INTRODUCTION

Epoxy resins are one of the most important classes of thermosetting polymers and their use is increasing day-by-day for a large number of applications and end uses due to their better mechanical, electrical, thermal, and chemical resistance properties. The epoxy resins find applications in wide range of areas such as in protective coatings, adhesives, body solders, and caulking compounds, dipping compounds, potting and encapsulation compounds, low pressure molding resins, and glass-reinforced plastics.^{1,2}

However, due to brittleness caused by their highly crosslinked systems formed during the curing process, epoxy resins have low ductility, poor heat resistance, and are also liable to yield cracks. The epoxy resins can duplicate the performance of most other thermosetting plastics such as phenol-formal-dehyde resins and exceed their performance in a variety of specialized applications.³ The blends of resole and epoxy will have improved properties than their counterparts.

The blends of epoxy and resole^{4–10} offer a versatile spectrum of superior properties such as outstanding strength and adhesion, good solvent and chemical resistance, high heat and thermal resistance, and so

forth. These blend systems are used in electronic industries as molding and sealing compounds for electronic packaging, protective coatings, composites, and many other application areas such as aerospace, marine, and satellite communications. The use of proper curing agents can convert such resins into a void-free highly crosslinked network, which ultimately can affect the thermal stability of the blend systems.^{11–14} By changing the type of phenol, in the resole, may also affect the properties of the blend systems. Therefore, the effect on various physicochemical characteristics while varying the curing agent concentration and changing the type of phenol in resole has been investigated in our present article. Such blend systems might be used for fast curing coating application areas.

EXPERIMENTAL

Materials

Phenol, *o-*, *p-*, and *m*-cresols, formaldehyde (37% w/ v), methyl ethyl ketone (MEK), sodium bicarbonate, (all from M/s Thomas Baker Chemicals, Mumbai), potassium hydroxide, sodium hydroxide, sodium carbonate, sulfuric acid and methanol (all from M/s CDH, New Delhi) were used during the investigation. Diglycidyl ether bisphenol-A (DGEBA) epoxy resin (Grade: *R*-100; EEW: 190 g/equiv) and polyamide (Grade: PH-851; Amine value: 240–400 mg

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Sample Designation												
S. no.	E/R_1	PA	Code	E/R_2	PA	Code	E/R ₃	РА	Code	E/R_4	PA	Code
1	0/100	0	E0R110	0/100	0	E0R210	0/100	0	E0R310	0/100	0	E0R410
		40	$E_0 R_{114}$		40	$E_0 R_{214}$		40	$E_0 R_{314}$		40	$E_0 R_{414}$
		50	$E_0 R_{115}$		50	$E_0 R_{215}$		50	$E_0 R_{315}$		50	E_0R_{415}
		60	$E_0 R_{116}$		60	$E_0 R_{216}$		60	$E_0 R_{316}$		60	$E_0 R_{416}$
2	25/75	0	$E_2 R_{170}$	25/75	0	$E_2 R_{270}$	25/75	0	$E_2 R_{370}$	25/75	0	E_2R_{470}
		40	E_2R_{174}		40	$E_2 R_{274}$		40	E_2R_{374}		40	E_2R_{474}
		50	E_2R_{175}		50	E_2R_{275}		50	E_2R_{375}		50	E_2R_{475}
		60	E_2R_{176}		60	E_2R_{276}		60	E_2R_{376}		60	E_2R_{476}
3	50/50	0	E_5R_{150}	50/50	0	E_5R_{250}	50/50	0	E_5R_{350}	50/50	0	E_5R_{450}
		40	E_5R_{154}		40	E_5R_{254}		40	E_5R_{354}		40	E_5R_{454}
		50	E_5R_{155}		50	E_5R_{255}		50	E_5R_{355}		50	E_5R_{455}
		60	E_5R_{156}		60	E_5R_{256}		60	E_5R_{356}		60	E_5R_{456}
4	75/25	0	$E_7 R_{120}$	75/25	0	$E_7 R_{220}$	75/25	0	$E_7 R_{320}$	75/25	0	$E_7 R_{420}$
		40	$E_7 R_{124}$		40	$E_7 R_{224}$		40	$E_7 R_{324}$		40	$E_7 R_{424}$
		50	$E_7 R_{125}$		50	$E_7 R_{225}$		50	$E_7 R_{325}$		50	$E_7 R_{425}$
		60	$E_7 R_{126}$		60	$E_7 R_{226}$		60	$E_7 R_{326}$		60	$E_7 R_{426}$
5	100/0	0	$E_1 R_{100}$	100/0	0	$E_1 R_{200}$	100/0	0	$E_1 R_{300}$	100/0	0	$E_1 R_{400}$
		40	$E_1 R_{104}$		40	$E_1 R_{204}$		40	$E_1 R_{304}$		40	E_1R_{404}
		50	$E_1 R_{105}$		50	$E_1 R_{205}$		50	$E_1 R_{305}$		50	E_1R_{405}
		60	$E_1 R_{106}$		60	$E_1 R_{206}$		60	$E_1 R_{306}$		60	E1R406

TABLE I Sample Designation

E, DGEBA-epoxy; R₁, resole from phenol; R₂, resole from *o*-cresol; R₃, resole from *p*-cresol; R₄, resole from *m*-cresol; PA, polyamide in weight %; E/R in wt/wt.

KOH/g) were taken from M/s Resinova, Nayaganj, Kanpur, for the preparation and curing of blends.

Preparation of blend samples

The resoles from various phenols were synthesized by reacting respective phenols and formaldehyde in a molar ration of 1 : 2 in basic medium at 70°C by a method adopted by Knop and Schieb.³ The DGEBAepoxy resin was mixed with various resoles, separately, in different weight ratios ranging between 0 and 100 wt % in the interval of 25 wt % according to the formulation given in Table I.

Curing of blend samples

The curing of blend samples was performed in an air oven at temperatures obtained from differential scanning calorimetric (DSC) scans under dynamic mode. For curing the samples, polyamide (40–60 wt % of total weight of blend of epoxy/resole) was used as curing agent during the studies.

Preparation of panels for chemical resistance

The films of pure resoles, DGEBA-epoxy and blends of resole (s) and epoxy were coated on sand blasted steel sheet panels of size 150 mm \times 100 mm \times 1.25 mm using Bird Film Applicator (M/s Sheen Instruments, UK). These panels were further sealed from three sides by using molten paraffin wax. The dry film thickness of about 150 µm was maintained on all the panels. These films were then cured as per the cure schedule. The panels were examined for a visible change in the conditions of the film samples at regular intervals when immersed in different chemicals like solvents, acids, and alkalies at ambient temperature for 6 months.

Fourier-transform infrared (FTIR) spectroscopic analysis

FTIR spectra of all pure resoles and blend samples were taken from "Bruker Victor 22 in. infrared spectrophotometer of USA in the wave number range 500–4000 cm⁻¹ with standard KBr pellets. The blend sample having equal weight ratios of resole, prepared from *p*-cresol, and DGEBA-epoxy has been considered for IR spectrum as this blend sample showed least cure time at 100°C. Although the blend sample containing equal weight ratios of resole, prepared from *m*-cresol, and epoxy showed least cure time but this was not considered as the resole prepared from *m*-cresol took only 30 min for the completion of reaction and so could not give higher molecular weight resole.³

Differential scanning calorimetric (DSC) analysis

The cure temperatures for the completion of curing reactions of epoxy and resole blend samples were determined by DSC of TA instruments, USA (model 2910) in dynamic mode at a heating rate of 10° C/min in the temperature range of $50-250^{\circ}$ C.



Figure 1 FTIR spectrum of uncured blend of *p*-cresolic resole and epoxy (E_5R_{350}) .

Thermogravimetric (TG) analysis

The thermal stability was determined by comparing the onset degradation temperature (5% weight loss) of cured samples by using thermogravimetric analyzer (TGA) of DuPont, USA (Model TGA VSIA DuPont 2100) at a heating rate of 10° C/min and in nitrogen atmosphere with flow rate 10 cc/min from ambient to 800°C.

Scratch hardness

The scratch hardness of cured films, prepared in the experimental section, was determined according to Indian standard (IS 101, Part 5, Sec. 2, 1988) using table type scratch hardness tester of M/s Sheen Instruments, UK for varying loads.

RESULTS AND DISCUSSION

FTIR analysis of uncured and cured blend samples

Figure 1 showed the IR spectrum of blend sample E_5R_{350} . From Figure 1, it is clear that a band appeared in the region of 3200–3500 cm⁻¹ that might be due to the presence of *p*-cresolic hydroxyl group in the blend system. Methylol and methylene linkages were found to be present, after blending, indicated that there occurred no chemical reaction between hydroxyl of the methylol group with the oxirane group of the epoxy resin. The peak appearance near 1040 cm^{-1} confirmed the same (Fig. 1). The shifting of peak related to p-cresolic hydroxyl, as reported in literature³ for the blend of phenolic resole and epoxy, indicated the reaction of oxirane group of the epoxy resin and the hydroxyl group of the *p*-cresol. The peak appearance near 1120 cm^{-1} , due to aromatic ether group, further supported the same. Also, the characteristic peaks of oxirane group of the epoxy resin appeared as sharp peaks at 970 and 910 cm⁻¹. Similar peak positions of various



Scheme 1 Reaction mechanism of resole (s) and DGEBA-epoxy resin.

functional groups have also been mentioned in the literature.^{8,9}

The preceding discussion, on IR, might be confirmed by the reaction mechanism as shown in Scheme 1 between *p*-cresolic resole (R_3) and epoxy resin (E). The mechanism was proposed in a similar fashion as proposed between phenolic resole and epoxy.³ Further, the blend of epoxy and other resoles might result similar types of products but of different reactivities, due to phenols of varying reactivities.

Resole itself can act as a curing agent for epoxy resin [3, 10.11], but the curing might proceed at a very slow rate. Therefore, three weight percentages of curing agent (polyamide), viz., 40, 50, and 60 wt %, with the total weight of the blend resin were considered in the present article. The concentration of curing agent was considered on the basis of the literature for phenolic resole.³ The effect of epoxy content, type of phenol, in resole and curing agent concentration on cure time of blend resins has been shown in Figures 2–4. These figures clearly indicated that the cure time of the blend samples, first, decreased up to 50 wt % epoxy content and then increased. Therefore, the blend containing equal weight ratios of



Figure 2 Variation in cure time of blend systems cured with 40 wt % polyamide.



ENDO 50 75 100 125 150 175 200 Temperature (°C)

Figure 5 DSC scan of blend sample E_5R_{354} .

Figure 3 Variation in cure time of blend systems cured with 50 wt % polyamide.

epoxy and resole was considered to be the optimum blend ratio. The cure time of blend samples E_5R_{154} , E₅R₂₅₄, E₅R₃₅₄, and E₅R₄₅₄ were found to be 60, 40, 35, and 30 min, respectively, cured with 40 wt % polyamide at 100°C. The cure temperature was taken from the maximum peak temperature in dynamic DSC scan of blend sample, E_5R_{354} (Fig. 5). Although the blend sample containing *m*-cresolic resole and epoxy showed least cure time, but this was not considered for further studies. The resole, based on *m*cresol, resulted in only 30 min. The reaction rate of *m*-cresol with formaldehyde is about three times higher than that for phenol based resole and also higher than o- and p-cresol systems. Therefore, during resole synthesis the *m*-cresol readily reacted with formaldehyde resulting high viscosity product while



Figure 4 Variation in cure time of blend systems cured with 60 wt % polyamide.

during this period other systems remained unaffected or partially reacted. Some time this could lead to the formation of more secondary hydroxyl groups as compared to other systems. During crosslinking reactions of *m*-cresolic resole with epoxy groups, the presence of such secondary hydroxyl groups might catalyze the curing reactions and hence showed minimum cure time^{3,8–12} that might not result better quality product. Therefore, *p*-cresolic resole based blend system has been considered to be the least cure time system.

Curing of blend sample

The reaction product "A" of Scheme 1 may be represented as "B" in Scheme 2. The curing might proceed with the reaction of reaction product "B" and polyamide forming secondary hydroxyl groups (Scheme 3). The reaction product "C", formed in Scheme 3, might further react with another "B" forming another secondary hydroxyl group and can be shown in Scheme 4. The product "D," formed in Scheme 4, might further react with another epoxy group of product "B," and so on. This could result



Scheme 2 Structures of various byproducts.

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Scheme 3 Curing mechanism of blend of resole and DGEBA-epoxy resin with polyamide.

in a three-dimensional network structure.^{3,10-12} The physical appearance of the cured product confirmed the same. The IR spectrum (Fig. 6) of the cured blend sample, E₅R₃₅₄, further confirmed the same which showed with the disappearance of characteristics peaks discussed in article 3.1 for similar uncured blend sample along with appearance of new peaks near 1620 and 1650 cm⁻¹ due to NH bending and CO stretching vibrations in the cured blend sample. Formation of stretched peak in the region of 850–950 cm⁻¹ and at 850–1050 cm⁻¹ were observed which might be attributed to O-H bending and C-O stretching vibrations as well as consumption of epoxy groups. All other characteristic groups formed as a result of curing with polyamide and according to the proposed reactions of curing given in Schemes 2–4.

Thermal stability

The temperatures of 1–10% weight loss in TGA curves at a heating rate of cured blend samples are given in Table II. The temperatures up to 5 wt % loss in TGA thermograms have been ignored as these might appear due to presence of impurities in the blends. Thus, the temperatures for 5% weight loss could be treated as an indicating temperature for the thermal stability of the blends and these temperatures have been shown in Table III. From Table III, it is clear that the blend sample containing *p*-cresolic resole and epoxy with 40 wt % polyamide showed the highest initial degradation temperature (IDT), that is, 324°C, among all other blend samples. Also, the percent char yield was found to be maximum in blend sample E_5R_{354} (Table III). Further, all the blend



Scheme 4 Propagation reaction of curing mechanism.

samples containing 40 wt % polyamide showed higher IDT's than that of blend samples containing 50 wt % polyamide. Hence, the blend samples containing 40 wt % polyamide were found to more thermally stable blend systems than the blend samples containing 50 wt % polyamide (Table III). This might be attributed to the presence of more crosslinks in the cured blend samples having 40 wt % polyamide.

Chemical resistance of blend samples

Effect of various acids, alkalies, and solvents on the cured films of pure resole (s) and DGEBA-epoxy resins

Figures 7–9 showed the comparative acids, alkalies, and solvent resistance, respectively, of the cured films of pure resole (s) and pure epoxy. A quick perusal of Figure 7 clearly illustrated that the film of coatings based on resole, prepared from *p*-cresol, and DGEBA-epoxy resins have offered maximum resistance towards different concentrations of acids and alkalies as compared to the films of other resoles. This behavior might be attributed to the fact that the resole, prepared from *p*-cresol offered greater reactivity resulting in a more complex structure to provide these resistance as compared to other resoles.

Effect of various acids, alkalies, and solvents on the cured films of resole and DGEBA-epoxy blend resins

The comparative acids, alkalies, and solvent resistance on the cured films of *p*-cresolic resole and epoxy resin blends has been shown in Figures 10–12. The cured films of all blend samples were completely unaffected by 10% acetic acid solution for the entire period of exposure of 12 months. The films when exposed to 10% sulfuric acid and hydrochloric acid solutions were found to be resistant for 10 months whereas in other solutions, they were resist-



Figure 6 FTIR spectrum of cured blend of *p*-cresolic resole and epoxy (E_5R_{354}).

1		0		0	5	1				
	Temperature for (K)									
Weight loss (%)	E_5R_{154}	E_5R_{254}	E_5R_{354}	E_5R_{454}	E_5R_{155}	E_5R_{255}	E_5R_{355}	E_5R_{455}		
1	384	420	491	416	355	440	428	344		
2	437	455	498	466	422	517	571	409		
3	527	502	527	523	462	540	582	473		
4	555	562	567	538	500	575	584	557		
5	591	589	597	593	587	580	587	573		
6	602	591	600	598	604	606	604	588		
7	623	595	605	609	622	615	609	595		
8	634	605	609	623	635	620	617	600		
9	641	613	613	630	644	624	626	609		
10	648	626	623	634	648	628	635	620		

 TABLE II

 Temperature of 1–10 Percent Weight Loss in Thermogravimetric (TG) Analysis of Cured Blend Samples

ant for less than 9 months. The film of blend samples E_5R_{254} and E_5R_{354} showed better resistance towards all acid solutions as compared to the film of blend samples E_5R_{154} and E_5R_{254} . The higher concentration of alkali solution less affected the film surface than lower alkali solutions (Fig. 11). It could also be seen from Figure 12 that the film surface were strongly affected by solvents like methanol, acetone, and MEK whereas the films retained their surface in solvents like tolune, xylene, and MTO for a period of 12, 9, and 10 months, respectively. This behavior might be attributed to the fact that the resole, prepared from *p*-cresol offered greater reactivity as compared to phenol and o-cresol resulting in a more complex structure to provide these resistance as compared to other resoles and might result greater degree of crosslinking also affected the same.^{13,14}

The blending of epoxy, separately, with different resoles improved the acid, alkalies, and solvent resistance of the resole resins (refer Figs. 7–12). Hence, the films of blend samples were found to more chemically resistant than their pure resole counterparts. This behavior might be attributed to the fact

TABLE III Degradation Temperature at 5 Percent Weight Loss of Blends of Resole/Epoxy Coatings in TG Analysis

S. no.	Code	IDT ^a (°C)	DT ₅₀ ^b (°C)	FDT ^c (°C)	CY ^d (%)
1.	E_5R_{154}	318	418	544	15.1
2.	E_5R_{254}	316	403	503	15.3
3.	E_5R_{354}	324	430	505	17.5
4.	E_5R_{454}	320	425	550	15.2
5.	E_5R_{155}	307	454	531	15.0
6.	E_5R_{255}	311	417	497	15.0
7.	E_5R_{355}	314	453	550	17.0
8.	$E_5 R_{455}$	300	440	515	15.7

^a IDT, Initial Degradation Temperature.

^b DT_{50} , Degradation Temperature at 50 percent weight oss.

^c FDT, Final Degradation Temperature.

^d CY, Char Yield.

that the formation of more crosslink structures by the addition of epoxy resin. It was also found that the blend samples based on *p*-cresolic resole and epoxy showed the best chemical resistant characteristics among other blend samples. This might be due to higher aromatic content and more crosslink sites along the backbone of the molecule.¹³

Scratch hardness

The variation of scratch hardness of the coating films prepared from different blend samples are shown in Figure 13. From figure, it is clear that the maximum hardness was found for pure epoxy resin. The scratch hardness of the pure resole (s) were improved when



Figure 7 Effect of various acids on the cured films of pure resole (s) and epoxy.



Figure 8 Effect of various alkalies on the cured films of pure resole (s) and epoxy.



Figure 10 Effect of various acids on the cured films of blends of resole and epoxy.

blended with epoxy resin. The scratch hardness of pure epoxy resin was found to be 5.0 kg. On blending resoles, separately, with epoxy resin, the scratch hardness of the blend sample E_5R_{354} was found to maximum, that is, 3.3 kg. This might be attributed to the formation of more crosslinks as a resulting chemical reaction between *p*-cresolic resole, epoxy, and poly-

amide. This could provide more complex structure to make this resin film more tough, hard, and higher resistance to cracking/crazing during services whereas the lower values of hardness in case of blend samples, E_5R_{154} , E_5R_{254} , and E_5R_{454} might form lower crosslink sites which might improve the flexibility of the cured film with a sacrifice to the hardness. The formation of



Figure 9 Effect of various solvents on the cured films of pure resole (s) and epoxy.



Figure 11 Effect of various alkalies on the cured films of blends of resole and epoxy.

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Figure 12 Effect of various solvents on the cured films of blends of resole and epoxy.

more char in case of blend sample E_5R_{354} confirmed the same as compared to other blend samples (refer Table III).

CONCLUSIONS

The infrared spectroscopic analysis was used to study the appearance and disappearance of various functional groups during the reactions of resole and epoxy as well as during curing which resembled the proposed reaction mechanism. The addition of 40 wt % polyamide resulted least cure time for all blend samples. Blend sample containing p-cresolic resole and epoxy (in equal weight ratios) with 40 wt % polyamide showed the highest thermal stability among all other blend samples. Also, all the blend samples containing 40 wt % polyamide resulted higher thermally stable blend systems as compared to all blend samples containing 50 wt % polyamide. The film of coatings based on resole, prepared from p-cresol, and DGEBA-epoxy have offered maximum resistance toward different concentrations of acids and alkalies as compared to other blend samples. This might be attributed to the formation of more crosslinks as a resulting chemical reaction between *p*-cresolic resole, epoxy, and polyamide. This could provide more complex structure to make this resin film more tough, hard, and higher resistance to



Figure 13 Variation in scratch hardness of blend systems cured with 40 wt % polyamide.

cracking/crazing during services. The formation of complex structure during curing resulted maximum scratch hardness in case of blend sample containing *p*-cresolic resole and DGEBA-epoxy among other blend samples.

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