Asian Journal of Chemistry; Vol. 36, No. 9 (2024), 2169-2178

ASIAN JOURNAL OF CHEMISTRY

https://doi.org/10.14233/ajchem.2024.32231

Epoxidized Novolac Modification in Resol Phenolic under Open Mold Heat Curing for Microvoid Reduction

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Received: 3 July 2024; *Accepted*: 12 August 2024; *Published online*: 30 August 2024; AJC-21744

Resol phenolics were generally cured by temperature assisted compression molding. In this study, resol phenolic was modified using epoxidized novalacs (EN) and cured by heat assistance without pressure to find the influence of EN on the reduction of microvoids in cured resol phenolics. Epoxidized phenolic novolac (EPN), epoxidized *p*-cresol novolac (EPCN) and epoxidized *o*-cresol novolac (EOCN) were synthesized and used for modification of resols. The modification led to reduction in both the size and number of voids and increase in the tensile strength, flexural strength and impact strength of the resol phenolics. Epoxidized novolacs with phenol: formaldehyde ratios 1:0.7 and 1:0.9 exhibit comparatively better results for the resols. The decrease in the % soluble matter in the cured resin and FTIR spectrum show the incorporation of epoxidized novolacs to the resol phenolics. The dynamic mechanical analysis (DMA) confirms better damping properties of the modified resols. Thermogravimetric analysis shows improved thermal properties for the resol samples modified with EPN and EPCN. The optimum amount of epoxidies novolacs required for the modification was ~7.5-10%.

Keywords: Resols, Epoxidized novolacs, Thermoset modification, Dynamic mechanical analysis, Thermogravimetry.

INTRODUCTION

Resol phenolic is one of the cheapest thermoset resin with a history of more than hundred years [1,2]. Because of its specialties like the ease of preparation, high strength, high heat and electrical resistance, good chemical and weather resistance and low water absorption, it still invites as a potential thermoset resin [3-6]. The voids in the cured resol phenolics makes it undesirable material for many applications. The formation of voids is mainly because of the condensation products having water, formaldehyde, *etc*. during curing of the resols. Numerous works have been done to improve the properties of resol phenolics [3,7-9]. The use of different types of phenols and aldehydes at the preparation stage is one of the easiest ways to modify the properties of resols [10,11]. The properties of resols can also be modified by incorporating rubbers, thermoplastics, particulate fillers and reinforcing with fibers. Other methods include chemical modification, process modification and other means [12,13].

Epoxidized novolacs (EN) act as a good modifier for various thermoset resins. The modification using EN achieves better mechanical and thermal properties [14-16]. Epoxidation of novolacs can be achieved by reacting novolac resin with epichlorohydrin. The reaction between the phenolic -OH group of novolac and the epoxide is catalyzed by acids, bases, triaryl or trialkyl nucleophile of Group VA compounds and quarternary ammonium complexes. Catalysts such as phosphine or tertiary amine are usually utilized, with triphenyl phosphine being the most used.

Epoxidized novolacs can join with two resol prepolymer molecules through either the methylol groups or the phenolic –OH groups since they have atleast two epoxy groups. Through the epoxy groups in the epoxidized novolacs and the methylol groups in the resol resin, it causes a concomitant crosslinking reaction [17]. This means that without compromising the structural integrity of cured resol, number of byproducts generated during curing and the crosslink density can both be decreased. Better phenolic resol resins are therefore anticipated as a result of incorporating epoxidized novolacs.

In this study, various epoxy novolacs based on simple phenol, *p*-cresol and *o*-cresol with varying phenol to formaldehyde ratios were synthesized and subsequently epoxidized using epichlorohydrin. These epoxy novolacs were used as modifiers to reduce the microvoids and improve the properties of resol phenolics.

EXPERIMENTAL

Phenol (m.w. 94.11, m.p.: 39.5-41 ºC), *p*-cresol (m.w. 108.14, b.p.: 202 ºC, 98% assay), *o*-cresol (m.w. 108.14, b.p.: 190 ºC, 98% assay), formaldehyde (37-41% w/v, $d^{20} = 1.08$), sodium hydroxide (m.w. 40, 97% assay) and oxalic acid (m.w. 126.07, 99.8% assay) were L.R. grade supplied by Loba Chemie, India. Epichlorohydrin (L.R., m.w. 92.53, 98% assay b.p.: 114-118 ºC) was supplied by Research Laboratory, Mumbai, India. Benzene (m.w. 78. 98% assay) and triphenyl phosphine (m.p.: 78-82 ºC, m.w.: 262.3, 98% assay) were obtained from E. Merck India. Commercial resol resin in alkaline medium was obtained from M/s Polyformalin (P) Ltd., Thripunithura, India. The physical properties of phenol-formaldehyde (PF) resin are given in Table-1.

TABLE-1
PHYSICAL PROPERTIES OF THE COMMERCIAL PHENOL-FORMALDEHYDE RESOL RESIN

Appearance	Deep brown colour
Viscosity	~2000 cps
Water tolerance	~1:3
Solid content	~50
F:P ratio	~1.85

The phenol-formaldehyde (PF) resol resin was made neutral with glacial acetic acid until the pH reached 7. It was kept overnight and the water layer was removed off. The resin was subsequently dried for 12 h using a vacuum oven to remove the water completely.

Synthesis of epoxy modifiers

Novolac resins: Initially, novolacs were synthesized by allowing phenol and formaldehyde, at a molar ratio of 1:0.7, to react in the presence of oxalic acid as catalyst in a three-necked flask with a mechanical stirrer, a water condenser and a thermometer. The reaction mixture was refluxed for 2-3 h. The compl-etion of the reaction was indicated by phase separation of water and the resin. Sodium hydroxide was used to neutralize the mixture before it was filtered, washed with water and vacuum dried. Novolac resins were synthesized from *p*-cresol and *o*-cresol using the same process. Novolac resins with phenol and formaldehyde in different molar ratios, 1:0.5 and 1:0.9, were also prepared using the same technique.

Epoxidized phenolic novolacs (EPN): Novolac resin (1:0.7) and epichlrohydrin were mixed in the ratio 1:6 and the mixture was heated in a boiling water bath. An aqueous NaOH solution (30%) was added to the reaction mixture dropwise with constant stirring and continued stirring for 16 h. The separated organic layer was dried with sodium sulphate and then fractionally distilled under vacuum. Novolac resins with varying phenol and formaldehyde molar ratios (1:0.5 and 1:0.9) were also subjected to epoxidation to form EPNs of different compositions [16]. These epoxy novolacs were designated as EPN5, EPN7 and EPN9, respectively. The same procedure was followed for the synthesis of epoxidized *p*-cresol novolac (EPCN) and *o*-cresol novolac (EOCN). Epoxidized *p*-cresol novolacs were designated as EPCN5, EPCN7 and EPCN9 whereas epoxidized ortho-cresol novolacs were designated as EOCN5, EOCN7 and EOCN9. The modified resol phenolics were designated as EPN5PR, EPN7PR, EPN9PR, EPCN5PR, EPCN7PR, EPCN9PR, EOCN5PR, EOCN7PR and EOCN9PR.

Weight per epoxide (wpe) values of the synthesized samples were determined by the pyridinium chloride method as per ASTM D 1652-11. Various epoxies used in the study are given in Table-2 with abbreviation of each epoxidized novolac.

TABLE-2
LIST OF EPOXIES USED AS MODIFIERS, THEIR ABBREVIATIONS AND WEIGHT PER EPOXIDE (WEP) VALUES

Type of epoxy	Abbreviation	WEP
Epoxidized phenolic novolac	EPN5	210
	EPN7	186
	EPN9	171
Epoxidized *p*-cresol novolac	EPCN5	221
	EPCN7	193
	EPCN9	217
Epoxidized *o*-cresol novolac	EOCN5	281
	EOCN7	247
	EOCN9	245

Sample preparation: Dried phenolic resol resin was mixed with varying proportions of epoxies (2.5%, 5%, 7.5%, *etc.*) dissolved in methyl ethyl ketone using a mechanical stirrer for 20 min then 0.5% of PPh_3 on resol basis was also added. The solvent was then removed by applying vacuum for about 45 min. The dried and degassed samples were then poured into a Teflon mould with 4 mm deep rectangular cavities and cured in an air oven according to the following time-temperature schedule (60 ºC, 2 h: 70 ºC, 15 h; 80 ºC, 2 h; 90 ºC, 1 h; 100 ºC, 1 h; 110 ºC, 1 h and 120 ºC, 2 h). The slow cure period helps the water of condensation to escape as and when formed.

Spectroscopic studies: FTIR spectra of the samples (in finely powdered form) were taken in Bruker FTIR spectrophotometer model Tensor 27 (spectral range of 7500-370 cm^{-1} with standard KBr beam splitter) in attenuated total reflectance (ATR) mode having zinc selenide as crystal material with high sensitivity DLATGS detector with KBr window.

Mechanical properties: Tensile and flexural strengths of the cured samples were tested on a Shimadzu Autograph AGI Universal Testing Machine. Testing samples were cast in a Teflon mould, fabricated as ASTM D-638 for tensile strength and ASTM D 790 for flexural strength. All samples were cured as per the time and temperature schedule given earlier. The impact strength of the cured samples was tested on a Resil Impact Analyser (Junior) as per ASTM D-256. A hammer with 4J capacity at a speed of 3.46 m/s was used for testing the samples.

Dynamic mechanical analysis (DMA): The dynamic mechanical analysis was performed using a TA Instruments DMA-Q 800. The tests were performed in the fixed frequency mode (1 Hz). A temperature ramp was run from room temperature to 250 ºC at a heating rate of 1 ºC/min.

Thermogravimetric analysis: A TA Instrument TGA Q 50 model was used to investigate thermal degradation. A temperature ramp was run from room temperature to 800 ºC at 20 ºC/min in nitrogen.

Soxhlet extraction: The samples were ground to fine particles and packets containing 2 g of the ground sample in Whatmann No. 1 paper were extracted with acetone in a Soxhlet apparatus for 48 h. The loss in weight of the packets after extraction gave the amount of soluble matter and the percentage soluble matter was calculated.

SEM analysis: Scanning electron microscope (JOEL JSM 840A Scanning Microscope) was used to investigate the morphology of the fractured surfaces.

Void size characterization and distribution: The voids in the cured sample are assumed to be uniformly distributed in the bulk. Magnified micrographs can be used to calculate the morphological parameters. The distribution of the void parameters was determined by measuring the diameters on the magnified SEM micrographs. These were calculated using eqns. 1-6 [18,19]:

Number-average diameter:

$$\overline{D_n} = \frac{\sum N_i D_i}{\sum N_i} \tag{1}$$

Weight-average diameter:

$$\overline{D_w} = \frac{\sum N_i D_i^2}{\sum N_i D_i} \tag{2}$$

Surface area -average diameter:

$$\overline{D_a} = \sqrt{\frac{\sum N_i D_i^2}{\sum N_i}} \tag{3}$$

Volume-average diameter:

$$\overline{D_v} = \sqrt[3]{\frac{\sum N_i D_i^3}{\sum N_i}} \tag{4}$$

where N_i is the number of particles having a diameter D_i.

The poly dispersity index (PDI), which is a direct measure of size distribution of the voids, is calculated as:

$$\text{PDI} = \frac{\overline{D_w}}{\overline{D_n}} \tag{5}$$

The volume fraction of void (V_D) may be calculated as:

$$V_D = \frac{\pi}{4}\left(\frac{\sum N_i D_i^2}{A_T}\right) \tag{6}$$

where A_T is the area of micrographs under analysis. Eqn. 6 assumes that the volume fraction is an isotropic property; hence the values measured in the micrograph plane are same as those in the real volume.

RESULTS AND DISCUSSION

Epoxide equivalents: The wpe (epoxy equivalents) values for EPN5, EPN7 and EPN9 were found to be 210 (4.76 eq/Kg), 186 (5.376 eq/Kg) and 171 (5.85 eq/Kg), respectively. EPN9 which contains phenol and formaldehyde in the ratio 1:0.9 was found to have greater epoxide content than the other two epoxy novolacs. The wpe (epoxy equivalents) for EPCN5, EPCN7 and EPCN9 were found to be 221 (4.52 eq/Kg), 193 (5.18 eq/Kg) and 217 (4.61 eq/Kg), respectively, whereas the wpe values for EOCN5, EOCN7 and EOCN9 were found to be 281 (3.56 eq/Kg), 247 (4.05 eq/Kg) and 245 (4.08 eq/Kg) respectively.

FTIR spectroscopy: The FTIR spectra of cured neat and EPN9 modified resol resin are shown in Fig. 1. The spectra of both the resins are identical. The increase in the peak intensity at ~2900 cm^{-1} and 1360 cm^{-1} is mainly due to the increase in number of $-CH_2-$ groups due to the reaction between resol prepolymers with EPN, which originally contained $-CH_2-$ groups. The enhancement in the peak intensities at ~1050 cm^{-1} and ~1220 cm^{-1} is due to the stretching vibrations of the C-O bond of the secondary alcoholic group, formed by the reaction of epoxy group in the EPN with the –OH groups of resol. The absence of epoxy ring peak at ~915 cm^{-1} in the modified resin indicates the ring opening of the epoxy group during cross-linking.

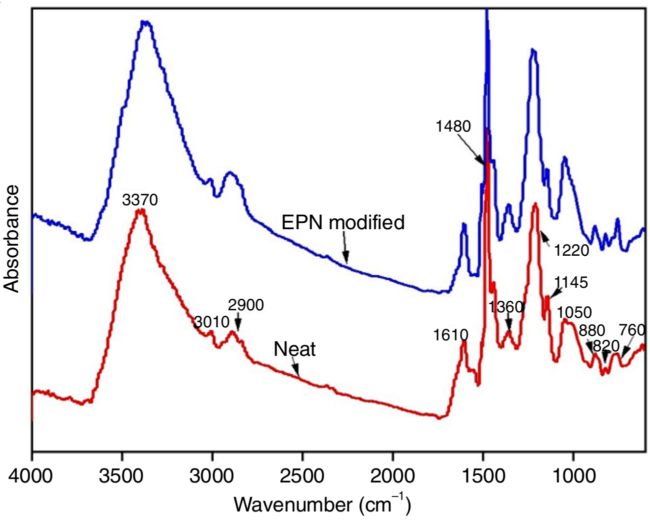

Fig. 1. FTIR spectra of cured neat and EPN9 modified resin

Mechanical properties: Fig. 2 shows the variation of tensile strength of the modified resol phenolics with the amount of epoxidied novolacs (EN) used.

In all cases the tensile strength is improved irrespective of the EN used for the modification. ENs with phenol to formaldehyde ratio 1:0.5 (EPN5, EPCN5 and EOCN5) show minimum improvement in the tensile strength. In all cases 7.5 to 10% epoxidized novolacs are sufficient to get maximum strength. Among the epoxidized novolacs, EPN9PR gives the highest strength with ~35% enhancement in tensile strength. The increase in the tensile strength may be due to the reduction in the condensates during curing, which reduces the void formation and the secondary bond forces offered by the -OH groups formed on ring opening of the epoxy group.

Figs. 3 and 4 respectively indicate the variation of flexural strength and impact strength with the amount of epoxidized

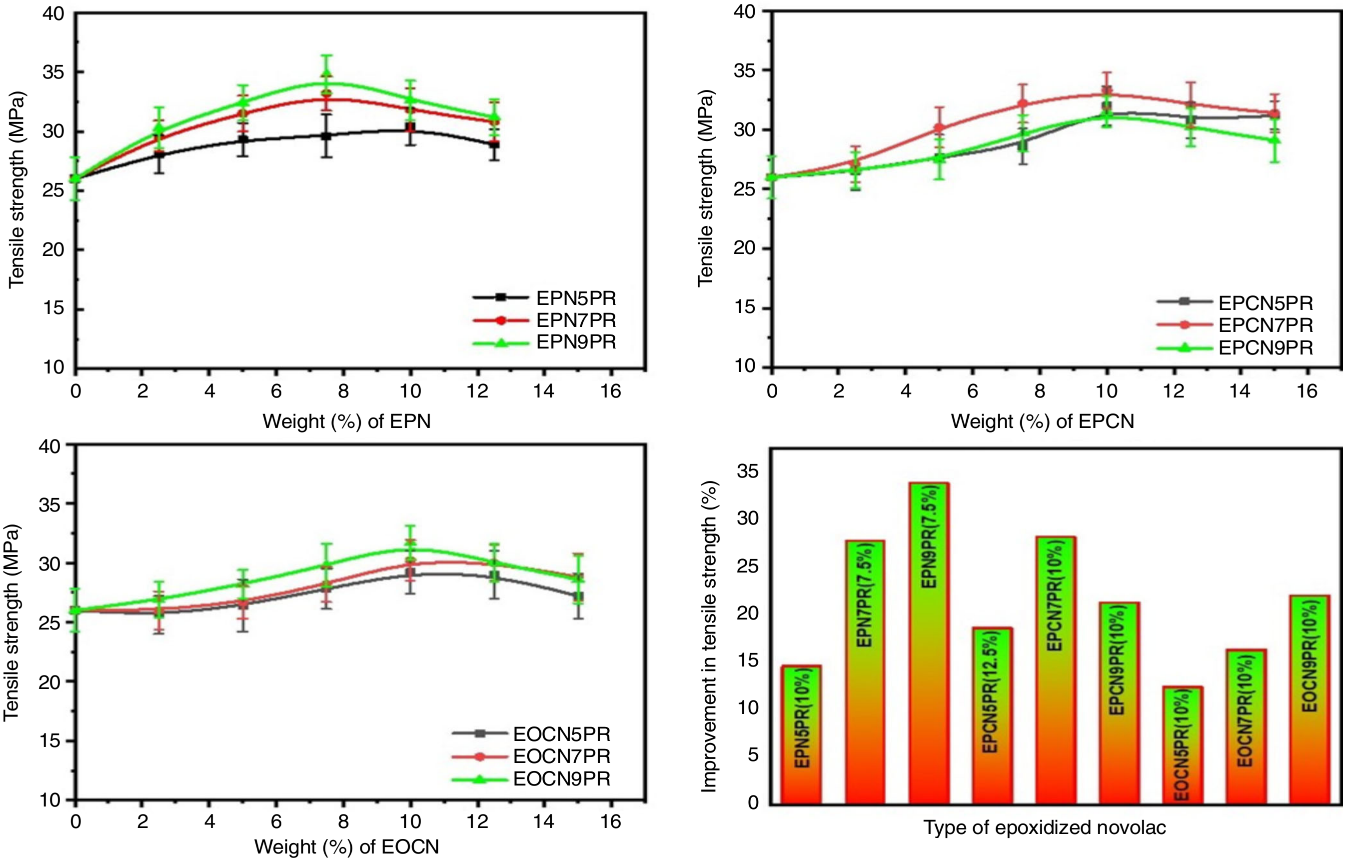

Fig. 2. Tensile strength of modified resin *versus* epoxidized novolac concentration

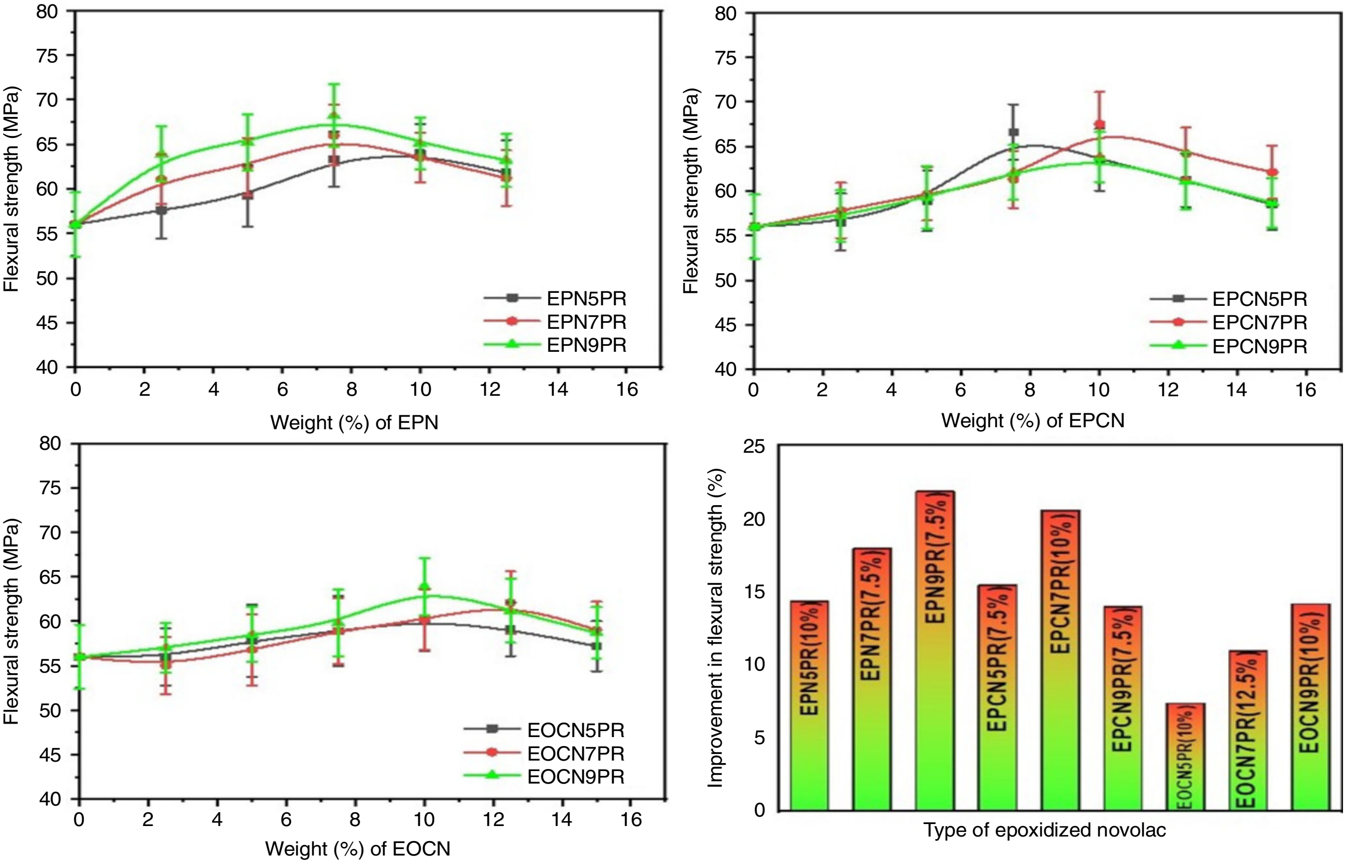

Fig. 3. Flexural strength of the modified resin *versus* epoxidized novolac concentration

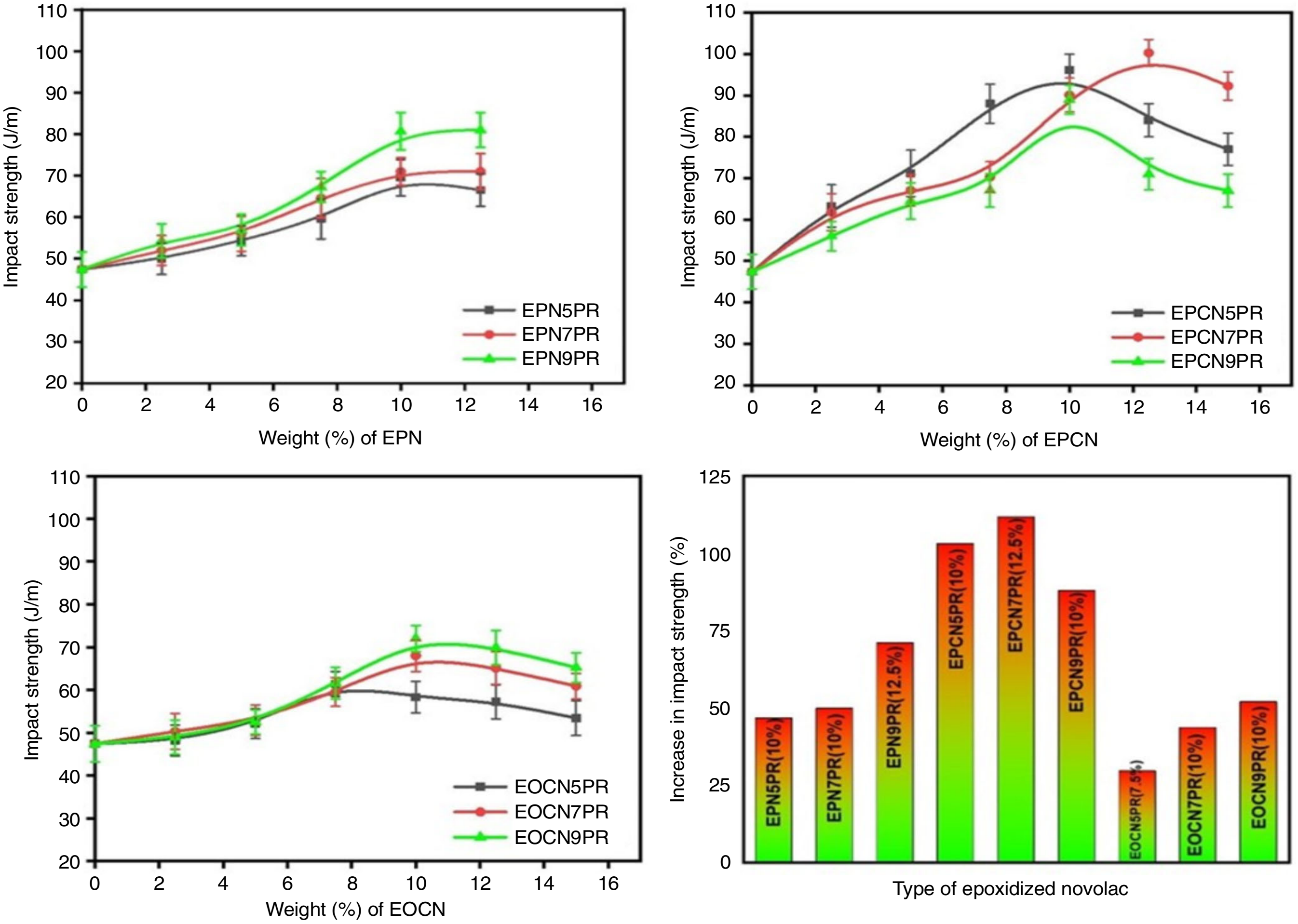

Fig. 4. Impact strength of the modified resin *versus* epoxidized novolac concentration

novolacs used for the modification of resol. It can be seen that epoxidized *o*-cresol novolac (EOCN) shows comparatively less improvement in strength than EPN and EPCN. ~20% in flexural strength can be achieved by both the EPN and EPCN modifiers with the incorporation of 7.5-10%.

The impact strength of the modified resol resin is improved appreciably in all cases. This indicates improved toughness of the modified resol phenolics. ~10% epoxidized novolacs in enough to get a reasonable improvement in strength for the cured samples. Further addition does not lead to enhancement in the properties. EPCNPR samples showed greater extend of improvement in the impact strength.

Soxhlet extraction: The % soluble content in the neat and modified phenolic resin with epoxidized novolacs, *viz.* EPN, EPCN and EOCN is shown in Fig. 5. The neat resol phenolic contains higher amount of % soluble matter. On modification with epoxidized novolacs the soluble matter decreases. But for EPNPR and EPCNPR resols the amount of soluble content remains almost constant above 7.5%. The decrease in the soluble matter indicates that epoxidized

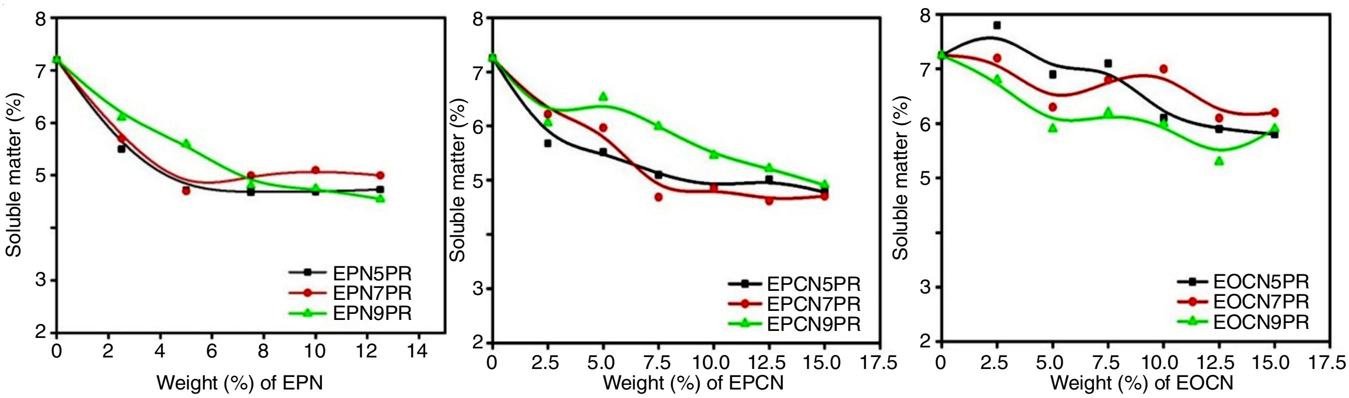

Fig. 5. % Soluble matter in the modified resin *versus* EPN concentration

novolacs are chemically anchored to the phenolic matrix and they reduce the amount of leachable material in the cured sample. It is also likely that the formation of the by-products of the condensation process is decreased and/or the escape of the condensation by-products is facilitated by epoxidized novolacs. It can be seen that the soluble matter in modified resin with EOCN decreases only to a smaller extent than the EPN and EPCN. The presence of methyl group at ortho position in *o*-cresol may retard the reaction between the -OH groups and epoxy functionality.

Morphological studies: The scanning electron micrographs of the fractured surfaces of the neat and modified phenolic resins (10 wt.% of each modifier) are shown in Fig. 6. All the samples contain microvoids. The size of the voids and crazes in the fractured surfaces are different for the neat and modified samples. As can be seen from the SEM images, the surface morphology has changed on modification.

In case of EPN modified samples, separate ductile deformed films and fibrils were observed. Both EPN7 and EPN9 modified resins show ductile deformed films with thicker boundaries. Referring to EPN9 modified resin, the fracture paths have excessive whitening with feathery texture. The EPCN modified resins contain layered structure in fractured surface. EPCN 7 modified resin has a wavy nature with valley and peaks in the fractured surface. Micrographs of EOCN modified resins show that size of the voids has decreased compared to neat sample. But compared to EPN and EPCN modified resin, EOCN modified resin exhibits more voids with bigger size. The excessive whitening, feathery texture and wavy nature of the fractured surface indicate improved toughness and load bearing characteristics of modified resin. This can be correlated with the enhancement in the mechanical properties of the modified resins.

Fig. 7 shows an insight in to the variation in the void size distribution on modification of phenolic resins with epoxidized

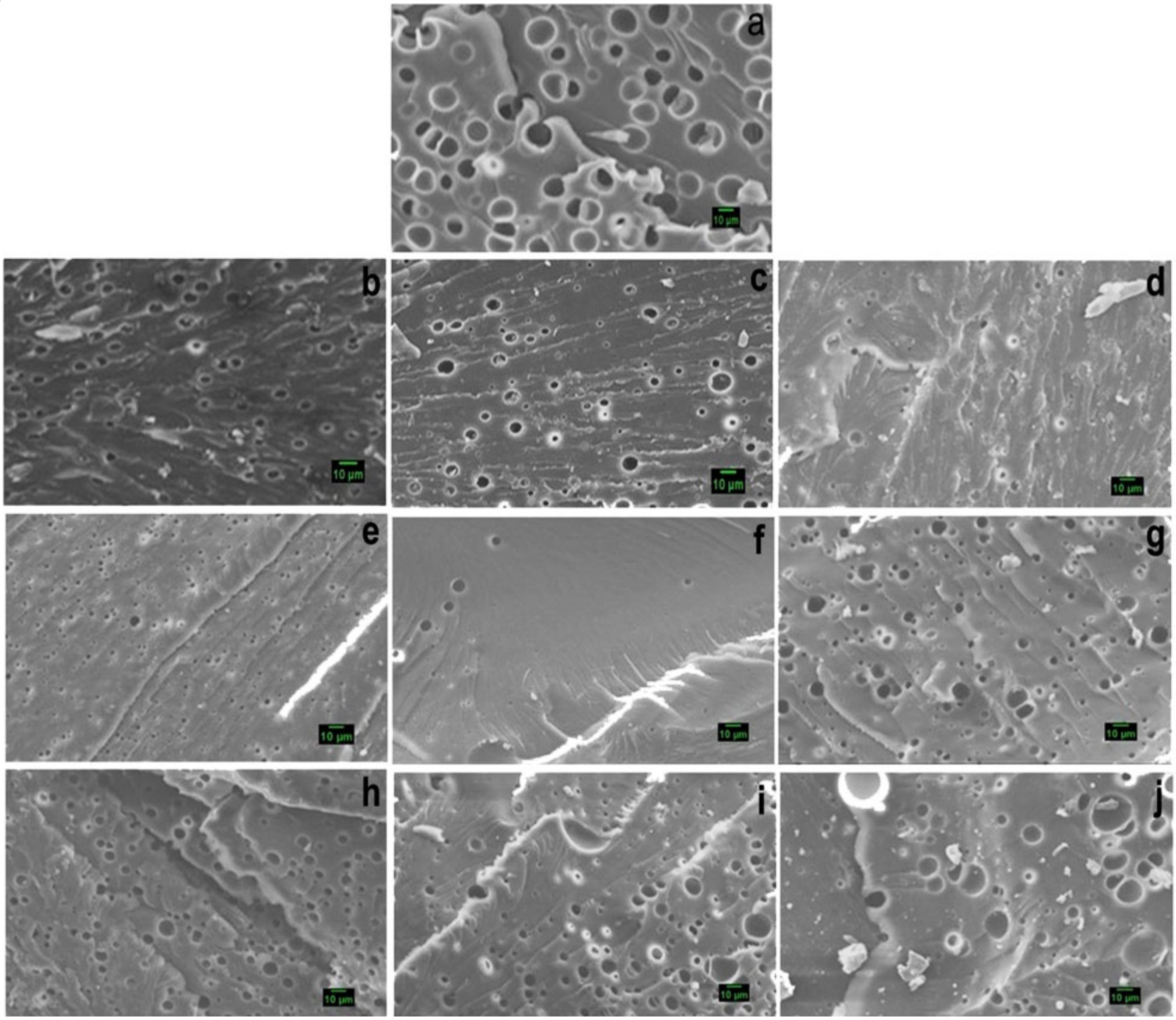

Fig. 6. Scanning electron micrographs of fractured surfaces of neat phenolic resin and modified resin (a) PR, (b) EPN5PR, (c) EPN7PR, (d) EPN9PR, (e) EPCN5PR, (f) EPCN7PR, (g) EPCN9PR, (h) EOCN5PR, (i) EOCN7PR and (j) EOCN9PR

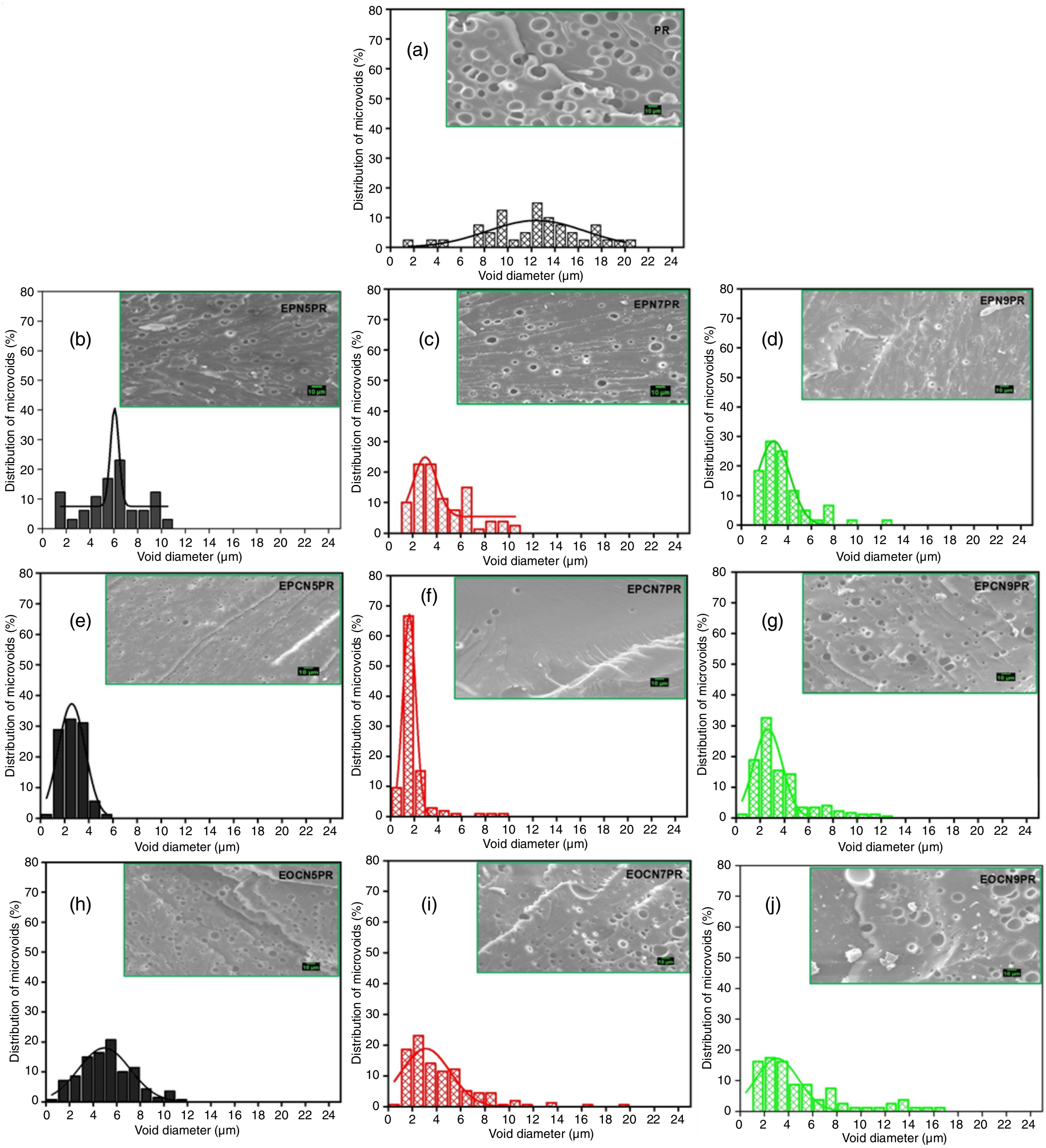

Fig. 7. Microvoid distribution diagram of the neat resin and epoxidized novolac modified samples, inset: SEM images of each resol phenolic

novolacs. In neat sample, majority of the voids are in the range of 10-15 µm and contains microvoids upto 20 µm. In all modified samples, the void size distribution curve shifts to the left with narrow distribution compared to neat resin. The size and number of voids were less in EPN and EPCN modified resins compared to EOCN modified resin. The size distribution is narrow in the EPCN modified samples in comparison with the EPN and EOCN modified resol phenolics.

The size characterization of voids $\overline{D}_n$, $\overline{D}_w$, $\overline{D}_a$, $\overline{D}_v$, PDI and V_D values of the neat and modified resins are presented in Table-3. It can be seen that void size in neat resin is very high compared to the all modified resol phenolics. The PDI values indicate that the void size remains in the same range in the neat sample but it is inconsistent in the modified samples. The void volume is considerably reduced in all modified resin especially in EPCN and EPN. The reduction in the void volume is

TABLE-3
SIZE CHARACTERIZATION OF VOIDS IN THE NEAT AND MODIFIED RESIN

Samples	$\overline{D_n}$ (μm)	$\overline{D_w}$ (μm)	$\overline{D_a}$ (μm)	$\overline{D_v}$ (μm)	PDI	V_D
Neat (PR)	11.95	13.16	12.54	13.75	1.11	0.2000
EPN5PR	5.74	6.78	6.24	4.02	1.18	0.0502
EPN7PR	4.27	5.48	4.83	5.37	1.28	0.0371
EPN9PR	3.52	4.74	4.08	4.71	1.345	0.0178
EPCN5PR	2.5	2.84	2.67	2.82	1.14	0.045
EPCN7PR	1.76	2.83	2.23	2.89	1.61	0.0093
EPCN9PR	3.57	5.05	4.25	4.96	1.41	0.056
EOCN5PR	5.08	6.04	5.54	5.94	1.19	0.0770
EOCN7PR	4.24	6.28	5.16	6.18	1.48	0.0767
EOCN9PR	5.5	9.38	7.22	8.90	1.69	0.0744

one of the reason for the betterment of strength of the modified resol phenolic. This is achieved by simple modification without applying pressure during curing.

Dynamic mechanical analysis: The elastic component of a polymeric material under dynamic conditions indicates the capacity to store the mechanical energy, the viscous property of a polymeric material indicates the capacity to dissipate the mechanical energy and the ratio between these two quantities, tan δ, in an index of damping property of the polymeric material.

Figs. 8a-c show the variation of storage modulus (E′) with temperature of neat and modified resins. The initial E′ values of modified samples are higher than that of the neat sample, which may be due to the decrease in the number of voids in the modified samples. The modulus values of the samples decrease with increase in temperature. This may be due to the increased segmental mobility at higher temperature. The modulus values of the neat and modified samples reach a minimum at ~200 °C and thereafter show a slight increasing tendency due to residual curing. The depth of the dip in the plots is prominent in case of neat and EOCN modified samples, which confirms that the EPN and EPCN modified resols had undergone increased degree of curing compared to the neat resin and EOCN modified resin.

The variation of tan δ values of the neat and modified samples with temperature is shown in Figs. 8d-f. The tan δ values of modified samples are higher than that of the neat resin. Broadening of tan δ plots and increase of tan δ values indicates a lowering of crosslink density and better damping properties for the modified samples. This observation supports the increase in the value of impact strength of the modified samples.

Thermal studies: Fig. 9 represents the thermograms of the neat resin and epoxidized novolac modified phenolic resins. The modified phenolics with EPNPR and EPCNPR showed marginally better thermal properties based on the weight loss of the samples with increase in temperature. As the pattern of

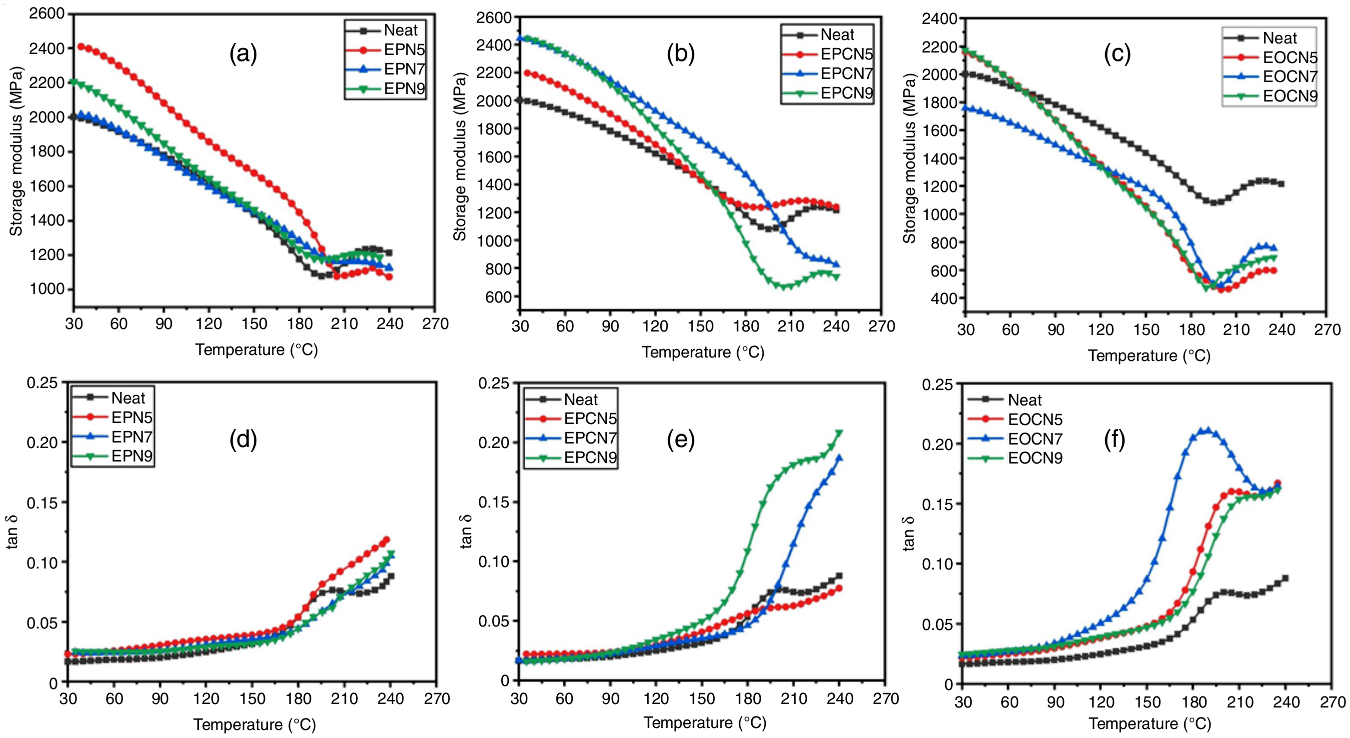

Fig. 8. (a-c) Storage modulus *versus* temperature of neat resol resin (PR) and (a) EPNPR (b) EPCNPR (c) EOCNPR modified resol resins; (d-f) tan δ *versus* temperature of neat resol resin (PR) and (d) EPNPR (e) EPCNPR and (f) EOCNPR modified resol resins

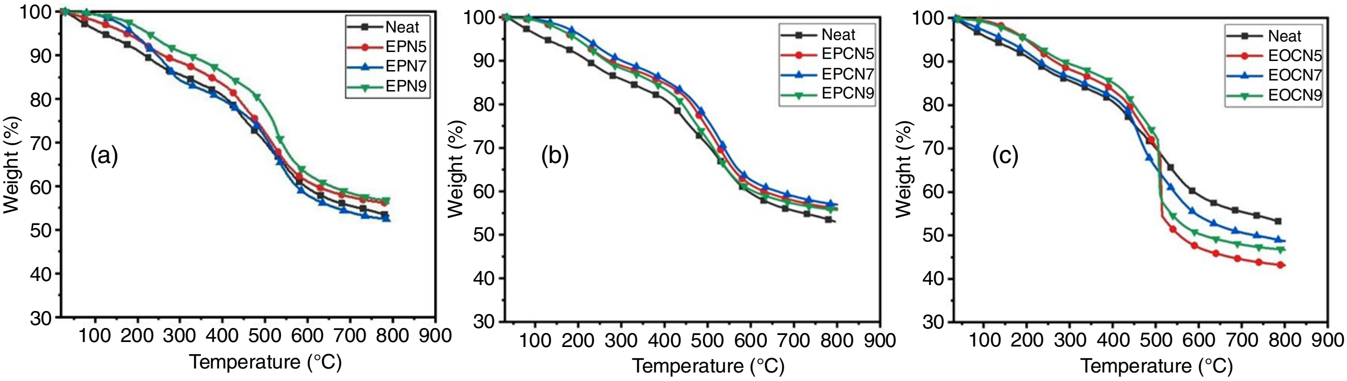

Fig. 9. Thermograms of the neat (PR), EPNPR (a), EPCNPR (b) and EOCNPR (c)

TABLE-4
THERMAL ANALYSIS OF THE NEAT AND MODIFIED RESINS

Sample	Temperature at different stages of decomposition (°C)					Temp. at max. degradation (°C)	Residue (%)
	10%	20%	30%	40%	50%		
Neat (PR)	218	410	501	589	>800	533	53
EPN5PR	260	437	516	622	>800	516	56
EPN7PR	246	396	508	573	>800	528	52
EPN9PR	322	483	542	658	>800	524	57
EPCN5PR	272	463	528	631	>800	528	56
EPCN7PR	301	473	538	661	>800	535	57
EPCN9PR	264	442	512	606	>800	523	56
EOCN5PR	267	463	527	541	765	505	50
EOCN7PR	282	435	517	600	>800	521	51
EOCN9PR	243	441	511	586	>800	512	53

the thermograms is similar for both the neat and modified resins, both follow the same mechanism of thermal degradation.

The thermal analysis data of the neat and modified samples are given in Table-4. It can be observed that the temperature at different stages of thermal degradation increases on modification with EPN and EPCN. The temperature of maximum degradation slightly decreased on modification whereas the final % residue has increased in the case of EPN and EPCN modified samples.

The TGA data can be used to study the kinetics of thermal decomposition, which provides an understanding of thermal stability. The kinetic parameters of thermal decomposition of polymeric materials can be investigated by using the Coats-Redfern method [20]. The Coats-Redfern equation to calculate the kinetic parameter is given in eqn. 1:

$$\ln\left(\frac{g(\alpha)}{T^2}\right) = \ln\left(\frac{AR}{\beta E}\right)\left(1-\frac{2RT}{E}\right)-\frac{E}{nRT} \qquad (1)$$

for $n \neq 1$, $g(\alpha) = \{1-(1-\alpha)1-n/(1-n)$; for $n = 1$, $g(\alpha) = -\ln(1-\alpha)$. where α is the fraction decomposed, T the temperature (K), n is the order of reaction, A is the Arrehenius constant, R is the universal gas constant, E_a is the activation energy and β is the heating rate. The plot of the lefthand side of eqn. 1 against 1/T should be a straight line with slope = E_a/R for the correct value of n.

In the case of crosslinked polymers, a first order kinetics is usually assigned since they undergo degradation by a random process. The activation energy (E_a) can be determined from the plot of $\ln[-\ln(1-\alpha)/T^2]$ against the reciprocal of absolute temperature (1/T). The Coats-Redfern plots for the neat and EPN modified resins are shown in Fig. 10. The kinetic parameters of all modified samples using Coats-Redfern plots are given in Table-5.

TABLE-5
KINETIC PARAMETERS OF THE THERMAL DEGRADATION OF MODIFIED RESINS

Samples	E (KJ/mol)	A ($\times 10^4$)	Correlation coefficient
Neat (PR)	94.6	2.24	0.9940
EPN5PR	108	2.44	0.9928
EPN7PR	114	3.18	0.9942
EPN9PR	116	7.24	0.9938
EPCN5PR	111	3.00	0.9970
EPCN7PR	107	1.31	0.9942
EPCN9PR	106	1.96	0.9943
EOCN5PR	93	0.09	0.9902
EOCN7PR	99	0.53	0.9966
EOCN9PR	98	1.20	0.9963

The activation energy values of the modified samples are higher than that of the neat sample. The Arrhenius constant (A) is higher for the EPN modified resins, but for both the EPCN and EOCN modified resins, it is lower than that of the plain resin. This difference may be attributed to the presence of the side chain $-CH_3$, which is vulnerable to thermal breakdown.

Conclusion

Epoxidized novolacs can be used to modify resol resins, which can reduce both the dimension and number of voids in the cured resol phenolics. This is reflected in the improvement

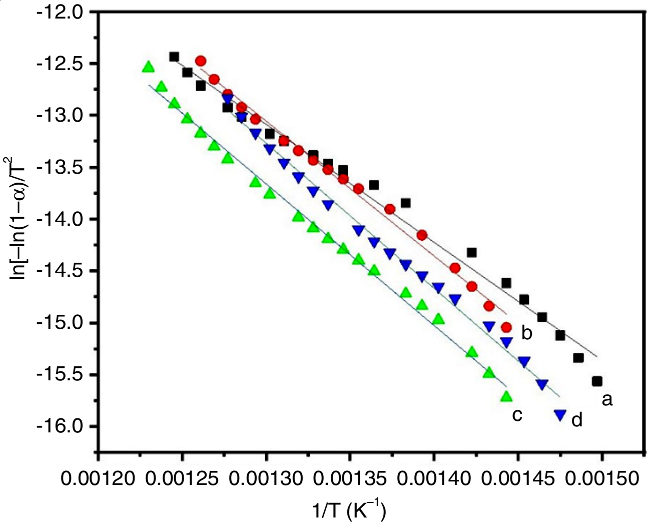

Fig. 10. Coats-Redfern plots for (a) neat (PR), (b) EPN5PR, (c) EPN7PR and (d) EPN9PR

of mechanical properties of the modified resins compared to the unmodified resol resin. The efficacy of the modifier depends on the P/F ratio of novolac resin and also on the epoxy content of modifier. Among the epoxidized novolacs, the EPN synthesized in the laboratory imparts the best tensile property whereas EPCN gives the greatest improvement in flexibility and impact properties. In all cases epoxidized novolacs with lower P/F ratio showed the better properties. The morphology of the fractured surface of modified samples shows that the modification leads to a considerable reduction in the microvoid dimensions and void density in case of EPN and EPCN. The increased tan δ values of the modified samples from DMA analysis indicate lowering of the crosslink density, which leads to better energy absorption by the modified samples. Thermal stability of the modified samples is comparatively better than that of the neat sample as indicated by the activation energies of the modified samples.

ACKNOWLEDGEMENTS

One of the authors, PSP, thanks Department of Polymer Science and Rubber Technology, Cochin University of Science and Applied Technology, Kochi, India, for providing all the research facilities to carry out this research work.

CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

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