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Synthesis and Characterization of New Epoxy Terminated Polymers

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Synthesis of epoxy terminated adhesive polymers based on a proprietary trifunctional heterocyclic compounds, 4,4'-sulfone diphenol, 4,4'-thiodiphenol and epichlorohydrin was carried out by the solution polymerization process using DMAc as solvent. These polymers were characterized by viscosity measurement, elemental analysis, IR spectroscopy, ¹H-NMR and ¹³C-NMR spectrometry and X-ray diffraction. The polymers were soluble in acetone, DMF, DMAc, HMPA, NMP and DMSO like polar solvent.

Keywords: Solution polymerization; sulfur containing epoxy; NMR study

INTRODUCTION

Since its discovery epoxy resin is an important class of speciality thermosetting materials [1–4]. Its broad spectrum properties originate from the versatility of reaction of the epoxy group and the wide range of properties of these polymers. For example, epoxy resins are unique among all the thermosetting materials because of their strength, excellent adhesion to variety of surfaces and good durability in various harsh environments. Depending on the curing agent [5, 6], curing schedule [7, 8] and the dihydroxy reactant used for its synthesis, epoxy resins exhibit excellent chemical and heat resistance, very good electrical insulation and mechanical properties.

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These desirable characteristics make epoxy resins as a good candidate for polymer composites such as fiber reinforced plastics (FRPs) [9]. Major limitations of these polymers are their poor high thermal stability and flammability. The latter shortcoming has been compensated commercially by substitution of bisphenol-A by halogenated diols [10] or by incorporation of suitable flame retardant additives [11]. Unfortunately, such attempts are not eco-friendly because during burning toxic hydrohalides are liberated which are highly harmful to health and environment. Attempts have also been made to increase the thermal stability of epoxy polymers by incorporating imide [12] and amide [13] linkages as well as heterocyclic thermostable moiety [14, 15] in the polymer chain.

This paper reports the synthesis and characterization of epoxy terminated polymers which are expected to be higher thermostable and intrinsically better flame retardant than commercial epoxy resins by reacting sulfur containing diphenols, epichlorohydrin and a proprietary nitrogen containing heterocyclic compound. It is expected that the presence of the heterocyclic moiety will increase the thermal stability while the sulfur and nitrogen synergistic effect will improve the flame resistance of these epoxy polymers.

EXPERIMENTAL

Materials

The *N,N'*-dimethyl acetamide (DMAc) (S.D. Fine Chem.) was allowed to stand over calcium hydride for 24 h and distilled under reduced pressure (10 mm-Hg) [16]. The 4,4'-sulfone diphenol and 4,4'-thiophenol were recrystallized from toluene. Their melting points were 240°C (lit. 240–241°C) [16] and 154°C (lit. 154–156°C) [16] respectively. Epichlorohydrin (S.D. Fine Chem.) was purified by vacuum distillation. Pyridine (BDH, India) was purified by refluxing with sodium hydroxide followed by distillation [17]. Concentrated hydrochloric acid (S.D. Fine Chem.), 30% hydrogen peroxide (S.D. Fine Chem.), thorin indicator, barium perchlorate (E. Merck), mercuric perchlorate (Aldrich) were used without further purification.

Synthesis of the Polymers

Polymer 1

In a three-necked 250 ml reaction flask fitted with a condenser, thermometer and pressure equalizing funnel. DMAc solution of 6 g (23 mmol) sodium salt of 4,4'-sulfone diphenol was placed in this reaction flask and the temperature was cooled down to 20–25°C. Next, 11.5 mmol of the proprietary heterocyclic compound in 10 ml DMAc was added to it dropwise through the dropping funnel. Reaction was continued upto half an hour and then 1.13 g (12.2 mmol) of epichlorohydrine was added to it. After this the temperature of the reaction mass was gradually raised to 100°C and the reaction was continued upto 6 h. The mass was cooled down to room temperature and the reaction mixture was poured slowly into chilled water by continuous stirring to obtain a sticky product. This was repeatedly washed with distilled water. Finally, the product was dissolved in acetone and reprecipitated, isolated and dried under vacuum at 50°C. Yield: 80%.

Polymer 2

Polymer 2 was synthesized exactly by the same way as was done for polymer 1 using sodium salt of 4,4'-thiodiphenol by two sets of experiment. In the first experiment epichlorohydrin was added to the above diphenol in the mole ratio of 1:1 with the proprietary heterocyclic compound. In the second experiment the above ratio is kept at 1:5. Yield in 1st and 2nd experiments are 85% and 75%, respectively.

Determination of Epoxy Content

The epoxy content of these polymers was determined by pyridinium hydrochloride method [18].

Estimation of Sulfur Content

The sulfur content of these polymers was estimated by Schöniger combustion method [19].

Estimation of Halogen Content

The halogen content was determined by Schöniger combustion method [19] using perchloric acid as titrant.

Polymer Characterization

The elemental analyses of the polymers were carried out by a Carlo–Ebra 1108 elemental analyzer. Chlorine and Sulfur were estimated by the Schöniger combustion method. IR spectra of the polymers were recorded with a Perkin–Elmer model 883 IR spectrophotometer using a KBr disc. $^1\text{H-NMR}$ and $^{13}\text{C-NMR}$ spectra of these polymers were recorded with a Bruker 200 MHz NMR spectrometer using $\text{DMSO-}d_6$ and CDCl_3 as solvent and TMS as reference. X-ray diffraction of the polymers was recorded with a Philips model PW 1710 X-ray diffractometer using Ni-filtered $\text{CuK}\alpha$ ($\lambda = 1.5420 \text{ \AA}$) radiation at 35 kV–100 mA and a scanning speed of $3^\circ/\text{min}$. Density of these polymers was determined by a pycnometer.

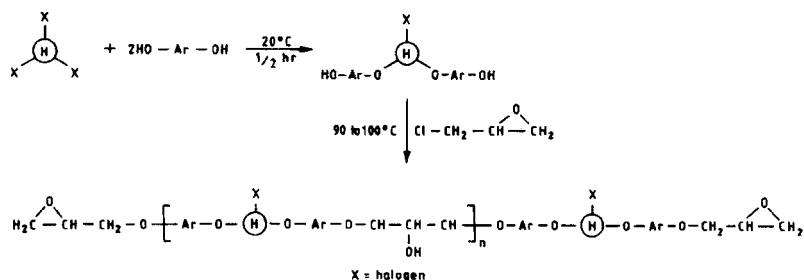
RESULTS AND DISCUSSION

Polymer Synthesis and Characterization

The epoxy polymers were obtained first by the reaction between the heterocyclic compound with sulfur containing diols followed by the reaction with epichlorohydrin. The reaction is shown in Scheme 1.

Polymer 1 is resinous in nature having the inherent viscosity 0.24 dL/g and polymer 2 is a viscous liquid with inherent viscosity 0.11 dL/g. The epoxy content of these polymers has been varied by variation of the reactant ratio *i.e.*, the diphenol to epichlorohydrin. The maximum epoxy content of the polymers obtained was 0.32 (Tab. I), while the commercial epoxy polymer possess the epoxy content of 0.52.

It is reported that epoxy content of the polymer depends on the molar ratio of diol and epichlorohydrine [4, 15]. As the concentration of the epichlorohydrine increases the molecular weight of the polymer decreases and the epoxy content value increases. Similarly in case of



Polymer	Aryl group (Ar)
1	
2	

SCHEME 1

polymer 2B under same reaction conditions using higher amount of epichlorohydrine the polymer becomes a viscous liquid and its epoxy content becomes high (0.32).

These polymers are soluble in polar solvents like dimethyl formamide (DMF), DMAc, hexamethyl phosphoramide (HMPA), *N*-methyl pyrrolidone (NMP), methyl ethyl ketone (MEK) and acetone but insoluble in hydrocarbon solvents like, petroleum ether, chloroform, *n*-hexane *etc.* This affinity towards the polar solvents may be due to the presence of epoxy group in the polymer chain [4].

The chemical structures of polymers 1 and 2 were assigned on the basis of the elemental analyses, estimation of the epoxy content, IR, $^1\text{H-NMR}$ and $^{13}\text{C-NMR}$ study, and X-ray analysis.

IR Analysis

The IR spectra of polymers 1 and 2 are shown in Figure 1. The strong absorption peak at 1090 cm^{-1} is assigned to the aryl-alkyl ether ($-\text{CH}_2-\text{O}-\text{Ar}$) linkage in the polymers. Similarly the strong absorption peak at 1225 cm^{-1} confirms the presence of the aryl-aryl ether ($\text{Ar}-\text{O}-\text{Ar}$) linkage [15]. Apart from these absorption bands, peaks at 1160 cm^{-1} and 700 cm^{-1} are due to the $\text{S}=\text{O}$ and $\text{C}-\text{S}$

TABLE I Characteristics of polymers

Polymer code	Color	Yield (%)	Inherent viscosity (η_{inh}) ^a (dL/g)	Density (gm/cc)	Softening point (°C)	Elemental analysis (%)						Epoxy content
						C	H	N	S	Cl		
1	colorless	80	0.24	1.38	85-90	F 50.4	F 4.56	F 7.26	F 9.48	F 5.19	0.19	
						C 53.9	C 3.30	C 6.30	C 9.59	C 5.30		
2A	colorless	85	0.21	1.30	77-80	F 62.2	F 5.77	F 8.90	F 10.00	F 5.62	0.18	
						C 59.7	C 3.66	C 7.00	C 10.60	C 5.88		
2B	colorless, liquid	75	0.11	1.20	--	--	--	--	--	--	0.32	

Note: F indicates found and C indicates calculated;
a = 0.5 percent solution in DMF solvent at 30°C.

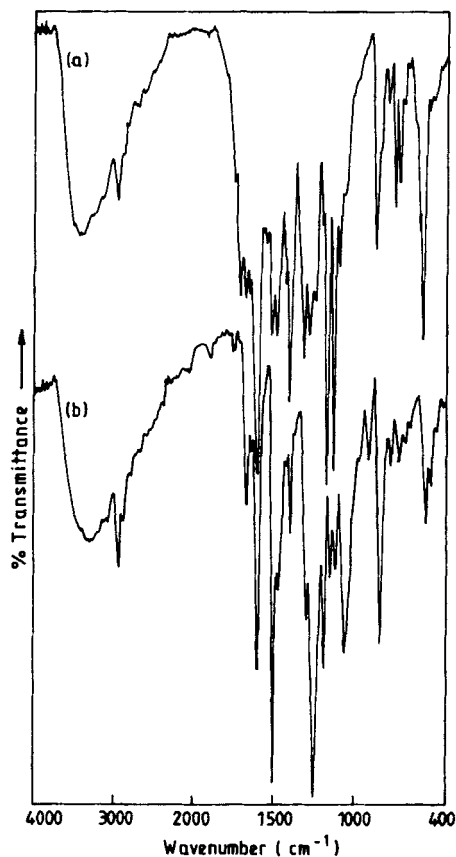


FIGURE 1 IR spectra of polymer 1 (curve a) and polymer 2 (curve b).

bonds in polymer 1 and polymer 2, respectively. Peaks near about $810\text{--}900\text{ cm}^{-1}$ can be assigned to the epoxy C—C bond stretching and at 750 cm^{-1} to the '12 micron band' [20]. This band strongly supports the presence of the epoxy ring in these polymers.

NMR Analysis

¹H-NMR Study

The ¹H-NMR spectra of polymers 1 and 2 are shown in Figure 2. In the aromatic region peaks appear for 4,4'-sulfone diphenol in polymer 1.

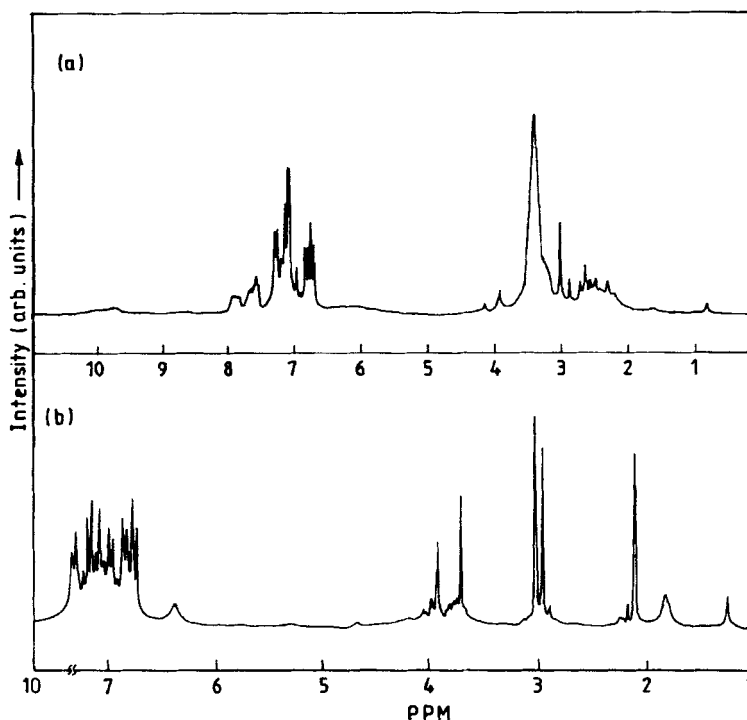


FIGURE 2 ^1H -NMR spectra of polymer 1 (curve a) and polymer 2 (curve b).

The doublet peak at 7.3 ppm may be assigned to the two ortho protons with respect to the $-\text{SO}_2-$ group. Another two protons chemically and magnetically identical with respect to the hydroxyl group of these polymers appeared at 6.9 ppm (d) [21]. The methine ($-\text{CH}-$) and methylene ($-\text{CH}_2-$) protons of the aliphatic part of the polymer chain appear at 3.9 ppm and 3.3 ppm respectively. The methine proton in the epoxy ring shows δ value at 3.31 ppm and the terminal ($-\text{CH}_2$) protons are chemically as well as magnetically non-equivalent. These are coupled to each other and appear at 2.9 ppm and 2.7 ppm with the coupling constant 6 Hz (Jab) [20].

Similarly, in case of polymer 2 peaks at the aliphatic zone appear almost in the same region. But peaks at 6.9 ppm (d) are assigned to for the two ortho protons with respect to the hydroxyl group, and peaks

at 7.3 ppm(d) are due to the two ortho protons with respect to — S — group of 4,4'-thiodiphenol moiety [21].

¹³C-NMR Study

The ¹³C-NMR spectra of the polymers are shown in Figure 3. For polymer 1 a singlet peak at 163 ppm is assigned to the halogenated carbon atom of the heterocyclic moiety [15]. Another peak at 155 ppm(s) is assigned to another two quaternary carbon atoms of this moiety. Two singlet peaks for the 4,4'-sulfone diphenol moiety appears at 123 ppm and 161 ppm for 'O' bearing and — SO₂ — bearing carbon atom respectively. Due to the electron withdrawing mesomeric effect of the — SO₂ — group the latter carbon atom appears at downfield. Peaks at 115 ppm and 107 ppm are assigned to ortho to the — SO₂ — group and ortho to the 'O' atom respectively. The chemical shifts at 41.6 ppm and 29 ppm are attributed to the —CH₂— and —CH— carbons of the epoxy moiety. The peak at

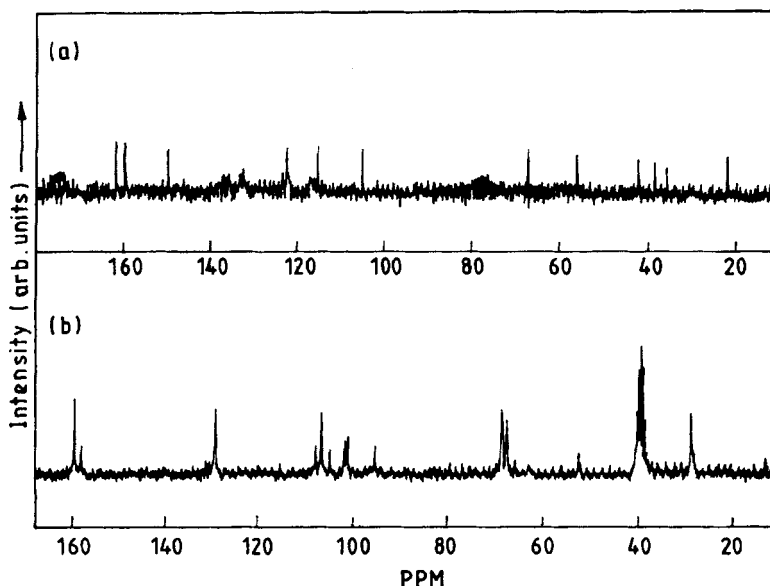


FIGURE 3 ¹³C-NMR spectra of polymer 1 (curve a) and polymer 2 (curve b).

68 ppm is due to the —CH— carbon atom containing the hydroxyl group.

Similarly in case of polymer 2 the peaks for the heterocyclic moiety and the aliphatic chain appear almost at the same region as in polymer 1. The peak at 136 ppm is assigned to the (—S—) linked carbon atom of the 4,4'-thiodiphenol moiety of polymer 2. The peak at 105 ppm is due to the 'O' bearing quaternary carbon atom of the phenyl ring. Another two peaks for ortho carbon atoms to the (—S—) linkage and the 'O' atom appear at 132 ppm and 118 ppm, respectively.

X-ray Study

X-ray diffraction study of both polymers (Fig. 4) reveals that the polymers are completely amorphous in nature. There is no peak for crystalline zone. This is consistent with the non-crystalline nature of epoxy polymers [15, 22].

CONCLUSION

The new epoxy terminated heterocyclic based polymers were synthesized by solution polymerization process. Their inherent viscosity and physical state vary with the epoxy content of the polymers. These polymers were characterized by usual analytical techniques for assignment of their structures.

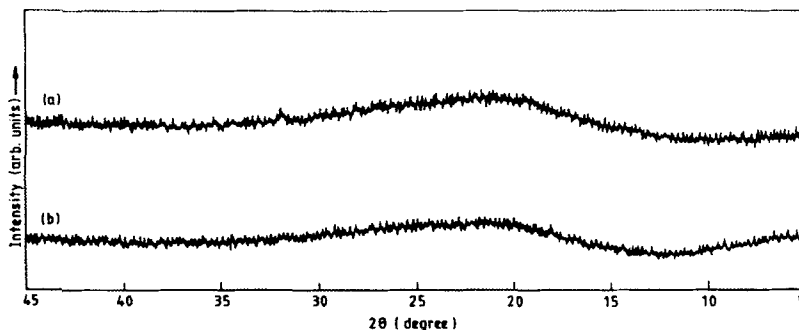


FIGURE 4 X-ray diffraction of polymer 1 (curve a) and polymer 2 (curve b).

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