Modification of Epoxy Resin with Optically Active Carboxylic Acid

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ABSTRACT: L-leucine was converted to *S*-2-chloro, 4-methyl pentanoic acid (CMPA) with retention of optical activity. CMPA was reacted with the epoxy resin to form chiral monoester and chiral diester compounds. The modified epoxy resin (MER) was characterized by FTIR spectrophotometer and polarimeter and was analyzed for epoxy content. The MER shows optical activity and the optical rotation increases with increasing concentration of CMPA. DSC studies indicate similar reactivity of the enantiomers of CMPA as well as the recemic mixture. The MER containing different concentrations of chiral modifier was cured with a stoichiometric amount of amine hardener. The cured film (obtained up to 21 mol % of CMPA) exhibits chiral property as well. Dynamic mechanical thermal analysis (DMTA) studies indicate high damping behavior. A shift in tan δ peak toward lower temperature was observed with increasing concentration of chiral modifier. The tan δ_{max} increases up to 14 mol % of CMPA in MER and decreases thereafter. However, storage modulus gradually decreases with an increase in CMPA. Cured film based on two enantiomer-modified epoxy samples shows different damping behavior. CMPA was also blended with poly(methyl methacrylate) and the blend films were studied similarly. The system behaves in a similar fashion as observed with cured MER films. © 2002 Wiley Periodicals, Inc. J Appl Polym Sci 86: 2523–2529, 2002

Key words: chiral; esterification; FTIR; toughness

INTRODUCTION

Optically active polymers make an important class of compound on their own merit. In recent years, these polymers have attracted much attention and many publications on synthesis and characterization of such polymers have appeared in the literature.[1–4] A large number of studies on chiral materials, reported in literature, are devoted to amino acids and carbohydrates. The choice of amino acids is due to their availability with high optical purity and lower price.[5] Synthetic peptides are important in the field of medicines, foods, fibers, and so on because of their high degree of biocompatibility and optical activity. Various vinyl monomers bearing peptide moieties in the side chain have been synthesized and corresponding polymers have been reported to work as functional materials.[6] L-leucine, an important amino acid, has a strong hydrophobic nature caused by its isobutyl group and plays an important role in α-helix formation and stabilization of peptides and proteins.[7] Poly(L-leucine) can form an α-helix by itself[8] and therefore has been examined as biocompatible material such as artificial skin[9] and fibers.[10] Synthesis of methacrylamide having L-leucine methyl ester structure has revealed its unique and interesting radical polymerization behavior such as inversion and increase of absolute value of specific rotation in the transformation of monomer to polymer.[11] Methenitis et al.[12] synthesized a series of polymers with various neutral amino acids and studied their properties complexing toward divalent metal ions. Further, the hydrocarbon tail present in L-leucine is expected to enhance the impact properties of corresponding polymers.

Extensive studies on modification by functionalized rubber and thermoplastic, to reduce its inherent brittleness, were reported.[13–16] The broad interest in epoxy resins originates from the versatility of epoxy group toward a wide variety of chemical reactions and the useful properties of the network polymers[17,18] such as high strength, low creep, excellent corrosion and weather resistance, elevated temperature service capability, and adequate insulation properties. However, to our knowledge, modification of epoxy resin with a chiral compound has not been reported.

In the present study, an attempt was made to modify epoxy resin by using optically active carboxylic acid to impart optical activity. The preliminary study on synthesis and characterization of modified epoxy resin is reported in this article.

EXPERIMENTAL

Materials

The epoxy resin was a liquid diglycidyl ether of bisphenol A (Ciba-Geigy, Araldite LY 556) with an equiv-

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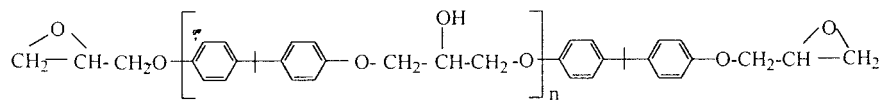
Diglycidyl ether of bisphenol-A

Figure 1   Chem structures of epoxy resin and hardener.

alent weight per epoxide group of 195 ± 5. An ambient temperature hardener, triethylene tetramine (TETA) (Ciba Geigy, HY 951), was used as the curing agent. The chemical structures of the epoxy resin are shown in Figure 1.

ᴅ-leucine and ʟ-leucine, sodium nitrite, hydrochloric acid, diethyl ether, triphenyl phosphine (TPP), and magnesium sulfate (AR grade) (M/s S. D. Fine Chemicals) were used without further purification.

Modification of amino acid

ʟ-leucine and ʟ-leucine were modified by replacing —NH_2 group with —Cl to get S-2-chloro, 4-methyl pentanoic acid (CMPA). Synthesis of CMPA was done by following the method of Perec and Oda.[19] ʟ-leucine was reacted with sodium nitrite and hydrochloric acid at 0–5°C. The product was distilled under vacuum to get a colorless liquid (yield: 50%, boiling point: 81–83°C).

Synthesis of modified epoxy and its curing

Epoxy resin (LY 556) (10 g, 0.055 mol) was taken in a round-bottom flask. Required amounts of CMPA (0.006–0.055 mol) were added and mixed in the flask. About 0.1 g TPP was added as catalyst. The mixture was constantly stirred at 140°C under nitrogen atmosphere until all the carboxyl groups were completely reacted. The reaction time was about 6 h. Modified epoxy resin (MER) obtained was light-brown in color and used as such for further reaction.

MER was mixed with a stoichiometric amount of hardener (HY951) and cured at room temperature for 16 h on a clean glass plate. The films, thus obtained, were further cured at 100°C for 4 h, cooled, and stored in a desiccator.

Blending of CMPA with PMMA

PMMA was dissolved in tetrahydrofuran to a concentration of 10% (w/v). CMPA was added to the solution in various amounts to make a PMMA/CMPA ratio at 10 : 2 to 10 : 6 (w/W). Films were cast on clean glass plates and dried at room temperature for 16 h, followed by heating at 40°C under vacuum.

Characterization of MER and cured networks

Epoxy equivalent

The modified epoxy resins were characterized for its epoxy equivalent by titration with hydrobromic acid.[20]

Polarimetry

The liquid samples were dissolved in methanol to a concentration of 10% (w/v) and 10 mL. Solution was placed in a polarimeter cell. The specific rotations were recorded at 25°C as an average of five readings at a wave length of 489 nm, employing a Jasco (P-1020) polarimeter. The film samples were directly placed in the path and optical rotations obtained under identical conditions.

Differential scanning calorimetry

The mixture of CMPA and epoxy were mixed thoroughly in a stoichiometric ratio and enclosed in an aluminum pan. DSC analysis was done by using a differential scanning calorimeter (TA Instruments; model Q 100) at a heating rate of 5°C per min under nitrogen atmosphere.

Infrared spectrometry

The liquid samples were spread in the form of a thin film on an NaCl window and solid film samples were directly mounted on the frame. FTIR spectra were recorded by employing a Perkin–Elmer FTIR spectrophotometer (1600 series).

Dynamic mechanical thermal analysis

Dynamic mechanical thermal analysis (DMTA) of the cured samples was done by employing a DMTA (Rheometric Scientific, MK III) instrument. The samples used were 15 × 6 × 0.2 mm and the measurements were carried out at 1 Hz using the tensile mode.

RESULTS AND DISCUSSION

ʟ-leucine is not miscible with epoxy resin and there is no common solvent as well. Hence, it cannot be incor-
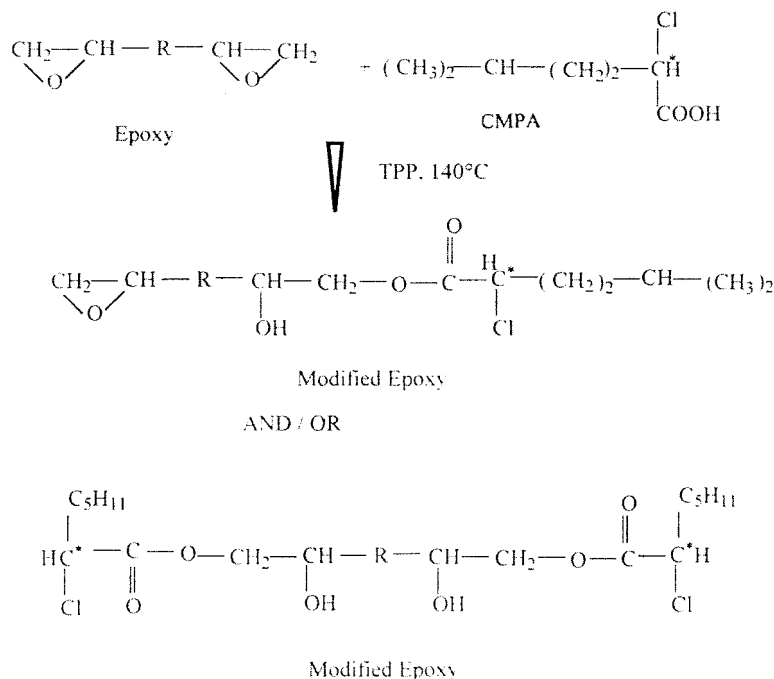
Figure 2 Prereaction of CMPA with epoxy.

porated into epoxy as such. For this reason, L-leucine was converted to CMPA, which is a liquid and miscible with epoxy. Further, this chemical transformation does not change the direction and magnitude of optical rotation. It was reacted with the epoxy resin in different concentrations. The idea is to attach the chiral moiety to one epoxy group and the other epoxy will get incorporated as chain end during curing with the hardener. The reaction is basically a carboxyl-epoxy esterification reaction, as proposed by Romanchick et al.[21] The reaction scheme is illustrated in Figure 2.

The final product consists of a mixture of mono- and diester by opening one or both of the epoxy groups. Thin-layer chromatography, using THF:hexane (1:2 v/v) mixture as eluant, shows two new closely spaced spots. The spots can be attributed to mono- and diester compounds. The epoxy equivalent of MER is shown in Table I. As expected, an epoxy equivalent of MER increases with incorporation of CMPA. This also indicates that the reaction between CMPA and epoxy resin takes place.

To understand if there is any effect of stereochemistry on carboxyl-epoxy reaction, epoxy/L-CMPA, epoxy/D-CMPA, and epoxy/recemic CMPA, having a composition corresponding to MER-4, were subjected to DSC analysis at the same heating rate. The DSC traces are shown in Figure 3. It was found from DSC analysis that both the enantiomers react in almost equal rates, as the peak exotherms are closely spaced in the temperature range of 163–166°C.

Figure 4 shows representative FTIR spectra of CMPA and MER. The FTIR spectra of L-leucine shows

a characteristic absorption peak of $—COO^{-}NH_{3}^{+}$ at 1584 cm^{-1}. In CMPA, the peak disappeared and a peak due to $—C{=}O$ appeared at 1724 cm^{-1}. MER shows absorption at 1744 cm^{-1}. This is due to conversion of carboxyl of CMPA to ester group of MER. A peak at 1606 cm^{-1} indicates the presence of a benzene ring and the peaks at 1271 and 1039 cm^{-1} are attributed to $Ar—O—CH_{2}$ group.

Table II incorporates the specific rotation of CMPA and MER samples. It can be seen that the specific rotation of CMPA is $-27.32°$. After reacting with epoxy resin, the specific rotation decreases. This is due to the dilution effect. The proportion of CMPA is much less than the nonchiral epoxy component in the mixture. However, the sign of rotation does not change and it increases with increasing proportion of CMPA. After MER 7, the rotation value does not increase

TABLE I
Modification of Epoxy Resin with CMPA

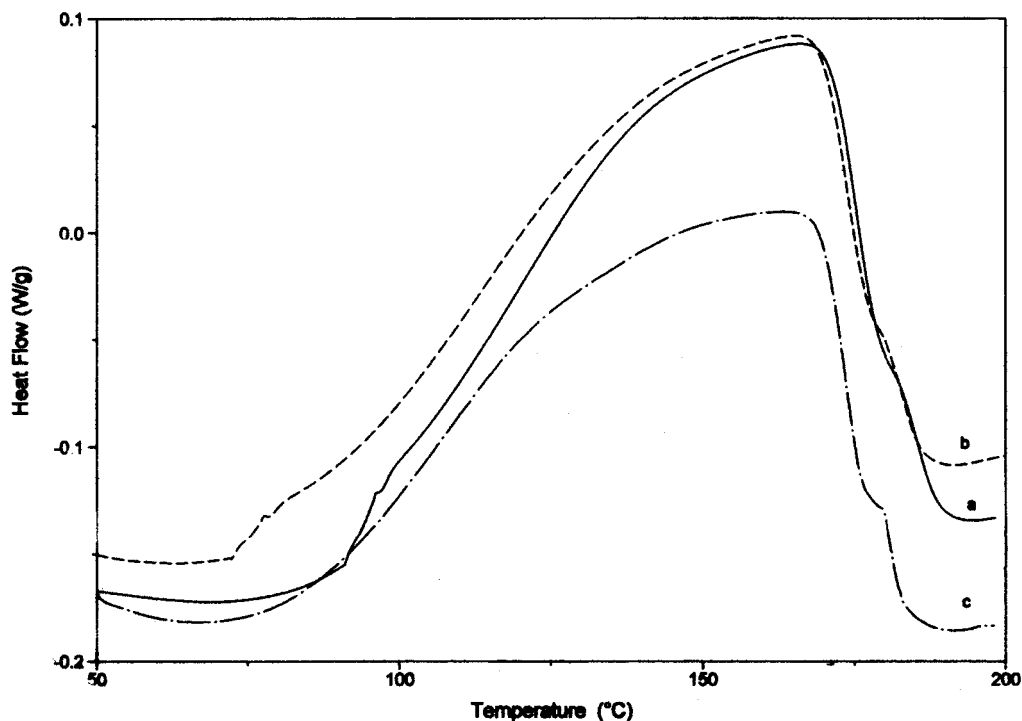| Sample no.	Sample	Epoxy resin (mol/mol)	CMPA (mol/mol)	Epoxy equivalent
1	MER0	0.055	0	184
2	MER1	0.055	0.006	241
3	MER2	0.055	0.009	284
4	MER3	0.055	0.012	373
5	MER4	0.055	0.015	459
6	MER5	0.055	0.018	540
7	MER6	0.055	0.026	745
8	MER7	0.055	0.031	1053
9	MER8	0.055	0.037	2243
10	MER9	0.055	0.050	4435
11	MER10	0.055	0.055	—

Figure 3 DSC traces for (a) epoxy/L-CMPA; (b) epoxy/D-CMPA; and (c) epoxy/recemic CMPA.

further. The cured films also show optical activity. Optical rotation of cured film of MER is shown in Table II. As expected, the rotation increases with an increase in the CMPA content in the film. The optical

rotations of D-MER-4 (reaction product of epoxy and D-CMPA) and the corresponding cured film were also presented in Table II. Optical rotation of D-MER and L-MER are opposite but not equal. The cured films based on D-MER and L-MER show almost equal and opposite optical rotation.

Figure 5 shows the variation of tan δ (loss factor) with temperature for the cured films. The tan δ is very low below the α-relaxation temperature, as the chain segments remain frozen. When the α-relaxation temperature is approached, tan δ increases as the micro-Brownian motion of molecular chain segments sets in. In that region, tan δ, representative of damping,
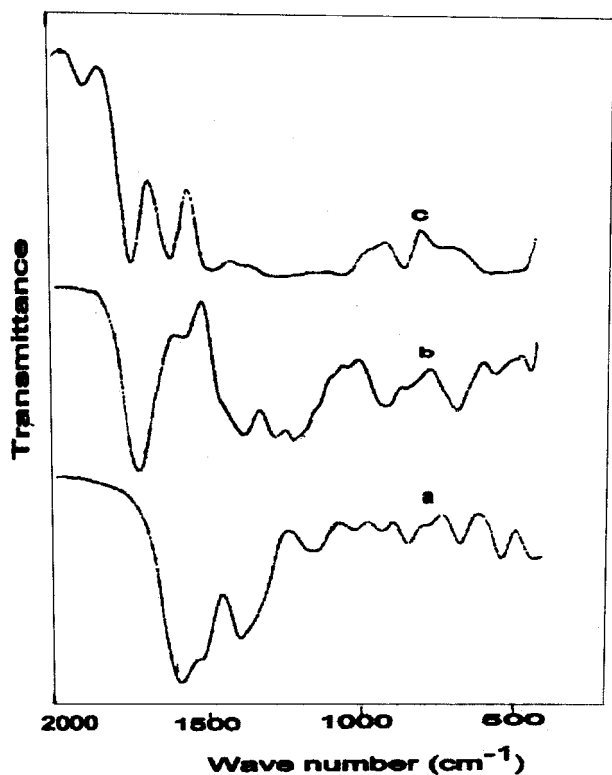

Figure 4 FTIR spectra of CMPA and MER (a) L-leucine; (b) CMPA; (c) MER.

TABLE II
Optical Rotations of MER and Cured MER Film

Sample no.	Sample	Specific rotation of solution $[\alpha]_D$ (°)[a]	Optical rotation of film[a] α (°)[b]
1	MER0	−0.004	−0.002
2	MER1	−1.52	−0.017
3	MER2	−1.61	−0.020
4	MER3	−1.70	−0.027
5	MER4	−2.23	−0.030
		(+4.26)[c]	(+0.027)[c]
6	MER5	−4.34	—
7	MER6	−5.44	—
8	MER7	−7.61	—
9	MER8	−7.71	—
10	MER9	−7.01	—
11	MER10	−6.82	—

[a] Measured by polarimeter at 25°C.
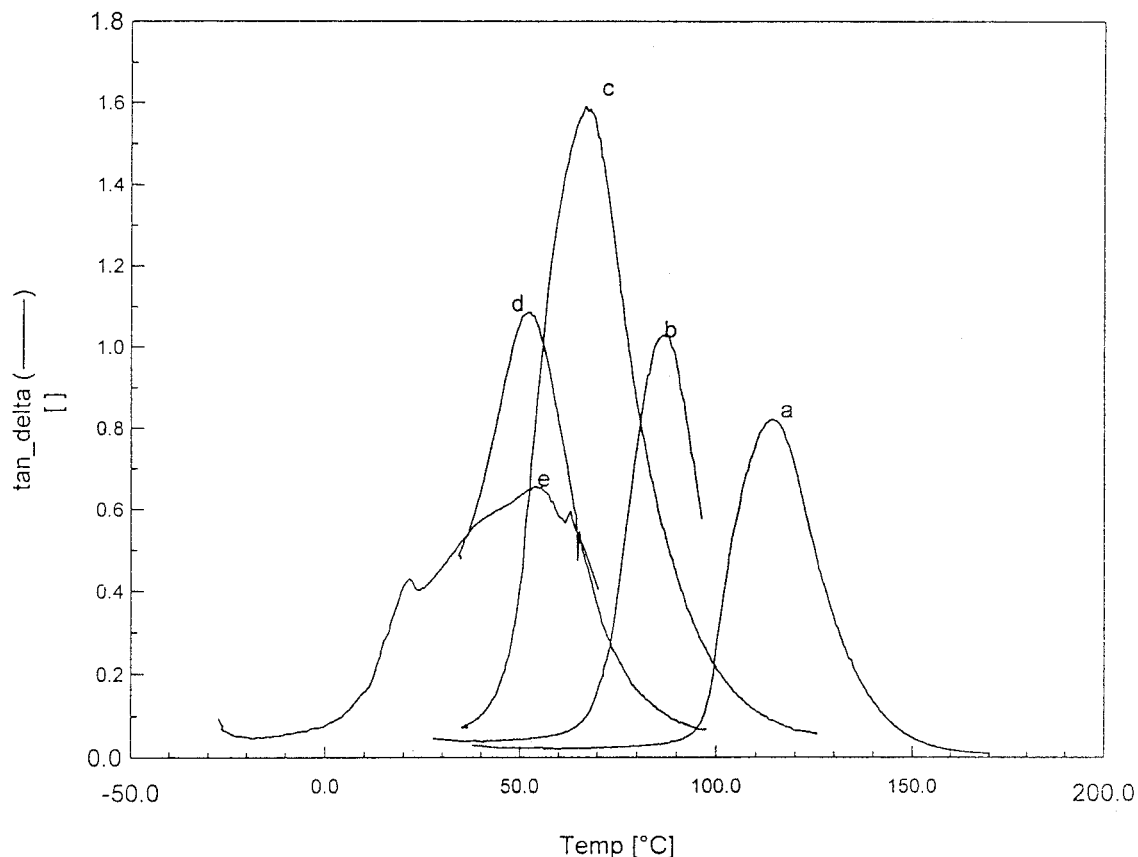[b] Film thickness was maintained at 0.7 mm.
[c] Value for D-MER4.

Figure 5 tan δ versus temperature plot of cured epoxy films: MER 0; (b) MER 1; (c) MER 2; (d) MER 3; (e) MER4.

reaches maximum when most of the chain segments take part in micro-Brownian motion. With a further increase of temperature, tan δ decreases as the sample is in the rubbery region and the segments are free to move, offering little resistance to flow.

From the DMTA curve, it was observed that both epoxy and modified epoxy films show a single relaxation peak. This indicates that phase separation has not taken place. Table III lists the values of E' at 35°C, tan δ, and tan δ peak temperature. The tan δ peak temperature for pure epoxy is at 120°C. It decreases on increasing the amount of CMPA in MER. This can be attributed to the increase of flexibility of the matrix as a result of incorporation of short chains/units with hydrocarbon tail. The short chain/unit acts as flexibilizer to epoxy resin. With a further increase of CMPA,

the tan δ peak temperature continuously decreases. It was not possible to form free-standing film beyond 21 mol % of CMPA. The mixture of MER and hardener remains soft and sticky even after long postcuring treatment. This may be attributed to a low degree of polymerization. This is possible in the case of a large amount of monofunctional epoxy produced during modification. The tan δ_{max} value increases with incorporation of CMPA up to 14 mol %. The enhancement of loss factor indicates a high dissipation of mechanical energy, which could result in higher toughness and impact strength. However, the tan δ_{max} value shows a decreasing trend after that. The same trend was reported while studying dynamic mechanical properties of carboxyl-functionalized polyester-modified epoxy resin.[22]

To study the effect of stereochemistry on dynamic mechanical properties of cured MER, cured films based on D-MER4, L-MER4, and recemic MER4 were characterized by DMTA. The results are shown in Figure 6. It can be seen that L-MER film shows a minimum tan δ peak temperature, whereas D-MER4 shows the maximum. The recemic mixture shows the intermediate value. Further, the area under the curve of D-MER film is much higher than the L-MER. This indicates that D-MER allows more movement of polymer segments under mechanical stress. MER contains

TABLE III
DMTA Analysis of Modified Epoxy (MER)-Based Films

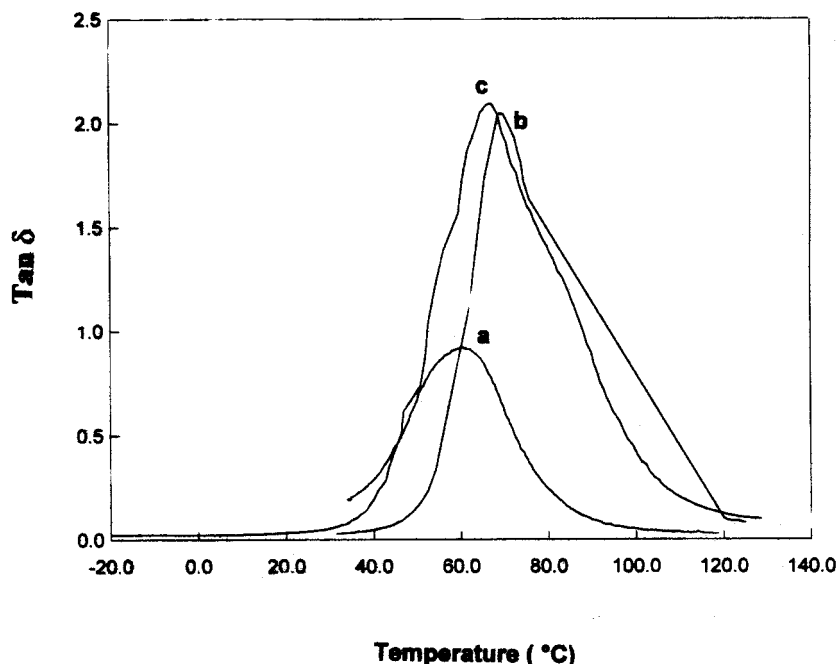| Sample	Storage modulus at 35°C (GPa)	tanδ peak temperature (°C)	tanδ$_{max}$
MER 0	1.84	114	0.82
MER 1	2.36	86	1.02
MER 2	1.99	67	1.60
MER 3	0.37	54	1.09
MER 4	0.18	53	0.64

Figure 6   DMTA plots of cured (a) ʟ-MER; (b) ᴅ-MER; and (c) recemic MER.

the mixture of mono- and diesters. The relative proportion of esters is also expected to affect the dynamic property of the cured polymer. Detailed study is beyond the scope of this article. The matter will be dealt with in a future communication. Recemic MER shows a higher area under the curve and half-peak width compared to ᴅ-MER. The peak expands over the temperatures corresponding to both MERs. This shows that after reaction with the hardener there is microphase separation between ᴅ-MER- and ʟ-MER-containing chains.

The effect of CMPA was also checked by physically blending it with poly(methyl methacrylate) (PMMA). The dried films were studied for optical rotation and dynamic mechanical properties. Table IV shows the optical rotation of PMMA/CMPA blend films. It can be seen that the blend films show optical rotation. Optical rotation of PMMA film is negligible. On increasing CMPA content, the optical rotation increases. DMTA curves are shown in Figure 7. It was observed

TABLE IV
Optical Rotation of PMMA/CMPA Blend Films

PMMA/CMPA (w/w)	Optical rotation of film[a] α^b (°)
10/0	−0.001
10/2	−0.012
10/3	−0.015
10/4	−0.021
10/5	−0.025
10/6	−0.042

[a] Film thickness was maintained at 0.30 mm.
[b] Measured by polarimeter at 25°C.

that E' and tan δ peak temperature decreases with the incorporation of CMPA into PMMA. PMMA is a hard matrix. The decrease of E' and tan δ peak temperature indicates the action of CMPA as flexibilizer. The result indicates that CMPA can influence the optical and dynamic mechanical properties of both thermoplastic and thermosetting resin.

CONCLUSION

Modification of epoxy with amino acid to get an optically active epoxy is reported for the first time. To react with epoxy, leucine was modified by replacing —NH₂ group with —Cl to get optically active CMPA. It was observed that the reactivity of both enantiomers of CMPA were almost equal. The CMPA was reacted with epoxy resin to form optically active monoester and diester compounds. Up to 36 mol % of CMPA was introduced. The modified epoxy resin was found to possess optical activity. It was cured with amine-based hardener to form free-standing film. The films (up to 21 mol % CMPA) were also found to exhibit optical activity. Dynamic mechanical analysis revealed good damping behavior of the films. The tan δ peak temperature and storage modulus decreases with incorporation of CMPA. The tan δ_{max} increases with CMPA addition up to 14 mol %, which is followed by a slow decrease. The cured film based on ʟ-MER shows lower tan δ peak temperature than the film based on ᴅ-MER. The damping of recemic MER-based film was found to be highest. CMPA was also incorporated into PMMA matrix as a physical mixture. The blend films show optical rotation and the
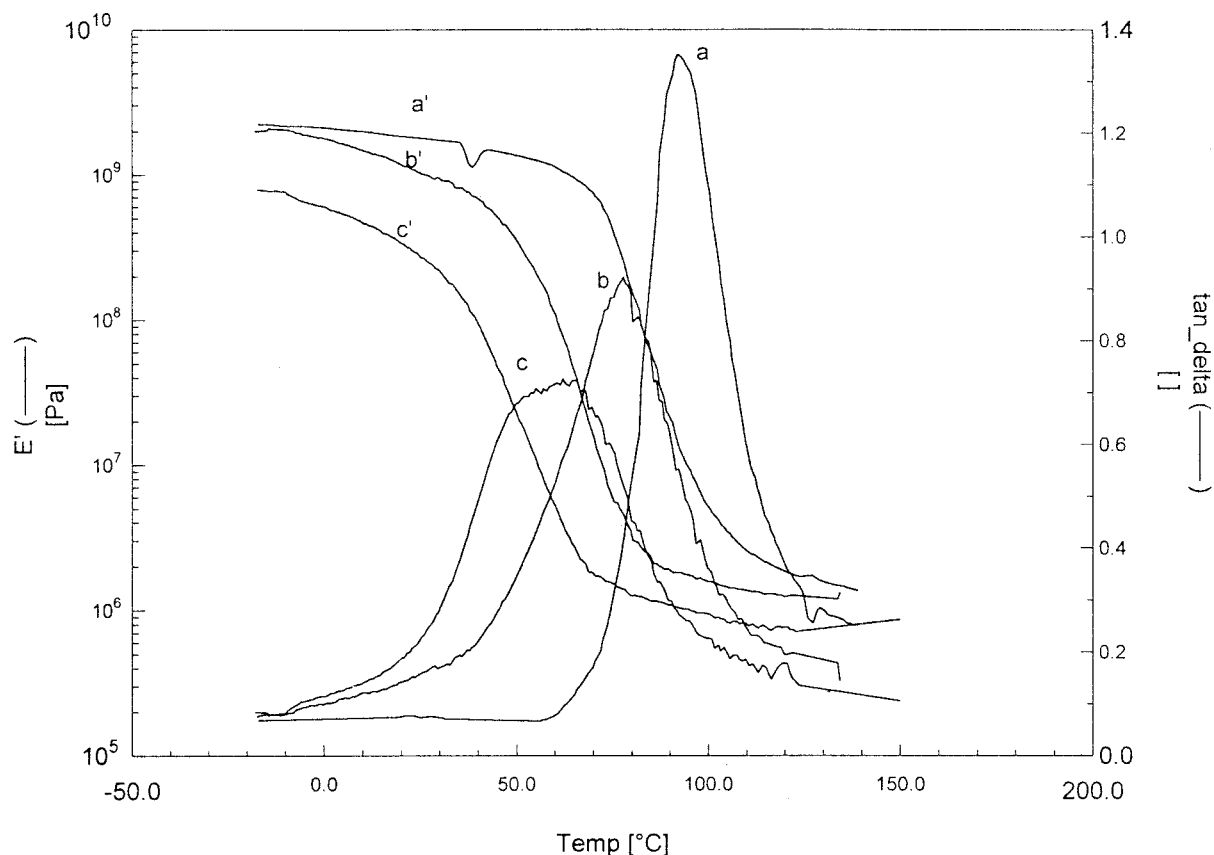
Figure 7 DMTA plot for PMMA/CMPA blend films: tan δ: (a) PMMA; (b) PMMA-30 wt % CMPA; (c) PMMA-40% CMPA. *E′*: (a′) PMMA; (b′) PMMA-30 wt % CMPA; (c′) PMMA-40% CMPA.

change in optical rotation is similar to that observed with cured MER. Storage modulus and tan δ peak temperature show a decline with increasing CMPA content.

References

1. Sridhara, S.; Ananthanarayanan, V. S.; Taylor, G. T.; Scheraga, H. A. Biopolymers 1977, 16, 2565.
2. Ishikawa, K.; Endo, T. J Polym Sci, Part A: Polym Chem 1990, 28, 3525.
3. Kihara, N.; Makabe, K.; Endo, T. J Polym Sci, Part A: Polym Chem 1996, 34, 1819.
4. Koyama, E.; Sanda, F.; Endo, T. J Polym Sci, Part A: Polym Chem 1997, 35, 345.
5. Sanda, F.; Takata, T.; Endo, T. J Polym Sci, Part A, Polym Chem 1995, 33, 2353.
6. Okamoto, Y. Adv Chem Ser 1985, 286, 361.
7. .Padmanabhan, S.; Marqusee, S.; Ridgeway, T.; Laue, T. M.; Baldwin, R. L. Nature 1990, 344, 268.
8. Ostroy, S. E.; Lotan, N.; Ingwall, R. T.; Scheraga, H. A. Biopolymers 1970, 9, 749.
9. Kuroyanagi, Y.; Koganei, Y.; Shioya, N. Nessho 1987, 13, 206.
10. Noguchi, J.; Nakamura, T.; Hayakawa, T.; Ohizumi, Kogyo Kagaku Zasshi 1967, 70, 1254.
11. Sanda, F.; Nakamura, M.; Endo, T.; Takata, T.; Handa, H. Macromolecules 1994, 27, 7928.
12. Methenitis, C.; Morcellet, J.; Pneumatikakis, G.; Morcellet, M. Macromolecules 1994, 27, 1455.
13. Ratna, D.; Banthia, A. K.; Deb, P. C. J Appl Polym Sci 2000, 78, 716.
14. Ratna, D.; Patri, M.; Chakrabarty, B. C.; Deb, P. C. J Appl Polym Sci 1997, 65, 901.
15. Ratna, D.; Banthia, A. K.; Deb, P. C. J Appl Polym Sci to appear.
16. Verley, R. J.; Hawthorne, D. G.; Hodgkin, J.; Simon, G. P. J Polym Sci, Part B: Polym Phys 1997, 35, 153.
17. Chen T. K.; Jan, Y. H. Polym Eng Sci 1994, 34, 778.
18. Bascom, W. D.; Hunston, D. L. in Rubber Toughened Plastics; Riew, C. K., Ed.; Advances in Chemistry Series 222, American Chemical Society, Washington, DC, 1989, p 135.
19. Perec, V.; Oda, H. Macromolecules 1994, 27, 4454.
20. Durbetaki, A. J. Anal Chem 2000, 28, 1956.
21. Romanchick, W. A.; Sohn, J. E.; Gaibel, J. F. Epoxy Resins Chemistry II; Bauer, R. S., Ed.; Advances in Chemistry Series 221; American Chemical Society, Washington, DC, 1983, p 93.
22. Ratna, D.; Chakraborty, B. C.; Deb, P. C. J Polym Mater 1997, 14, 185.