

Synthesis and Thermally Stimulated Current Study of Molecular Relaxations of the Grafted Polymethylphenylsiloxane Segment in Thiodiphenol-Modified Epoxy Resin

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ABSTRACT: A series of grafted polymethylphenylsiloxane (PMPS) segments in thiodiphenyl-containing epoxy resin (ESTP) was prepared. The structure was evaluated by IR, $^1\text{H-NMR}$, and $^{13}\text{C-NMR}$ measurements. DSC measurements on the grafted ESTP epoxy resins showed a decreasing trend for T_g with increasing content of PMPS siloxane. The TSC measurements further confirmed this trend. This result suggests that the matrix of ESTP copolymer was less rigid with grafting of PMPS oligomer, due to the Si—O—C linkage at the opened glycidyl ether chain located approximately between the BPA and 4,4'-thiodiphenoxyl chains in the epoxy backbone. A new and broad sub- T_g transition appeared at -60°C in the TSC spectrum was observed for the cooperative motion of this siloxane moiety. All copolymers showed sub- T_g relaxations of γ - and δ -modes, observed at -100 and -130°C , respectively. These two relaxations may be attributed to the motions of BPA and the terminal groups in the epoxy matrix. © 1998 John Wiley & Sons, Inc. *J Appl Polym Sci* 69: 1523–1530, 1998

Key words: epoxy resin; PMPS segment; molecular relaxation; Sub- T_g ; TSC

INTRODUCTION

Polyphenylene sulfide (PPS) with phenyl-S linkage has been known to possess characteristics such as thermal stability with ductile behavior^{1,2} and thermal-induced molecular mobility, characterized by thermally stimulated depolarization current (TSDC),³ among other mechanical properties.^{4,5} Synthesis of a structure resembling this phenylsulfide linkage by incorporating 4,4'-thiodiphenol (TDP), $\text{HO}-\text{C}_6\text{H}_4-\text{S}-\text{C}_6\text{H}_4-\text{O}-\text{H}$, in the epoxy system may produce a less rigid matrix and provides a hydroxyl reaction site, resulting from partial opening of the epoxy group. This

newly formed hydroxyl group may then be used for grafting of another flexible siloxane through condensation, such as methoxyl-terminated PMPS oligomers.^{6–10} With such siloxane modification, the rigidity of the epoxy matrix may be greatly reduced, so that the use of toughening agent, which often needs to be incorporated in the epoxy formulation, may be avoided.

The grafted siloxane oligomers in the epoxy matrix can be effectively studied by an instrument consisting of a highly sensitive detector, such as the electrometer, in thermally stimulated current (TSC).^{3,9–15} A sub- T_g relaxation related to the grafted segments in a cured epoxy matrix has been observed in flexible epoxy system (AL-BIFLEX) by TSC technique^{9,10} as a broader baseline in the temperature range of -30 to -60°C . On the other hand, for the rigid matrix of epoxy

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resins, TSC usually provides a very limited polarization of the dipoles or electrets. The corresponding relaxations upon depolarization show a few relaxation modes, generally with a weak intensity and a simple spectrum. This limited response hampers the observation of molecular relaxations, due to the restricted motions of the electrets in the rigid system. Therefore, intentionally partially cured rigid samples¹¹ or modified epoxy resins possessing a less rigid backbone^{12,13} are used for the observations of such relaxations.

The aims of the present investigation were, hence, to prepare a series of grafted PMPS in thiodiphenol-modified epoxy resins, and to use the TSC technique for observation of the relaxation movements of the grafted PMPS segments in the epoxy matrix.

EXPERIMENTAL

Materials

The DGEBA epoxy resin of Epikote 828 (E 828) possessing an epoxide equivalent weight (EEW) of 185–192 g/mol was locally purchased from Shell Chemical Co. DC-3074, a poly(methylphenyl) siloxane (PMPS) containing Si—phenyl/Si—CH₃ in 50/50 ratio was supplied by Dow Corning Co., Taiwan. 4,4'-Thiodiphenol (TDP) from Aldrich Co., 2,4,6-Tris(dimethylamino-methyl) phenol (DMP-30) from Anchor Chem Co., tetrahydrofuran (THF) from J. T. Baker Co., and tetra-isopropyl titanate (TPT) from Du Pont Co. were used directly without further purification.

Epoxy Equivalent Weight (EEW) Measurements

A method employing HCl/pyridine was used for EEW determination, following a procedure reported in the literature.¹⁶

DSC Measurements

Du Pont 9000 thermal analyzer, coupled with a TA-2000 data analysis system, was used with a heating rate of 10°C/min under N₂ atmosphere for T_g measurements.

TSC Measurements

Solomat TSC/RMA model 9100 (Solomat Instrument Co., Stamford, CT) was used. The sample was polarized at constant $V_p = 100$ V/mm (polar-

ization voltage) and $T_p = 110^\circ\text{C}$ (polarization temperature), with polarization time (t_p) of 5 min, and then cooled rapidly at the rate of $-20^\circ\text{C}/\text{min}$ to a stabilization temperature $T_o = -150^\circ\text{C}$, in order to freeze the oriented dipoles. The sample was then maintained at T_o for 2 min for equilibration. The current due to dipoles and electrets associated with the grafted segments was measured by using a picoammeter, at a heating rate of $10^\circ\text{C}/\text{min}$.

Infrared (IR) Measurement

IR measurements were performed on a JASCO IR-700 spectrophotometer. The samples were prepared by dissolving them in acetone and casting on a NaCl plate. The solid samples were mixed in KBr and pressed into KBr pellets.

¹H-NMR and ¹³C-NMR Measurements

The structural data of hydrogen and carbon atoms pertaining to their local environment that manifests in the form of individual chemical shifts, were measured by ¹H-NMR and ¹³C-NMR, respectively, using the Bruker AM-300 WB FT-NMR instrument in the NSC Instrument Lab.

Gel Permeation Chromatography (GPC)

The GPC instrument was equipped with Physical Spectra P1000 HPLC system in which four columns of 300×7.7 mm (with porosity of 100, 500, 1000, 10,000 Å) Phenogel-10 from the Phenomenex and a Spectra 100 UV at 254 nm were used. THF was used as mobile phase with a flow rate of 1 mL/min at ambient temperature.

Size-Exclusion Chromatography (SEC) Viscometer

The SEC viscometric instrument, coupled with a TriSEC GPC software from Universal Calibration model, was performed with a GPC chromatographic apparatus equipped with a refractive index (ERC-7515A from ERC Inc.) and an on-line differential viscometer (T-50A from Viscotek Co.). A set of AM-gel columns of 10 μm, 5 μm, and 100 Å from American Polymer Standards Co., were used. THF was utilized as eluent and the flow rate of 1 mL/min at ambient temperature.

Preparation of TDP-Containing Siloxane-Modified E 828 Epoxy Copolymers (ESTP)

Preparation of ETP-1-2 Copolymer

A hot-melt method was used for this preparation.^{6,7,9,10} A 2000 mL three-necked round-bottom flask, equipped with a reflux condenser and mechanical stirrer was placed on an oil bath. The ETP-1-2¹⁷ epoxy copolymer, consisting of a mixture of TDP and E 828 in 1-to-2 molar ratios, was prepared at 120–130°C. The crude product was washed with chloroform to remove unreacted TDP. The final product was dried in vacuum oven at 60°C for 24 h. The EEW was found to be 515 g/mol. The data for ETP-1-2 and ESTP copolymers are listed in Table I. The infrared (IR) spectrum of the ETP-1-2 product (cast on NaCl plate) exhibited absorptions associated with —OH at 3450 cm⁻¹, [—C(CH₃)₂—phenyl—] at 1378 cm⁻¹, [—C—O—C—] at 1231 cm⁻¹, oxirane at 911 cm⁻¹, and [—C—S—] at 700–600 cm⁻¹. The ¹H-NMR spectrum in ppm (CDCl₃) showed peaks (δ) associated with [—(CH₃)₂C—phenyl—] at 6.79, 6.81, 7.10, 7.12; [—S—phenyl—] at 6.81, 7.24; [oxirane for —O—CH₂] at 2.73, 2.88; [oxirane for —O—CH—] at 3.33 and [—C(CH₃)₂—phenyl—] at 1.62. The ¹³C-NMR spectrum (CDCl₃) showed the major peaks (δ) at 157.77, 156.13, 132.70, 115.35 ppm [—S—phenyl—], 156.26, 143.60, 127.96, 127.74, 113.94, 113.86 ppm [—C(CH₃)₂—phenyl—], 50.19, 44.77 ppm [—oxirane], 41.69, 30.97 ppm [—(CH₃)₂C—phenyl—].

Preparation of ESTP-74X Copolymers

ETP-1-2 was mixed with a premeasured quantity of DC-3074 and placed in a flask equipped with stirrer.^{6,7,9,10} Then, 0.5 wt % of TPT catalyst was added and the reaction temperature was maintained at 130°C for 2–3 h. The reaction time was determined by the EEW measurement. The product was washed three times with xylene and was dried in a desiccator under reduced pressure. A notation ESTP-74X is used hereafter for the siloxane-modified TDP-containing E 828 epoxy resins, where X represents the weight percent of DC-3074 in ETP-1-2, i.e., ESTP-7410, -7420, -7430, -7440, and -7450 represent 10, 20, 30, 40, and 50 wt % of DC-3074 in ETP-1-2, respectively. The ESTP-system has EEW of 675 for ESTP-7410, 703 for ESTP-7420, 761 for ESTP-7430, 804 for ESTP-7440, and 865 for ESTP-7450. The data of ETP-

1-2 and ESTP copolymers are listed in Table I. Infrared (IR) spectrum of ESTP-7430 (cast on NaCl plate) exhibits absorptions at 3392 cm⁻¹ [—OH], 2954, 1254, 805 cm⁻¹ [—Si—CH₃], 1589, 1425, 697, 487 cm⁻¹ [—Si—phenyl], 1379 cm⁻¹ [—C(CH₃)₂—phenyl], 1233 cm⁻¹ [—C—O—C—], 1179 cm⁻¹ [—Si—O—C—, —Si—O—CH₃], 1032–1097 cm⁻¹ [—Si—O—Si—], and 911 cm⁻¹ [oxirane]. The ¹H-NMR spectrum (CDCl₃) showed major peaks (δ) at 7.91, 7.41 ppm [—Si—phenyl], 6.79, 7.11 ppm [—C(CH₃)₂—phenyl—], 6.82, 7.26 ppm [—S—phenyl], 3.33 ppm [oxirane for (—O—CH—)], 2.74, 2.88 ppm [oxirane for (—O—CH₂)], 1.62 ppm [—C(CH₃)₂—phenyl—], and 0.09 ppm [—Si—CH₃]. The ¹³C-NMR spectrum (CDCl₃) showed major peaks (δ) at 157.82, 132.74, 115.40 ppm [—S—phenyl—], 134.30, 130.67, 127.66, 127.66 ppm [—Si—phenyl], 156.30, 156.18, 143.61, 127.98, 127.79, 113.92 ppm [—C(CH₃)₂—phenyl—], 50.26, 44.81 ppm [—oxirane], 41.73, 31.03 ppm [—(CH₃)₂C—phenyl—], and 0.85 ppm [Si—CH₃].

Curing Process of Siloxane-Modified ESTP-74X Copolymers

Epoxy resins of ESTP-74X series were mixed with an appropriate amount of curative (5–10 g) and the curing procedure was conducted under the hot-melt condition as follows. An amine curative (DMP-30, 2 wt %) was added to the ESTP copolymer and was well mixed, degassed, placed on an aluminum or Teflon-coated sample holder, and subjected to curing at 120°C for 1 h and postcured at 140°C for 1 h. The cured sample, in the form of 50-mm wide and 2-mm thick sheets, were used for TSC and DSC measurements.

RESULTS AND DISCUSSION

Synthesis and Structural Determination

There exist several ways to incorporate a siloxane oligomer in an epoxy resin.^{18–21} In the present synthesis, E 828 epoxy resin was first reacted with thiodiphenol to form a copolymer containing a hydroxyl group in the glycidyl segment. With this hydroxyl group as a reaction site, polycondensation with methoxy-terminated siloxane (PMPS) was carried out by a hot-melt method. The stripping of methanol molecules was accomplished heating the samples at 130°C. This epoxy copolymer was used for condensation with PMPS, viz.

Table I Preparation and Properties of ETP-1-2 and ESTP Copolymers

Epoxy Resins	Siloxane Content (wt %)	T_g (°C)					
		PS	SEC-IV	Cured			
		M_w/M_n^a	M_w/M_n^b	Uncured DSC ^c	DSC ^c	TSC ^d	EEW ^e
Epikote 828	0	394/392	—	-16.0	84.2	80.2	188
DC-3074	100	1130/826	—	-63.0 ^f	—	-59.3 ^g	—
ETP-1-2	0	1352/918	2440/1080	24.1	102.7	100.3	515
ESTP-7410	10	2830/1690	2580/1070	23.0	101.8	97.1	675
ESTP-7420	20	3382/2208	2730/1190	21.9	101.0	96.4	703
ESTP-7430	30	4920/2740	3210/1450	21.0	100.5	96.1	761
ESTP-7440	40	5930/3208	4200/1370	19.4	97.9	93.5	804
ESTP-7450	50	6290/2760	4360/1660	17.2	96.0	92.0	865

^a GPC measurements with UV detector and polystyrene standards.

^b SEC-IV detects by refractive index on-line with viscometer.

^c T_g was measured by DSC at a scanning rate of 10°C/min.

^d TSC measured at a depolarization rate of 10°C/min.

^e EEW was determined by the HCl/pyridine method.

^f From ref. 4.

^g Liquid sample (resin).

DC-3074. The PMPS-containing ETP-1–2 resins, abbreviated as ESTP-74X where X represents the wt % of DC-3074 from 10 to 50 wt %, were thus prepared, as outlined in Scheme 1.

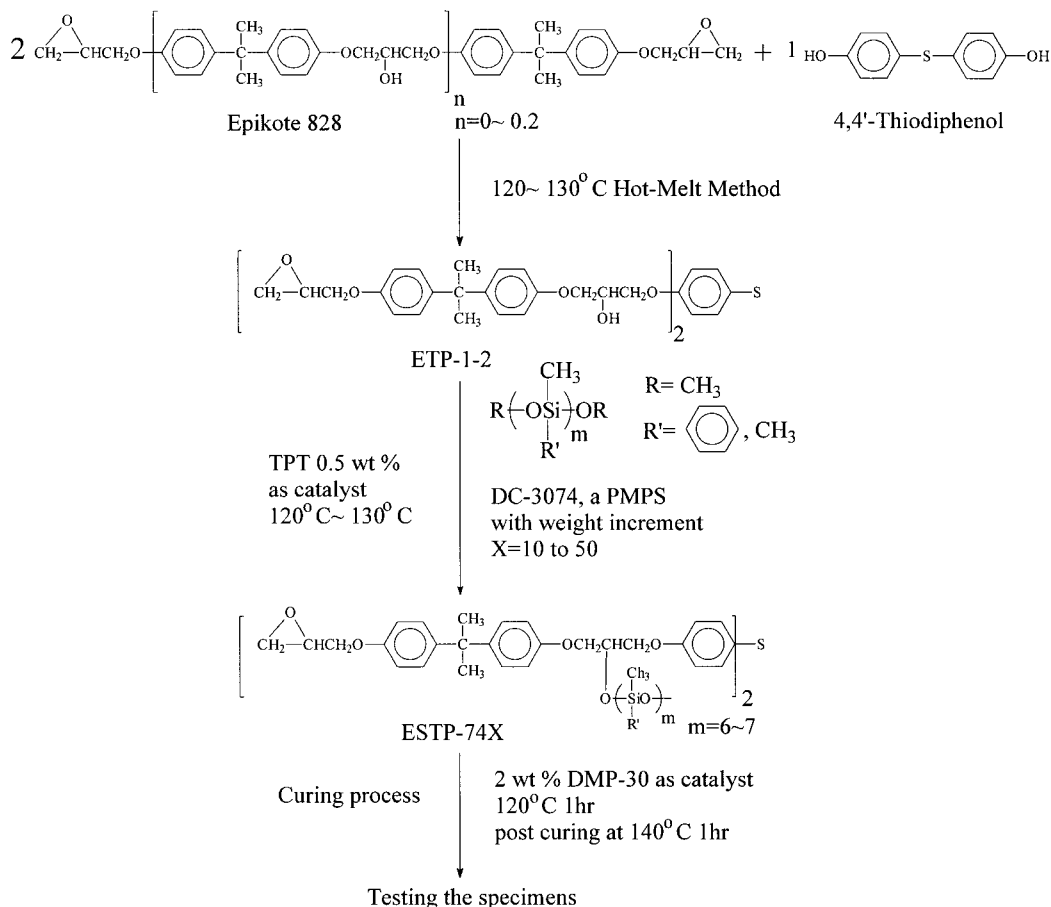
Evaluation of the Structure of PMPS-Containing Epoxy Resin and ESTP

Copolymer by IR, ¹H-NMR, and ¹³C-NMRs

The modified resin ESTP-7430 was used as a representative sample to examine the structure of ESTP copolymer. The IR spectra of ESTP-7430, ETP-1–2 and DC-3074 are presented in Figure 1 for comparison. The spectrum of ESTP-7430 in Figure 1(a) exhibits additional phenyl—Si— absorptions peaks, viz. A, E, and F at 1425, 697, and 487 cm⁻¹, respectively, as compared to the starting epoxy resin of ETP-1–2 shown in Figure 1(b). This confirms the same —Si—phenyl absorption peaks appearing in the spectrum of DC-3074 [Fig. 1(c)]. Other absorptions in this spectrum are peak B of isopropyl [—C(CH₃)₂—] at 1379 cm⁻¹, peak C of an oxirane at 911 cm⁻¹ and peak D of —Si—CH₃ at 805 cm⁻¹. The corresponding peaks A to F for ESTP-7430 are labeled in Figures 2 and 3, for ¹H-NMR and ¹³C-NMR data, respectively. These data, with the diminishing Si—O—CH₃ in DC-3074 in the ¹H-NMR (chemical shift appearing at 3.80 ppm) and in ¹³C-NMR (at 50.18 ppm) confirm the condensation of demethanolysis and the structure.

Molecular Properties of ESTP Copolymers

Results of the measurements on relative molecular weight of the ESTP copolymers by GPC with PS standards are presented in Table I. These relative molecular data were used because most of the related molecular data of PMPS-modified epoxy copolymers^{6,7} were based on the PS standards. Increase in relative M_w/M_n (1352/918) of the unmodified epoxy resin of ETP-1–2 to M_w/M_n (6290/2760) of ESTP-7450 can be noted with an increase in PMPS content. These results were then further checked with Size-Exclusion Chromatography (SEC) Viscometer^{4,22,23} coupled with a TriSEC GPC software for Universal Calibration model. It was performed with a GPC chromatographic apparatus equipped with a refractive index (RI) and an on-line differential viscometer (DV). Based on the universal calibration,²³ the molecular data from M_w/M_n of 2440/1080 for the starting epoxy resin of ETP-1–2 to M_w/M_n of 4360/1660 for ESTP-7450 copolymer were obtained and listed in Table I. This trend of increasing M_w , based on either relative molecular data or SEC molecular measurement, indicates that the bulky PMPS segment in the epoxy matrix may become a steric hindrance that prevents formation of the tight network. The softening of the matrix was also observed by the DSC measurements. T_g of the resins decreased from 24.1°C for the ETP-1–2 to 17.2°C for ESTP-7450. T_g of the cured specimens also decreased from 102.7°C for ETP-1–2 to 96.0°C for



Scheme 1 Preparation and curing process of siloxane-modified epoxy (ESTP-74X) copolymers. X is the wt % increment of PMPS, DC-3074 is an epoxy resin.

ESTP-7450. These results support the less rigid matrix concept. To confirm this structure, the TSC was used and the results are discussed as follows.

TSC Measurements on ESTP-74X Series

The TSC spectra of ESTP-74X series, where X = 10 to 50 wt %, and starting epoxy resins of ETP-1-2 and E 828 are shown in Figure 4. The peak temperatures of $T_{g,\alpha}$ -transition for these ESTP copolymers are also listed in Table I. A similar trend of decreasing $T_{g,\alpha}$ for the ESTP-74X series can be observed with increasing X content, i.e., from X = 0 at 100.3°C for ETP-1-2 to X = 50 at 92.0°C for ESTP-7450. This result may suggest that the matrix of ESTP was less rigid. The grafting of PMPS oligomer with the —Si—O—C-linkage at the opened glycidyl ether chain located approximately between the BPA and 4,4'-thiodiphenoxyl chains in the epoxy backbone may become too bulky and sterically hindered to prevent the for-

mation of the rigid matrix. One of the advantages of TSC spectra towards the evaluation of polymeric specimens over DSC is its capability to reveal the additional sub- T_g transitions. As can be seen from Figure 5, three sub- T_g transitions occur for this polymer. The depolarized relaxations for these sub- T_g transitions are designated as β , γ , and δ in the order of decreasing temperature. An additional small peak appearing as a shoulder at -35.0°C [as shown in Fig. 5(b)] along with broadening of the $T_{g,\gamma}$ peak on the high temperature side can be observed for ETP-1-2 specimen, while the E 828 shows a normal descending curve in this region. The same shoulder peak can also be observed in the ESTP-7410 spectrum, but is absent in TSC spectra of the samples with higher contents of PMPS and E 828 specimens as well. Therefore, this peak is believed to be unrelated to the PMPS segments in the epoxy matrix and could not be identified as yet. The assignment of this shoulder peak, however, may require further in-

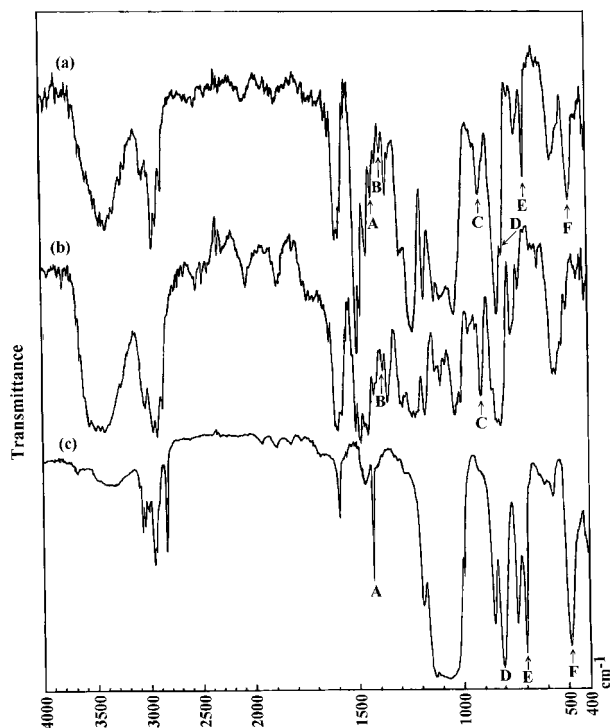


Figure 1 IR spectra of the starting materials and ESTP-7430: (a) ESTP-7430, (b) ETP-1-2, (c) DC-3074. The peaks are designated as A: (Si—phenyl); B: ($-\text{C}(\text{CH}_3)_2-$); C: (oxirane); D: (Si— CH_3); E: (Si—phenyl); F: (Si—phenyl).

vestigations probably with relaxation mapping analysis (RMA) to further elucidate the nature of this transition.²⁴

The γ and δ peaks in the low temperature regions can be observed for all epoxy copolymers including E 828, and may be attributed to the presence of free terminal groups for the δ mode, and the relaxation of phenyl methylene/thio moieties for the γ mode.²⁵⁻²⁷

The β transition is unique and occurs as a new peak only in the siloxane-grafted epoxy samples. It was observed as a broad peak previously for more flexible epoxy system, such as ALBIFLEX 108 (A 108), comparing the same grafted PMPS segment.^{9,10} However, it was not clear enough in the flexible A 108 system, presumably due to the overlap with other relaxation modes. For the present ESTP-74X matrix, a broad yet distinct peak in the region of -60°C , associated with the grafted PMPS segment, is observed. The intensity of this β -mode can be seen to increase from ESTP-7410 to ESTP-7450, i.e., with increase in PMPS content from 10 to 50 wt %, as shown in Figure 5. The intensity of β relaxation curve increases gradu-

ally in curves (d) to (h) before reaching the same intensity as that of the γ peak. A less rigid matrix offering ease of movement has been assumed to exhibit a higher depolarization response than the rigid one. Therefore, this β relaxation may be attributed to the cooperative movement of the grafted PMPS (see Scheme 1 for structure). Notably, the location of PMPS is in the proximity of these two phenyl methylene/sulfide groups of BPA and TDP. The intensity of this $T_{g,\beta}$ relaxation is higher than those of phenyl methylene/sulfide groups appearing on $T_{g,\gamma}$, because it contains a polymethyl-phenylsiloxane moiety in $[-\text{O}-(\text{CH}_3)\text{Si}(\text{phenyl})-\text{O}-]_n$. TSC measurements were also carried out for a liquid resin of PMPS (DC-3074). The corresponding TSC spectrum, as seen in Figure 5(c), shows a relaxation at -59.3°C . Because the motion of PMPS

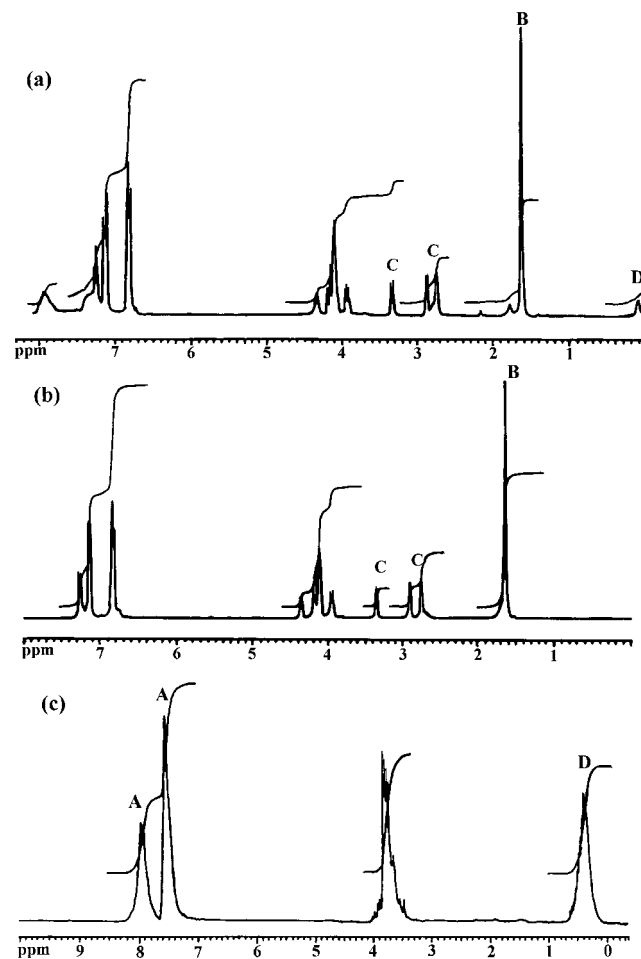


Figure 2 $^1\text{H-NMR}$ spectra of the starting materials and ESTP-7430: (a) ESTP-7430, (b) ETP-1-2, and (c) DC-3074. The peak assignments are the same as those in Figure 1.

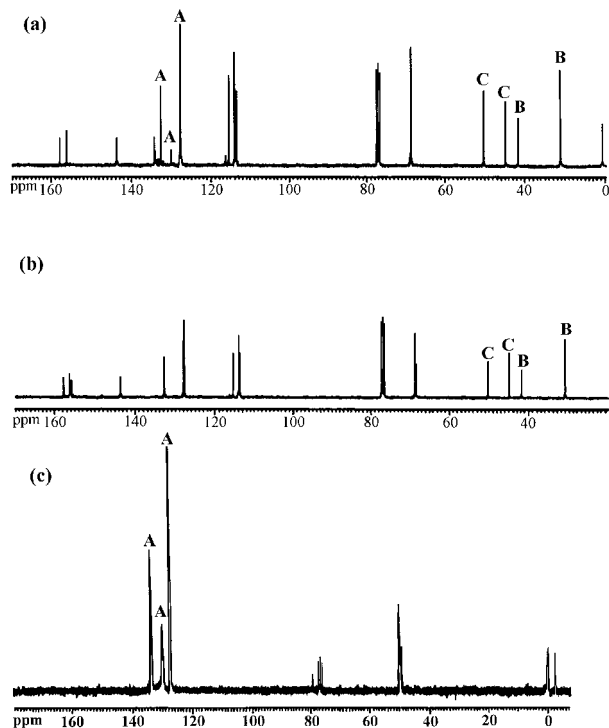


Figure 3 ^{13}C -NMR spectra of the starting materials and ESTP-7430: (a) ESTP-7430, (b) ETP-1-2, and (c) DC-3074. See Figure 1 for peak assignments.

oligomer may be more freer in liquid resin than that of the grafted segment in the epoxy resin, a slightly lower temperature for the relaxation transition occurs in the liquid. This result is thus in good agreement with the observed PMPS transition in the epoxy matrix.

CONCLUSION

PMPS grafted thiophenoxy-containing epoxy resins are prepared by hot-melt method. The low-

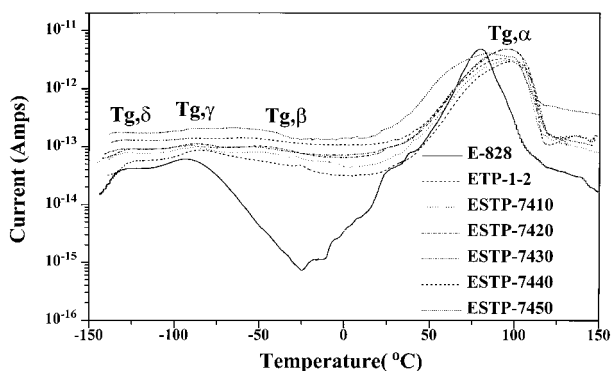


Figure 4 The global TSC spectra of ESTP copolymers.

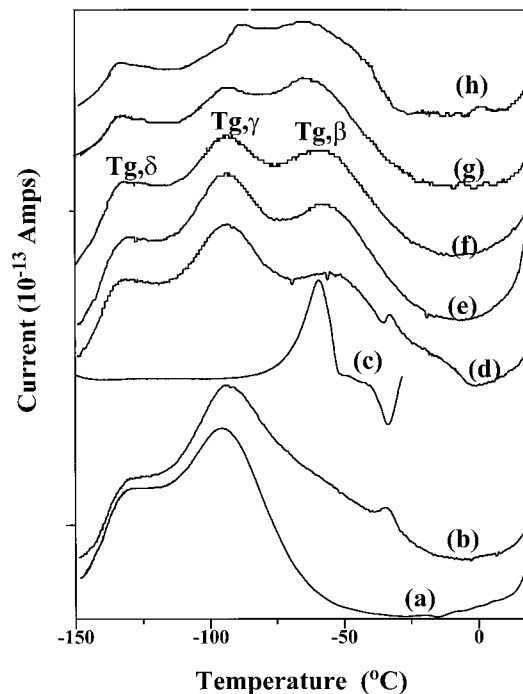


Figure 5 Enlarged TSC spectra of siloxane-modified ESTP-74X in the region of transitions $T_{g,\beta}$, $T_{g,\gamma}$, and $T_{g,\delta}$. Curves are designated as (a) E 828, $T_g = 80.2^\circ\text{C}$, (b) ETP-1-2, $T_g = 100.3^\circ\text{C}$, (c) DC-3074, $T_g = -59.3^\circ\text{C}$, (d) ESTP-7410, $T_g = 97.1^\circ\text{C}$, (e) ESTP-7420, $T_g = 96.4^\circ\text{C}$, (f) ESTP-7430, $T_g = 96.1^\circ\text{C}$, (g) ESTP-7440, 93.5°C , and (h) ESTP-7450, 92.0°C .

ering of T_g with an increase in PMPS content, observed from the DSC data, indicates reduction in the rigidity of the epoxy structure. This grafted soft segment of PMPS in the thiophenoxy epoxy matrix shows a relaxation as β mode at -60°C . Additional relaxations appear at -100 and -130°C , and the corresponding transitions are attributed to the phenyl methylene/sulfide moieties and the free terminal groups in the solid-state structure.

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REFERENCES

1. B. G. Risch, S. Srinivas, G. L. Wilkes, J. F. Geibel, C. Ash, S. White, and M. Hicks, *Polymer*, **37**, 3623 (1996).

2. M. F. Cheung and H. K. Plummer, Jr., *Polym. Eng. Sci.*, **36**, 15 (1996).
3. S. X. Lu and P. Cebe, *J. Appl. Polym. Sci.*, **61**, 473 (1996).
4. D. Daoust, S. Bebelman, P. Godard, J. M. Coisne, and C. Strazielle, *Polymer*, **37**, 3879 (1996).
5. S. S. Schwartz and S. H. Goodman, *Plastics Materials and Processes*, Van Nostrand Reinhold, New York, 1982.
6. S. T. Lin and S. K. Huang, *J. Polym. Sci., Part A: Polym. Chem.*, **34**, 869 (1996).
7. S. T. Lin and S. K. Huang, *J. Polym. Sci., Part A: Polym. Chem.*, **34**, 1907 (1996).
8. T. Kobayashi, H. Saitoh, and N. Fujii, *J. Appl. Polym. Sci.*, **51**, 483 (1994).
9. T. Y. Lo, W. C. Shau, and S. K. Huang, *Proceeding of the 19th ROC Polymer Symposium*, vol. 1, Hsin Chu, Taiwan, 1996, p. 61.
10. T. Y. Lo, W. C. Shau, and S. K. Huang, *J. Polym. Res.*, **4**, 73 (1997).
11. M. Goel, P. S. Viswanathan, and P. Vasudevan, *Polymer*, **19**, 905 (1978).
12. M. Topic and Z. Katovic, *Polymer*, **35**, 5536 (1994).
13. S. M. Shin, D. J. Byun, B. G. Min, Y. C. Kim, and D. K. Shin, *Polym. Bull.*, **35**, 641 (1995).
14. J. P. Ibar, *Fundamentals of Thermal Stimulated Current and Relaxation Map Analysis*, Imperial Graphics Communication, Bridgeport, CT, 1993.
15. G. Collins and B. Long, *J. Appl. Polym. Sci.*, **53**, 587 (1994).
16. L. T. Lee and C. P. Yang, *J. Appl. Polym. Sci.*, **46**, 991 (1992).
17. T. Y. Lo and S. K. Huang, *J. Appl. Polym. Sci.*, to appear.
18. E. M. Yorkgitis, N. S. Eiss, Jr., C. Tran, G. L. Wilkes, and J. E. McGrath, *Adv. Polym. Sci.*, **72**, 80 (1985).
19. J. L. Hedrick, B. Haidar, T. P. Russell, and D. C. Hofer, *Macromolecules*, **21**, 1967 (1988).
20. O. Mitsukazu and Y. Hideo, *Jpn. J. Polym. Sci. Technol.*, **49**, 499 (1992).
21. O. Mitsukazu, K. Toshio, M. Kenji, and Y. Hidekazu, *Jpn. J. Polym. Sci. Technol.*, **50**, 621 (1993).
22. R. A. Sanayei, K. G. Suddaby, and A. Rudin, *Makromol. Chem.*, **194**, 1953 (1993).
23. H. G. Barth, *J. Polym. Sci., Part B: Polym. Phys.*, **34**, 1705 (1996).
24. T. Y. Lo and S. K. Huang, submitted.
25. S. M. Shin, D. J. Byun, B. G. Min, Y. C. Kim, and D. K. Shin, *Polym. Bull.*, **35**, 641 (1995).
26. S. Pangrle, C. S. Wu and P. H. Geil, *Polym. Compos.*, **10**, 173 (1989).
27. W. F. A. Su, S. H. Carr, and J. O. Brittain, *J. Appl. Polym. Sci.*, **25**, 1355 (1980).