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Study on the depolarization transitions of the modified epoxy resins containing penta-coordinated aromatic phosphate by thermally stimulated current technique with the relaxation mapping analysis

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Abstract

Thermally stimulated current/relaxation map analysis (TSC/RMA) study on the T_g transition of the phosphate-containing epoxy copolymers reveals that the cooperative motion of the penta-coordinated phosphate group with 4,4′-thiodiphenol as the tribranched segment is the prime factor responsible for the lowering of the T_g for the copolymer. Thermal windowing technique of RMA leads to compensation search that produced with compensation points in "Z" structure. From this Z data, a convenient method is used for the verification of the T_g value. Thermokinetic data of enthalpy (ΔH) and entropy (ΔS) also provide additional supporting data for the determination of T_g based on the compensation search from the RMA measurement.

Keywords: Phosphate-thiodiphenol epoxy resin; Relaxation transition; TSC/RMA; Entropy; Enthalpy

1. Introduction

Epoxy resins are characterized by a tight network, which often gives rise to a brittleness and hence limits the applications. One method to solve this rigid epoxy matrix is by blending the toughening agents [1–3] such as carboxyl terminated butadiene nitrile (CTBN) rubber [4,5] in the formulation to give the needed toughening strength. Another approach is to undertake the modification on the resin's structure. A modification on the structure with a flexible oligomer may give the needed toughening property. A grafting of the flexible polymethylphenyl-siloxanes (PMPSs) in the epoxy side chains [6–11] have provided the needed toughening property with a showing of a 3- to 5-folds improvement on the impact strength [12]. The measurement on the glass transition temperature (T_g) is often carried out by DSC, TMA and DMA among other thermal analyzers. The measurement of T_g is essential in the evaluation of the polymeric modification. T_g is an important thermal characteristic that reflects the main chain motion in terms of the temperature. In general, a higher T_g may indicate a better thermal stability and may refer indirectly or correlate to the rigidity of the matrix, if the T_g's of the related samples are available for the comparison. By the same token, a lower T_g may be used to indicate the ease in backbone's motion as expressed by the depolarization relaxation [13] in the thermally stimulated current (TSC) technique. The present approach in this line

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of research is to incorporate a bulky aromatic phosphate in the epoxy backbone. This may envisage that the phosphate in a penta-coordinate form may serve as the tribranched center that may produce a branched or ideally a cascade-typed linkage that may soften the otherwise rigid epoxy matrix. This may provide the needed toughening property for the epoxy resin.

It is the purpose of this investigation to characterize the thermal transition of the phosphated copolymers by the depolarization technique of the TSC with the relaxation mapping analysis (RMA) and with the reference of the thermal data from conventional differential scanning calorimeter (DSC).

2. Experimental

2.1. Materials

Phosphorus oxychloride ($POCl_3$) from Riedel-de Haën, 2-methoxyethyl ether from Acros and 4,4′-thiodiphenol (TDP), from Aldrich, were purchased locally. Bisphenol A (BPA) was supplied by Nan Ya Plastic. 2,4,6-Tris(dimethylaminomethyl) phenol (DMP-30) was purchased from Anchor and was used directly. Tris-*p*-thiodiphenol phosphate (designated as P3-TDP) and tris-*p*-phenol A phosphate (designated as P3-BPA) were prepared in the lab. The P3-TDP modified DGEBA epoxy copolymers (P3-ETP and P3-EBPA) were prepared according to the hot-melt method described previously [14,15].

2.1.1. DSC measurements

The T_g measurements were carried out on Du Pont 900 DSC instrument couple with a TA-2000 data analysis system. Samples of both uncured resin as well as cured specimens were measured at a scanning speed of 10°C min^{-1}, in the temperature range −50°C to 200°C.

2.2. TSC measurements

TSC measurements were carried out on a TSC/RMA Model 9100 (Solomat) instrument. The voltage applied during the polarization stage was 100 V mm^{-1}. These measurements were carried out by polarizing the sample at 20°C above its T_g temperature measured by DSC. The depolarization process was carried out by heating the sample at the rate of 7°C min^{-1}. The sample thickness was generally 2 mm.

2.3. RMA measurements

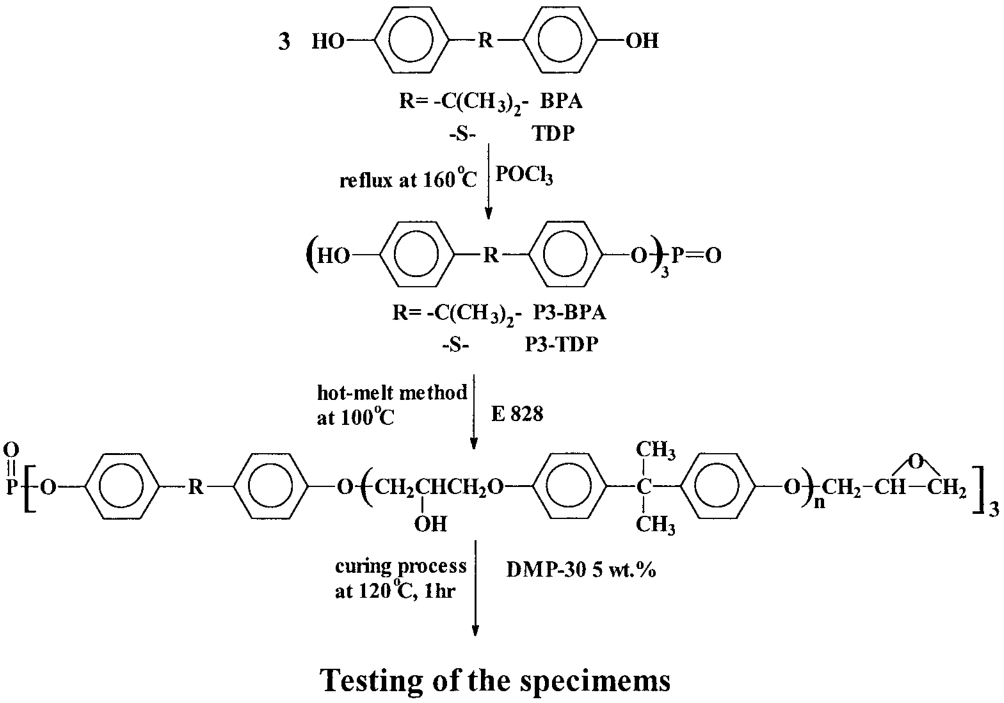
The thermal windowing technique of a fractional polarization in RMA consisted of application of the static electric field at T_p for 5 min. This allows the orientation of only those units having a relaxation time of less than 5 min. The temperature was then lowered till $T_d=T_p-5°C$, the field was then cut off and the sample was short-circuited for T_d=2 min, so as to allow relaxation of units with short relaxation times. Then the sample was quenched until $T_0=T_p-30°C$. The depolarization current was recorded by using the sample protocol as the complex spectrum. Thus, an elementary spectrum composed of a single peak was analyzed with the Debye integration option.

3. Results and discussion

3.1. TSC measurements

The preparation [14,15] and the representative structure for the penta-coordinated aromatic phosphate with P3-TDP and its epoxy copolymer (P3-ETP) are outlined in Scheme 1. The structural identifications on P3-TDP and related copolymers have been described elsewhere [15].

The thermal transition of P3-TDP, a phosphate with the tris-thiodiphenol and P3-ETP, the modified epoxy copolymer of P3-TDP with E-828, in resin form was first subjected to the depolarization measurement. Fig. 1 shows the TSC spectra of phosphate-modified copolymers and unmodified compounds in resin and cured states. The T_g of P3-TDP was observed as a peak at 0.5°C. The low T_g of this phosphated P3-TDP triol reflects the effect of the tribranched constitution. The low T_g of P3-TDP is significant when comparing to other phenolic materials used in the epoxy modifications. For example, the melting temperature of BPA is 150°C and TDP is 155°C. This low temperature of P3-TDP is favorite for the modification work. For the preparation of P3-ETP copolymer with P3-TDP and the liquid E-828, a much lower temperature can be used in the hot-melt condition. This may avoid the



Scheme 1. Preparation of P3-ETP copolymer.

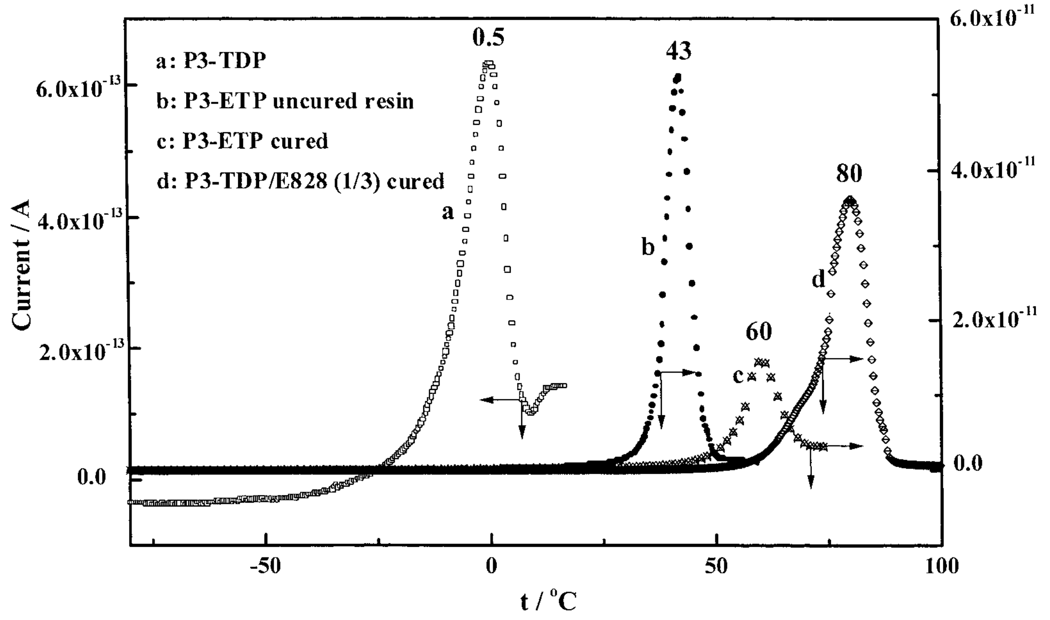


Fig. 1. TSC spectra of the phosphate-modified copolymers. Curve a: P3-TDP, curve b: P3-ETP resin, curve c: P3-ETP cured sample and curve d: P3-TDP/E828 blend and cured sample (mole ratio=1:3).

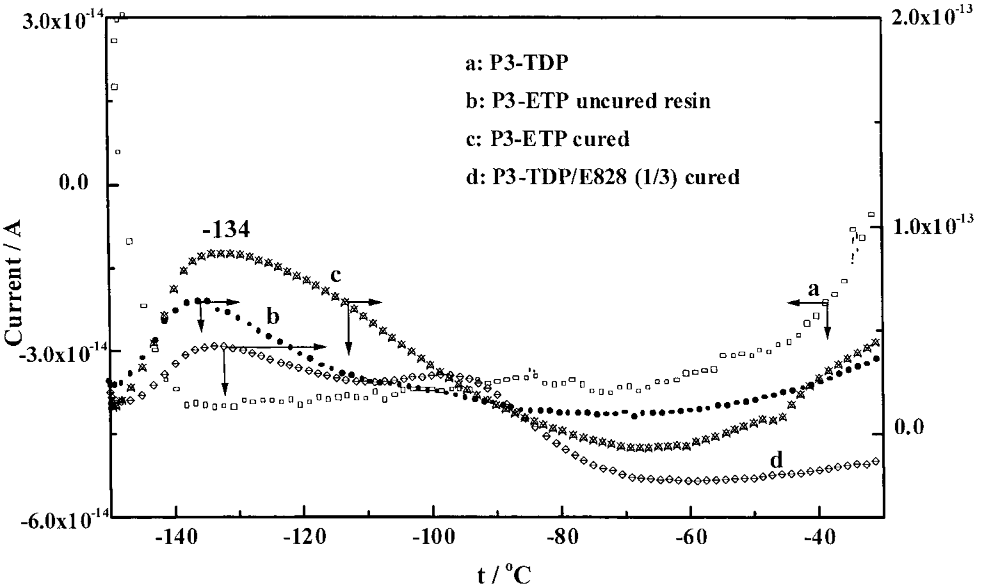


Fig. 2. TSC spectra of the sub-T_g transitions. Curve a: P3-TDP, curve b: P3-ETP resin, curve c: P3-ETP cured sample and curve d: P3-TDP/E828 blend and cured sample (mole ratio=1:3).

formation of the unwanted higher homologies in the P3-ETP epoxy copolymer. The TSC measurement of P3-ETP in the epoxy resin form is shown as the curve "b" in Fig. 1. It shows a low T_g of 43°C. A low temperature of 60°C of the cured specimen of P3-ETP with DMP-30 can be seen in Fig. 1, curve "c", while the temperature of 89°C for the cured E-1001 (in Fig. 2). A blended specimen, P3-TDP/E-828, with the ratio of 1/3 in P3-TDP/E-828 showed a T_g of 80°C (curve "d" in Fig. 1) after it was subjected to the same curing agent and the curing conditions. The T_g of 60°C of the copolymeric P3-ETP vs. the 80°C of the blended P3-TDP/E-828 specimen indicated that the tribranched P3-ETP, formed through copolymerization, is in advantage and in favorable condition since branched oligomer is already established, and a branched or a possible cascaded matrix may be formed upon the self-crosslinking condition. On the other hand, the blended formulation may be constituted many possible chain linkages such as a linear or a tight network formed through a competing self-polymerization of E-828 to E-828 under the initiation of the DMP-30 curative and a matrix of E-828 with the tris-thiodiphenols through random polymerizations and resulted in a higher T_g at 80°C.

The sensitive TSC measurements also show the sub-T_g transition in low temperature. The sub-T_g transition that appeared at −134°C to −137°C in Fig. 2 is often related to the relaxation transition of free terminal groups [11,16]. Little change for these epoxy specimens is observed either in resin or matrix states.

The DSC measurements on T_gs for P3-ETP and other specimens are listed in Table 1 for the reference.

The TSC spectra of the phosphated epoxy specimens in comparison with the unmodified DGEBA epoxy specimens are combined and shown in Fig. 3. Fig. 3(a) and (b) shows the T_g and sub-T_g transitions. P3-ETP shows the lowest T_g, followed by the ETP, then the E-1001 and the P3-EBPA at the highest. This result indicates that the incorporation of tribranched phosphate moiety does not necessarily reduce the rigidity of the epoxy matrix. The tribranched junction could serve as a hard crosslinked center with BPA segment in P3-EBPA with the highest T_g of 105°C or it may serve as a soft junction with the low T_g of 60°C in P3-ETP with the flexible divalent –S– linkage. The combination of the penta-coordinated phosphate with tribranched thiodiphenolic segment may provide the flexibility for the epoxy matrix in P3-ETP. A similar trend of P3-EBPA>E-

Table 1
TSC data on the thermal transitions of phosphate-containing epoxy specimens

Specimens	TSC						DSC		EEW (g mol^{-1})
	Sub-T_g (°C)				T_g (°C)		T_g (°C)		
	Terminal		Aromatic segment						
	Uncured resin	Cured resin	Uncured resin	Cured resin	Uncured resin	Cured resin	Uncured resin	Cured resin	
P3-ETP	−136	−134	–[a]	–[a]	43	60	32	46	715
P3-TDP/E828[d]	–[b]	−134	–[b]	−98	–[b]	80	–[b]	59	–[b]
ETP	−135	−137	−101	−96	24	86	27	75	643
E 828	–[a]	−129	−112	−95	−12	82	−16	95	196
P3-EBPA	−135	−134	−122	−90	31	105	34	82	–[c]
E1001	−132	−132	−103	−93	40	89	33	99	580

[a] Not observed.

[b] Not available or not applicable.

[c] Not measured

[d] Specimens was prepared by blending P3-ETP and E 828 in 1/3 ratio with 5 wt% DMP-30 curative and cured at 120°C for 1 h.

1001>ETP>P3-ETP may also be seen in the aromatic sub-T_g transitions at −90 to −96°C region, even with the broad peaks as shown in Fig. 3(b).

This enhanced flexibility of the epoxy matrix with the combination of the penta-coordinated phosphate with the flexible divalent –S– linkage in P3-ETP was further probed by the thermal windowing technique [17] employed in the RMA. The TSC measurement on the relaxation peak alone gives a limited information and is often required to carry out the confirmation on the peaks such as T_g and/or $T_{g,\rho}$ in TSC spectrum. The verification task on the T_g can be fulfilled by the RMA measurement. In addition, one can obtain thermokinetic data of ΔH, ΔS, ΔG and log τ, the relaxation parameter that may provide data to support the flexibility correlated to the low T_g data from the TSC measurement.

3.2. RMA measurements

The thermal windowing technique [17] is often used for RMA of the peaks appearing in the TSC spectrum. The narrowed depolarization process in this technique result to a series of peaks that can be converted to straight lines, if the transitions follow the Arrhenius equation,

$$\tau(T) = \tau_0 \exp(\Delta H/kT), \qquad (1)$$

where τ_0 is the pre-exponential factor, ΔH the activation enthalpy and k is the Boltzmann constant.

The plot of these Arrhenius lines provides the compensation search. Figs. 4 and 5 show the RMA data for P3-ETP and P3-EBPA epoxy copolymers, respectively, where (a) shows the thermal windowing curves, (b) depicts the Arrhenius lines that leads to the compensation points in the “Z” structure.

The following important observations can be noted from the above RMA data:

(1) The linear connection of T_c^+ and T_c^- forms a “Z” structure. This “Z” structure indicates that the specimen is an uniformed copolymer and is in amorphous state in this temperature region.

(2) The “Z” structure provides vital data for the verification of T_g. There exist methods that can be used to calculate T_g value from compensation data. A method has been used to calculate T_g from the equation $T_g=[(\Delta H_g-a)/(\Delta S_g+b)]$ [17]. The ΔH_g and ΔS_g can be obtained from the entropy–enthalpy plot. The entropy–enthalpy plot (E–E plot) of P3-ETP is shown in Fig. 6. For many polymeric systems, it is often found that $a=0$ and $b=0.0293$ kJ K^{-1} mol^{-1} [17]. The T_g values calculated with this equation are listed in Table 2.

For example, the T_g calculated by using $a=0$ and $b=0.0293$ kJ K^{-1} mol^{-1} is 61°C, which is in agree-

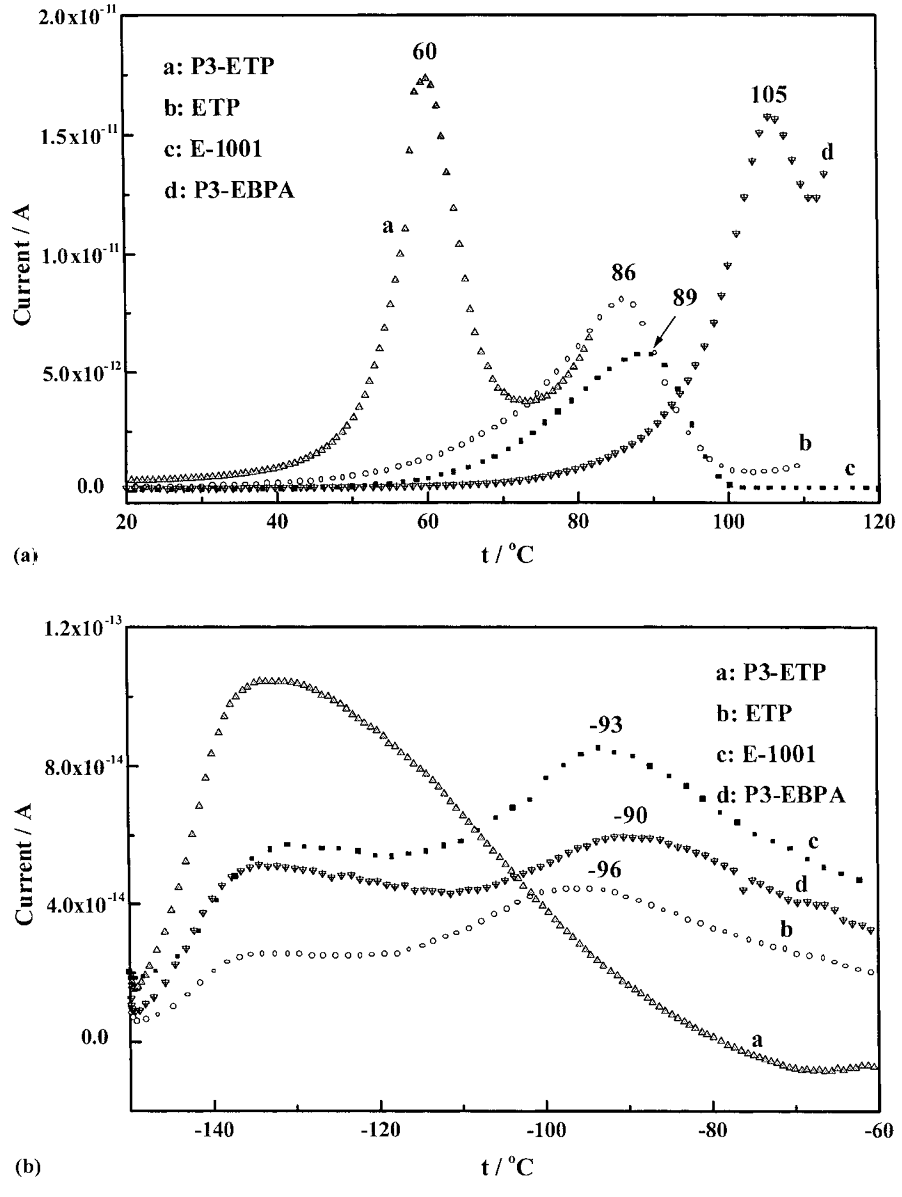


Fig. 3. TSC spectra of the phosphated epoxy copolymers. (a) The glass transitions: curve a: P3-ETP, curve b: ETP, curve c: E-1001 and curve d: P3-EBPA; (b) the sub-T_g transitions: curve a: P3-ETP, curve b: ETP, curve c: E-1001 and curve d: P3-EBPA.

ment with the T_g of 60°C from the TSC measurement for the P3-ETP copolymer.

3.2.1. Thermokinetic data of the P3-ETP and P3-EBPA copolymers

The quest on the flexibility of the matrix consists of a penta-coordinated phosphate with the tris-thiodipehnol segments in the main chain was further investigated with the thermokinetic properties in free energy (ΔG), enthalpy (ΔH) and entropy (ΔS).

Two specimens were used for the comparison. One with the penta-coordinated phosphate with the thio-linkage of the TDP in the tribranched segment in P3-ETP and the other with the isopropyl-linkage of

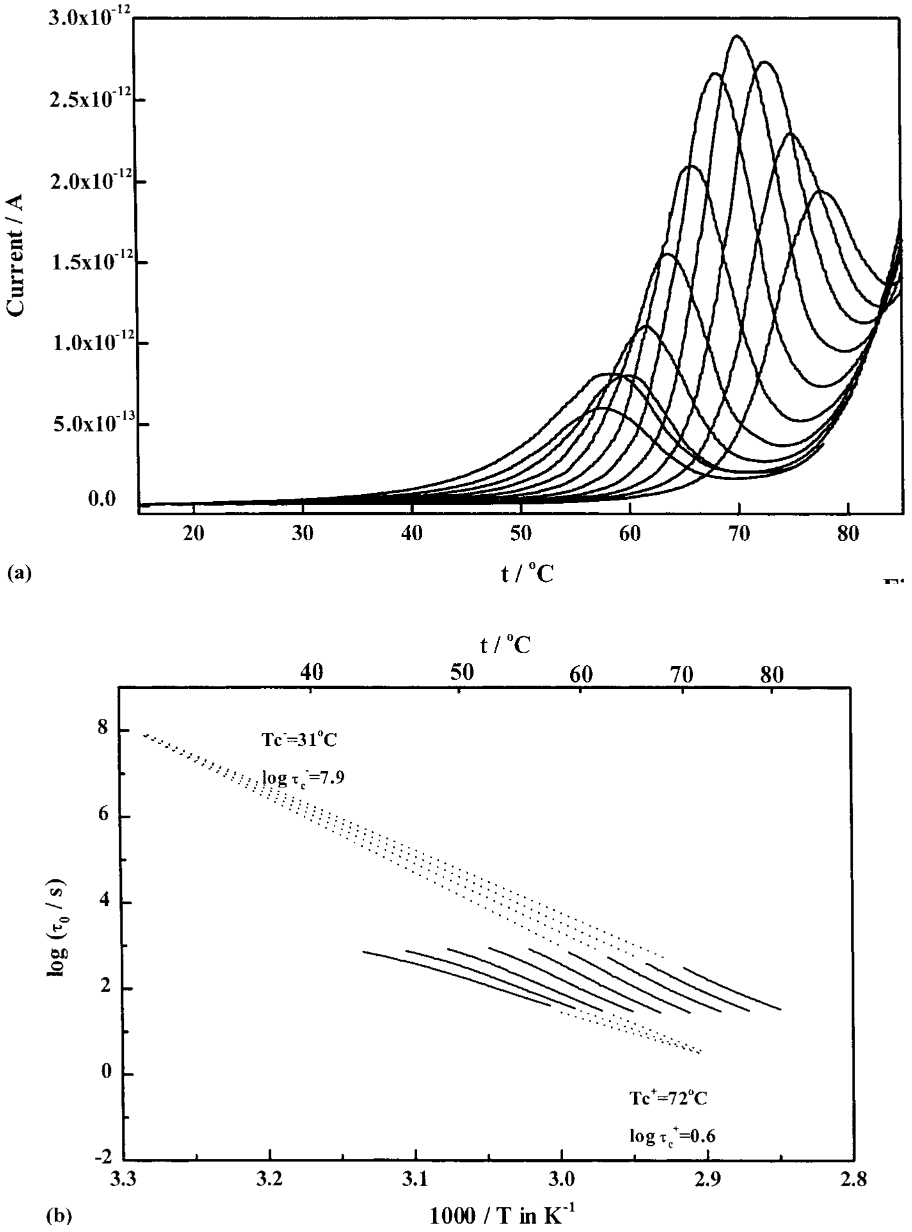


Fig. 4. RMA data of P3-ETP copolymer: (a) RMA spectrum and (b) "Z" structure.

the BPA in the same phosphate-contained P3-EBPA copolymer.

3.3. Arrhenius transform

The compensation search from the RMA measurement provides the temperature correlation of the enthalpy (ΔH) and relaxation in terms of log τ by the Arrhenius transform.

Eq. (2) is derived according to Debye model [17],

$$\tau(T) = J(T)/P(T), \tag{2}$$

where $\tau(T)$ is the true relaxation time of material, $J(T)$

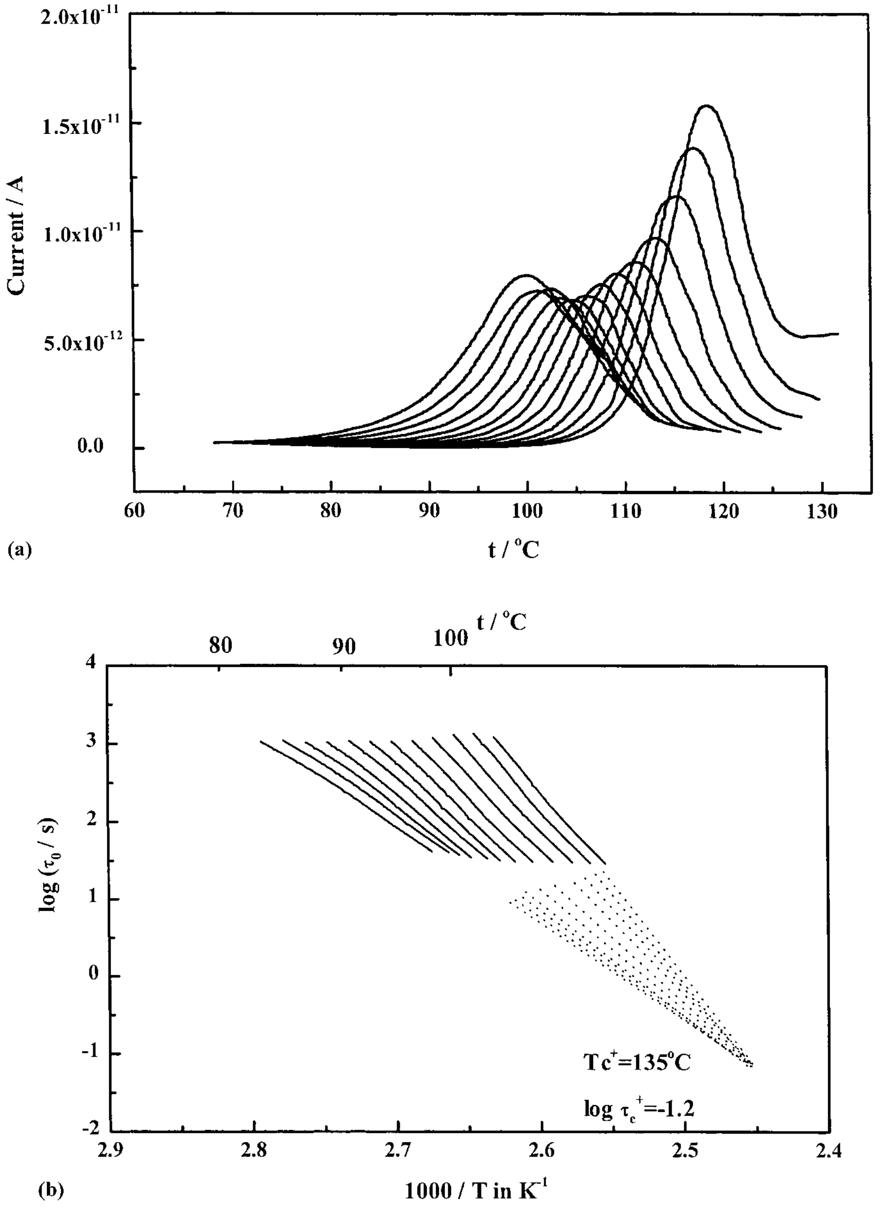


Fig. 5. RMA data of P3-EBPA copolymer: (a) RMA spectrum and (b) "Z" structure.

the depolarization current density and $P(T)$ is the surface area.

Combine the Arrhenius Eqs. (1) and (2) gives Eq. (3) in logarithm form;

$$\log\tau = \log\tau_0 + \Delta H/kT. \qquad (3)$$

The ΔH value can then be obtained by the plot of log τ to the reciprocal of the temperature ($1/T$).

3.4. Eyring transform

Another treatment by Eyring [18] provides the correlation of the thermokinetic properties in free energy (ΔG), enthalpy (ΔH) and entropy (ΔS).

The Eyring transform can be started with Eq. (4),

$$\log\tau_i = \log\tau_{i0} + \Delta G/kT. \qquad (4)$$

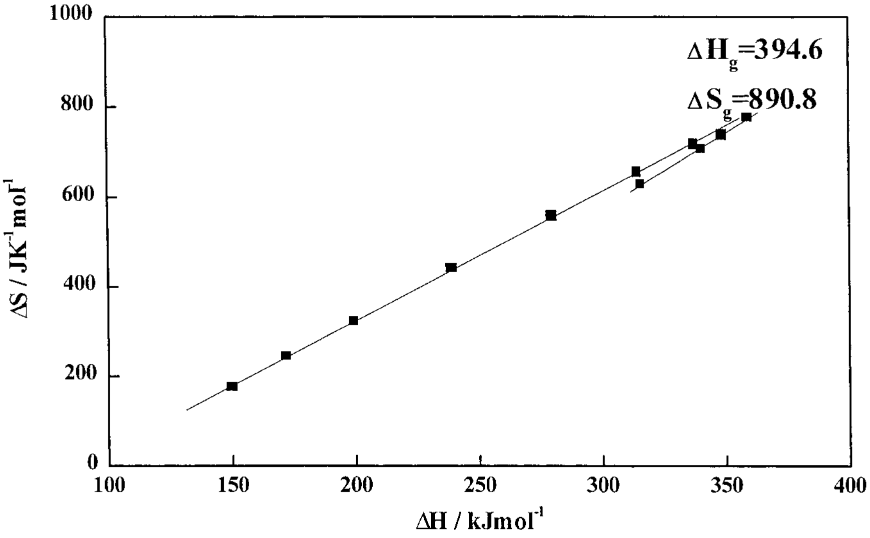


Fig. 6. The Entropy vs. enthalpy diagram of P3-ETP.

Eyring [18] defines log τ_{i0} in Eq. (5),

$$\log \tau_{i0} = -\log(kT/h), \quad (5)$$

where k, h are Boltzmann and Planck's constants.

The combination of Eqs. (4) and (5) leads to Eq. (6):

$$\tau_i = (h/kT)\exp(-\Delta S_p/k)\exp(\Delta H_p/kT). \quad (6)$$

The "Eyring plot" of [log τ_i+log T+log (k/h)] vs. the temperature ($1/T$) gives enthalpy in $\Delta H_p/k$ and entropy in $-\Delta S_p/k$ and the ΔG_p can be obtained from Eq. (7),

$$\Delta G_p = \Delta H_p - T\Delta S_p. \quad (7)$$

Fig. 7 shows the temperature correlates to the maximum of the enthalpy (ΔH) with the corresponding minimum of log τ_0 from the Arrhenius transform. The P3-EBPA showed the temperature at 112°C, with the higher temperature than the temperature at 66°C for the P3-ETP. The temperature correlates to the maximum values of enthalpy (ΔH) and entropy (ΔS) can be also obtained from the Eyring transform and from the entropy–enthalpy plot (Fig. 6). Based on these ΔH_{max} and ΔS_{max} values, the temperature corresponds to the T_g can be obtained from each treatment. Fig. 8 shows the temperatures correlate to the maximum of ΔH and ΔS curves at 112°C for P3-EBPA and at 66°C for P3-

Table 2
Confirmations by thermal techniques

Method	T_g (°C)		Note
	P3-ETP	P3-EBPA	
TSC	60	105	From Fig. 1
RMA	61[a]	105[a]	From Figs. 4 and 5
Arrhenius transform	66	112	For P3-ETP: log τ_{min} (s)=−53.8 ΔH_{max} (eV)=3.8 For P3-EBPA: log τ_{min} (s)=−52.9, ΔH_{max}(eV)=4.2
Eyring transform	66	112	For P3-ETP: ΔS_{max} (J K^{-1} mol^{-1})=775.3 ΔH_{max} (kJ mol^{-1})=359.4 For P3-EBPA: ΔS_{max} (J K^{-1} mol^{-1})=756.5 ΔH_{max} (kJ mol^{-1})=403.3

[a] $T_g=(\Delta H_g-a)/(\Delta S_g+b)$, a=0, b=0.07 [17].

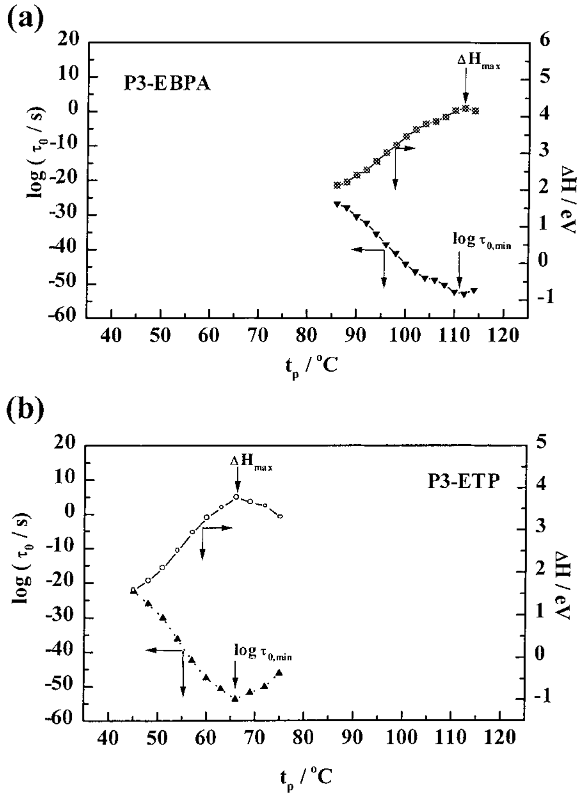


Fig. 7. Correlations of ΔH and log τ with temperature: (a) P3-EBPA and (b) P3-ETP.

ETP specimens. Both treatments lead to the conformation on the T_gs for P3-ETP and P3-EBPA.

The measurements of the T_g transition of the phosphated epoxy copolymers have been carried out by DSC, TSC and confirmed by an empirical equation of $T_g=(\Delta H_g-a)/(\Delta S_g+b)$, where $a=0$ and $b=0.0293$ kJ K^{-1} mol^{-1} in RMA and from the plots from the Arrhenius transform as well as Eyring transform, both based on the data from compensation search [17]. Table 2 lists the T_g values of P3-ETP and P3-EBPA from these measurements. The verification on T_g value from RMA is in good agreement with the TSC measurement. The P3-ETP possesses with the lower T_g than the P3-EBPA. P3-ETP therefore possessed a less rigidity in matrix than that of P3-EBPA. P3-ETP possesses the higher entropy and lower enthalpy than P3-EBPA. These thermokinetic data can be summarized as follows:

P3-ETP : $\Delta S_{\max} = 775.3\,\mathrm{J\,K^{-1}\,mol^{-1}}$,
$\Delta H_{\max} = 359.4\,\mathrm{kJ\,mol^{-1}}$,
$T_g = 61°\mathrm{C}$, $T_c^+ = 70°\mathrm{C}$; $\log \tau_c^+ = 0.7\,\mathrm{s}$,
P3-EBPA : $\Delta S_{\max} = 756.5\,\mathrm{J\,K^{-1}\,mol^{-1}}$,
$\Delta H_{\max} = 403.3\,\mathrm{kJ\,mol^{-1}}$,
$T_g = 105°\mathrm{C}$, $T_c^+ = 116°\mathrm{C}$; $\log \tau_c^+ = 0.5\,\mathrm{s}$.

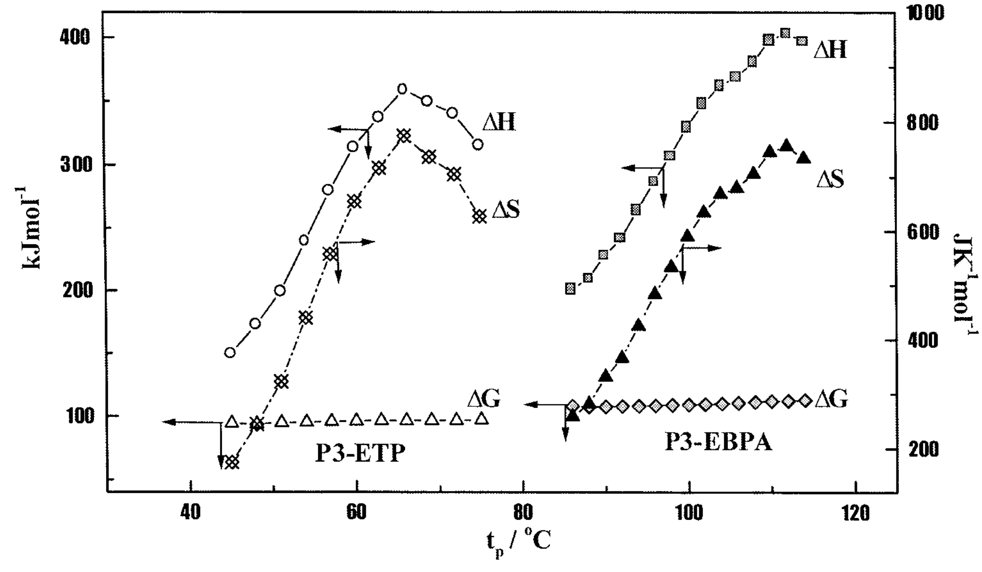


Fig. 8. Correlation of ΔH and ΔS with temperature.

4. Conclusion

Phosphate-containing epoxy copolymer with thiodiphenol in the tribranched segment (P3-ETP) are studied by TSC/RMA. Significant lowering of the T_g of P3-ETP as compared to other related samples indicates that the observed softening effect arises from the rightful combination of the penta-coordinated phosphate with the divalented thiophenol as the tribranched segment.

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