Studies on the Cure Kinetics and Networks Properties of Neat and Polydimethylsioxane Modified Tetrafunctional Epoxy Resins

Tar-Hwa Hsieh,[1] Tsung-Han Ho,[1] Ko-Shan Ho,[1] Ho-Ruei Chen,[1] Po-Hsing Li,[1] Shin-Shiao Yang,[1] Shi-Hao Ye,[1] Yu-Chen Chang[2]

[1]*Department of Chemical and Materials Engineering, National Kaohsiung University of Applied Sciences, Kaohsiung, Taiwan*
[2]*Institute of Materials Science and Engineering, National Sun Yat-Sen University, Kaohsiung Taiwan*

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ABSTRACT: The cure kinetics of tetrafunctional epoxy resins with three different backbone structures and their modification by polydimethylsioxane (PDMS) were studied by means of differential scanning calorimetry with dynamic approach. The development of epoxy networks was characterized by dynamic viscoelastic measurements. Results showed that all the epoxy resins obeyed the autocatalytic reaction mechanism with a reaction order of about 3. Epoxy resin with softer aliphatic backbone demonstrated a higher cure reactivity and stronger tendency towards autocatalysis, as well as lower crosslinking density. The PDMS-modified epoxy resins showed higher early cure reactivity and a lower crosslinking density due to the plasticization and restriction effect of the dispersed PDMS phase, respectively. Based on cure kinetics and dynamic viscoelastic results, the α_m was found to be an effective precursor for describing the developing of epoxy networks during the course of cure.
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Key words: tetrafunctional epoxy resins; polydimethylsioxane; cure kinetics; autocatalytic reaction; epoxy networks; crosslinking density; plasticization effect

INTRODUCTION

Epoxy resins have been widely used in printed circuit board as semiconductor encapsulating materials due to their well-balanced properties including excellent heat, moisture, solvent, and chemical resistance, superior electrical and mechanical properties, and good adhesion to many substrates.[1] *o*-Cresol-formaldehyde novolac epoxy (CNE) is the resin widely employed to encapsulate microelectronic devices. Upon cure, this multifunctional epoxy resin provides a densely crosslinked protective layer.

However, the trend toward miniaturization and thinner electronic equipment and continuing decrease in the scale of integrated circuits (IC) have forced the design of smaller chips, finer patterns, and high pin counts that are more susceptible to thermal stress failure.[2,3] Therefore, it is necessary to develop a low-stress, high glass transition temperature (T_g) and low-moisture-absorbing resin system for high-reliability semiconductor devices.

Many approaches have been reported to improve the heat resistance of epoxy resins, for example, by increasing the crosslink density of cured epoxy resin,[4] preparation of stiff main chain[5] or introduction of a bulky structure such as biphenyl or naphthalene.[6] However, these epoxy systems may also result in brittle and high stress characteristics of the cured epoxy resin. Recently, lots of studies have focused on the enhancement of mechanical properties, especially the toughness of cured epoxy resin, by the incorporation of low level reactive liquid rubber such as carboxy-terminated butadiene-acrylonitrile copolymer (CTBN),[7–10] acrylate rubber[11] or the modification with a ductile engineering thermoplastic polymer like bisphenol-A-based polycarbonate[12] or polyetherimide.[13] As reported in our previous study,[14] a low-stress, high T_g, and low moisture absorbing tetrafunctional epoxy (EP) resins were successfully synthesized by condensing a dialdehyde with phenol followed by epoxidation of the resulting tetraphenol with epichlorohydrin. The long-chain aliphatic group builds the needed flexibility into a cured epoxy resin (EP_3), leading to lower mechanical properties (i.e., storage shear modulus, flexural moduli and flexural strength) and T_g; the rigid aromatic group including the cured epoxy resin (EP_2) exhibited higher mechanical properties and T_g. Amine-terminated polydimethylsiloxane (PDMS)-modified epoxy resins (EP-AS) effectively reduce the stress of the synthesized EP resins by

Correspondence to: T.-H. Hsieh (thh@cc.kuas.edu.tw).

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creating dispersed phases of sea-island dissipation morphology.

In the present study, the effect of different backbone structures on the cure kinetics of EP or EP-AS resins were further investigated by means of DSC with dynamic scans. In combination with our earlier rheological results, the relationship between cure kinetics, morphology and the development of epoxy networks were discussed.

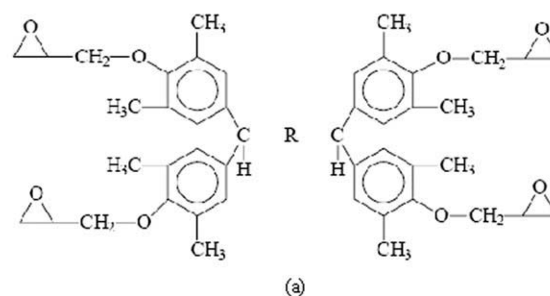
EXPERIMENTAL

Materials

EP resins with three different types of backbones and amine-terminated PDMS-modified ones were received from our earlier study.[14] Structure of the EP and EP-AS resins are shown in Figure 1, respectively.

In the present study, three different backbone structures of unmodified EP resins (designated here as neat EPresins) and their silicone PDMS-modified resins were designed as EP_1, EP_2, EP_3, EP_1-AS, EP_2-AS, and EP_3-AS, respectively, where the subscript of 1, 2, and 3 indicate, —, —C_6H_4— (phenyl) and $(CH_2)_3$ in the backbone of EP resins, respectively. According to our previous study,[14]the epoxy equivalent weight (EEW) values of EP_1, EP_2 and EP_3 are 192, 206 and 202 respectively. The EP-AS resins contained ca. 10 wt % bonded to PDMS.

The EP resins and EP-AS resins were used as the base epoxy resin. 4-4′-diaminodiphenyl sulfone (DDS) and triphenylphosphine (Ph_3P) were used as curing agent and curing accelerator, respectively, which were obtained from Merck Co.



EP_1, R = ----- 1,1,2,2-teuakis(4-glycidyloxy-3,5-d1methylphenyl)ethane

EP_2: R = [phenyl] 1,1,2,2-teuakis(4-glycidyloxy-3,5-d1methylphenyl)ethane

EP_3: R = $(CH_2)_3$ 1,1,5,5-tefrakis(4-glycidyloxy-3,5-dimethylphenyl)pentane

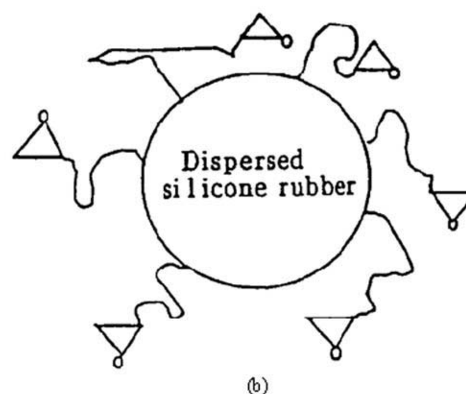


Figure 1 Schematic diagrams of structure of (a) EP and (b) EP-AS resins.

Sample preparation

A 1 : 1 stoichiometric ratio of epoxy to DDS samples and 1 wt % Ph_3P were compounded by a low temperature milling at 5°C, followed by immediately immersed in ice water to terminate the cure reaction before the kinetic studies.

Differential scanning calorimetry (DSC)

The cure kinetic analysis was conducted by a Perkin–Elmer 7 series DSC with heating rates (ϕ) of 40, 20, and 10°C/min ranged from 50 to 300°C. Nitrogen gas was purged at a flow rate of ca. 10 mL/min. Calibration of the calorimeter was conducted for each heating rate on the indium standard. With the presumption that the heat flow as measured by DSC, dH/dt, is proportional to the rate of reaction dα/dt, it is possible to determine the extent of fractional conversion, α, directly from the experimental curve by partial integration[15]

$$\alpha = \frac{1}{\Delta H_T} \int_0^t \left(\frac{dH}{dt}\right) dt \quad (1)$$

where ΔH_T stands for the total heat of reaction as determined by dynamic DSC scans and it was assumed to be specific to each heating rate and that the total heat was chosen such that conversion was 100%.

Dynamic viscoelastic measurements

Dynamic viscoelastic properties were performed on a Rheometrics RDA-II rheometer between −150 and 450°C, with a heating rate of 5°C/min at a frequency of 1 Hz. The rectangular torsion mode was chosen and the cured specimens with the dimensions of 51 × 12.7 × 0.76 mm were prepared under 210°C for 4 h. The storage modulus G' and tan δ were then determined.[14]

RESULTS AND DISCUSSION

Cure behavior

The conversion curves of curing of EP and EP-AS resins are shown in Figure 2. It can be seen that the

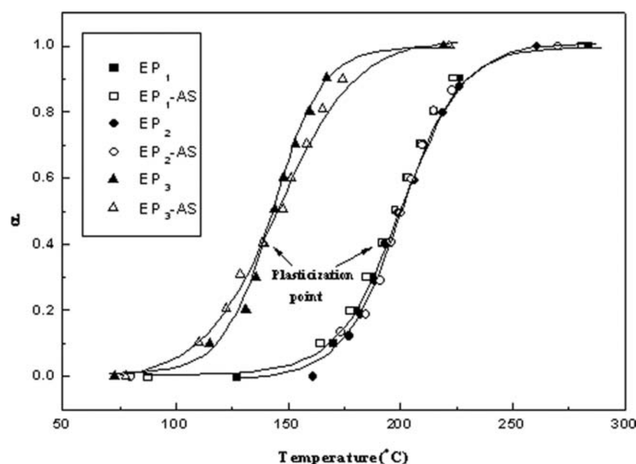


Figure 2 Typical conversion curves of curing of EP and EP-AS resins during cure at a heating rate of 20°C/min.

initial temperature (T_i) of cure reaction of EP_3, EP_1,and EP_2 are 72.9, 127.1 and 161°C, respectively, indicating the long-chain aliphatic group builds a more flexible backbone of the epoxy system, which leads to the occurrence of cure reaction at lower temperatures. As compared to the EP resins, in the early stage of cure (ca. $\alpha < 0.4$), the conversion curves of EP-AS resins display the lower T_i and higher initial curing rate (the slop of conversion curve extrapolating to the temperature axis as α equals to zero), as the cure is proceeding, the EP-AS conversion curve turns into intercepting with the EP conversion curve at α near 0.4 (i.e., plasticization point), after the plasticization point, the curing rate is gradually slowing down, and eventually the behavior becomes similar to those of neat epoxy resins. It suggests that the presence of the dispersed PDMS phases within the epoxy resin may act as a diluting agent which can effectively induce the cure reaction at lower temperatures and increases the curing rate of the initial stage,[16]contributing more effective collusion between epoxide with amine species in the plasticized matrix, while reduces the curing rate after the plasticization point, due to the formation of the curing network of PDMS as well as an uneven distribution of epoxide and amine species in the dispersed phase after phase separation.[17,18] It demonstrates that in the early stage of cure the chemically controlled mechanism of cure of EP-AS resin is strongly influenced by the dispersed morphology caused by the plasticization effect, after the plasticization point the cure reaction becomes a diffusion-controlled and mainly depends on the backbone structure rather than on the dispersed morphology.

Cure kinetics

In the present study, we have chosen to start with a simplified, general rate expression of

$$d\alpha/dt = \mathrm{A}f(\alpha)\ \exp(-E_a/RT), \quad (2)$$

where A is the pre-exponential factor, $f(\alpha)$ is a function of conversion, E_a is the apparent activation energy, R is the gas constant, and T is the cure temperature. For systems obeying eq. (2), Prime[19] suggested that E_a could be estimated through the dependence of the peak temperature (T_p) on the heating rate according to

$$E_a = -0.951\,R[d\ln\phi/d(l/T_p)]. \quad (3)$$

As shown in Figure 3(a,b), a good linear relationship between ln ϕ and the reciprocal of T_p of EP_3 and EP_3-AS resin are observed. Using Equationeq. (3), E_a values of the epoxy systems are also shown in Figure 3. As seen from Figure 3, E_a value of EP_3 is apparently lower than that of EP_1 or EP_3, due to the presence of the aliphatic, soft backbone. It suggests that owning more flexible backbones by epoxy resin may improve the cure reactivity. As compared to the EP resin, EP-AS resin displays the lower E_a

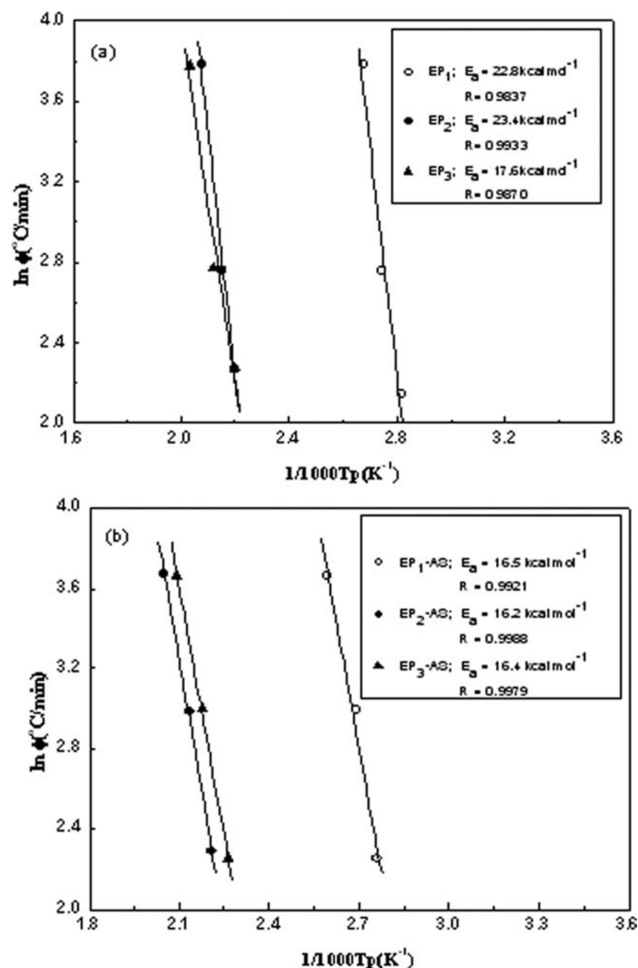


Figure 3 ln ϕ vs. the reciprocal peak temperature for (a) EP and (b) EP-AS resins.

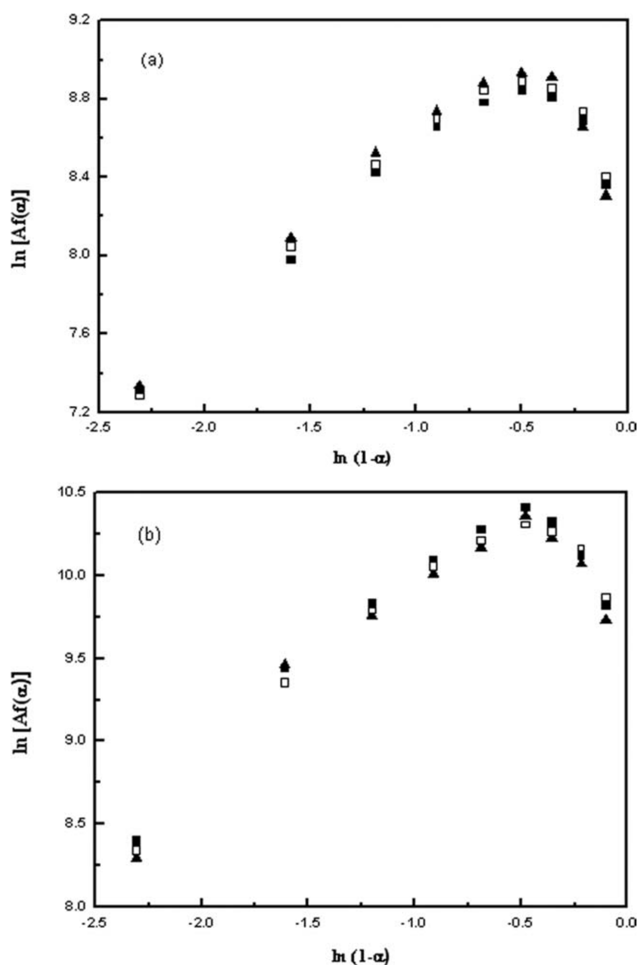


Figure 4 Variation of ln [Af(α)] with ln (1-α) for (a) EP_3 and (b) EP_3-AS resin at different heating rates; (▲) 10 °C/min; (□) 20 °C/min; (■) 40 °C/min.

The typical plot of ln [Af(α)] vs. ln (1−α) of EP_3 and EP_3-AS resin at different heating rates are given in Figure 4(a,b), respectively. It can be seen that the results at different heating rates also fall into a single master curve representing a heating rate independent expression, with the existences of the maximum, α_m, in the master curve of all epoxy resins, supporting that the cure reaction in each system is autocatalytic in nature and does not follow a simple *n*th-order. The master curves of curing of EP and EP-AS resins and the $\alpha_m$value are shown in Figure 5(a,b), respectively. It can be seen that α_m value of EP_3 is larger than that of EP_1 or EP_2, suggesting the crosslinking is easier to occur due to its aliphatic, soft backbone. As compared to the EP resin, α_m value of EP-AS resin is lower than that of neat epoxy resin, leading to the delaying crosslinking due to the plasticization effect. It demonstrates that the α_m is strongly influenced by its composition,[21,22] backbone flexibility, and morphology during cure. It is worthy to note that, α_m values of EP-AS resins are very close value than that of neat EP resin due to the dilution effect of PDMS modifier. It is worthy of noting that, as for EP-AS resins, E_a is about 16 kcal/mol exhibiting its independence from the backbone flexibility of epoxy resin. It suggests that the cure reaction of PDMS-modified epoxy resin is mainly affected by its resulting dispersed morphology rather than their backbone flexibility.

Since Prime's original method prove to be unacceptable in obtaining [Af(α)] values in a long extrapolation procedure. We have chosen to rewrite eq. (3) as[20]

$$\ln[\mathrm{Af}(\alpha)] = \ln[d\alpha/dt] + E_a/RT, \quad (4)$$

where ln [Af(α)] values can be further recalculated from experimentally determined $d\alpha/dt$ and E_a/RT. For *n*th-order reaction, i.e., $f(\alpha) = (1-\alpha)^n$ in eq. (3), Friedman suggested that the relationship

$$\ln[\mathrm{Af}(\alpha)] = \ln A + n \ln(1-\alpha). \quad (5)$$

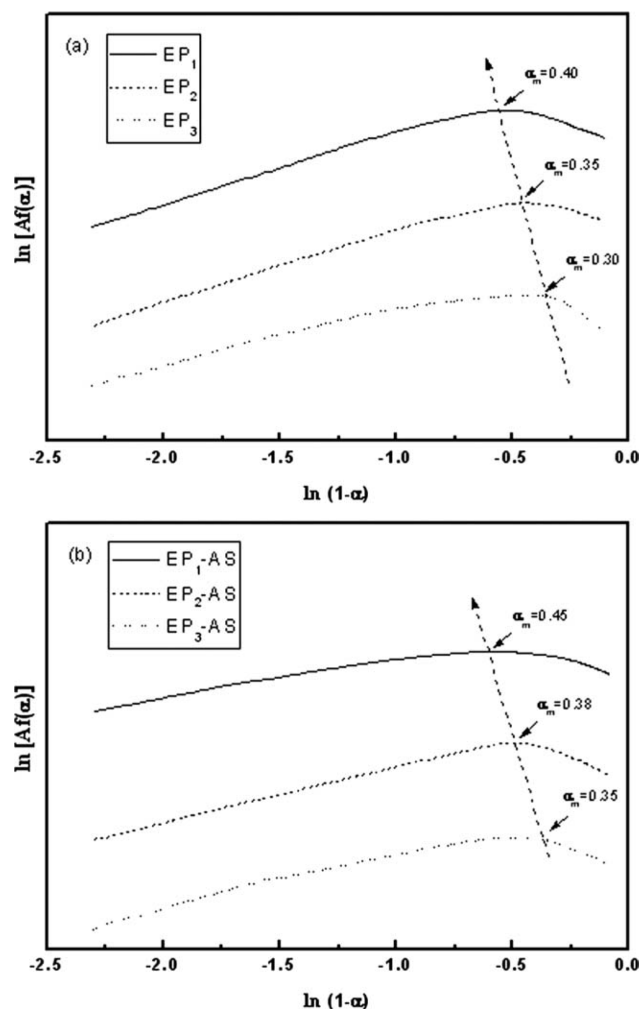


Figure 5 Master curves of ln [Af(α)] with ln (1-α) for (a) EP and (b) EP-AS resins.

TABLE I
The Kinetic Parameter of Epoxy Resins

Sample	$A_1/10^6$ (sec^{-1})	$A_2/10^6$ (sec^{-1})	m	n	Correlation coefficient
EP_1	5.57	1.72	1.1	1.4	0.999
EP_2	1.20	2.70	1.1	1.7	0.968
EP_3	27.86	11.50	1.3	1.7	0.990
EP_1-AS	0.06	0.016	1.4	1.3	0.998
EP_2-AS	4.87	3.21	1.5	1.5	0.999
EP_3-AS	3.81	3.22	1.5	1.5	0.966

to the plasticization point (see Fig. 2), implying the epoxy networks is being developed when α is near 0.4.

Due to the strongly autocatalytic nature of the cure reaction, Kamal and Sourour's[23] approach can be used as

$$d\alpha/dt = (k_1 + k_2\alpha^m)(1-\alpha)^n, \quad (6)$$

where k_1 and k_2 are kinetic rate constants characterized by an Arrhenius temperature dependency, and m and n represent reaction orders. When E_a is taken as a constant,[20–22] eq. (6) may be rearranged as

$$d\alpha/dt = \exp(-E_a/RT)(A_1 + A_2\alpha^m)(1-\alpha)^n, \quad (7)$$

where A_1 and A_2 are the pre-exponential factors. Corresponding to eqs. (2) and (7) gives

$$\mathrm{Af}(\alpha) = (A_1 + A_2\alpha^m)(1-\alpha)^n, \quad (8)$$

where the average values of $\mathrm{Af}(\alpha)$ are adopted here in the kinetic analysis due to the conversion independence of heating rate. The kinetic parameters of A_1, A_2, m, and n for the epoxy systems are determined by the nonlinear least squares curve fitting method[21,22] using eq. (8), with values thus obtained given in Table I. It is observed from Table I, the present curing reactions of epoxy resin follow the reaction order of about 3. It is worthy of noting that, the EP_3 have a stronger tendency towards autocatalysis than those of EP_1 or EP_2 ($m = 1.3$ as compared to the case of EP_1 or EP_2 where m is about 1.1), due to the flexibility of aliphatic backbone. Moreover, the PDMS-modified EP resin also shows a stronger autocatalysis than that of neat EP resin, resulting from the plasticization effect.

Networks studies

As from our earlier study,[14] the storage modulus (G') and tan δ curves for the cured EP and EP-AS resins are shown in Figure 6(a,b), respectively. As seen from Figure 6(a), the tan δ curves for the cured EP network exhibit two major relaxations: a high temperature or α-transition (above 240°C) corresponds to a major T_g of the cured epoxy resins above which significant chain motion takes place; the low temperature or β-transition (ca. −80°C) is attributed predominantly to the motion of the CH_2—CH(OH)—CH_2—O (hydroxyether) group of the epoxy.[14] It can be seen that the EP_3 resin shows lower T_g and G', whereas the EP_1 has higher T_g and G'. It suggests that the long aliphatic chain builds the flexibility within EP_3 and lowers the T_g and matrix's stiffness; the rigid group including the aromatic structure (EP_2) increases the T_g and matrix's stiffness. As seen from Figure 6(b), the exception of the epoxy α and β peaks, the tan δ curve for the PDMS-modified resin shows a significant, additional small peak from −130 to −105°C with a center near −120°C corresponding to the T_g of the siloxane phase, supporting the presence of the multiphase separation morphology. It is noted that the siloxane phase's T_g of EP-AS resins is around −120°C exhibiting its independence on backbone flexibility. As compared to the EP resins, T_g and G' values of EP-AS resins are lower than those of neat EP resins, indicating an increase in the number-average molecular weight between crosslinks (M_c) of epoxy networks created by the introducing of dispersed

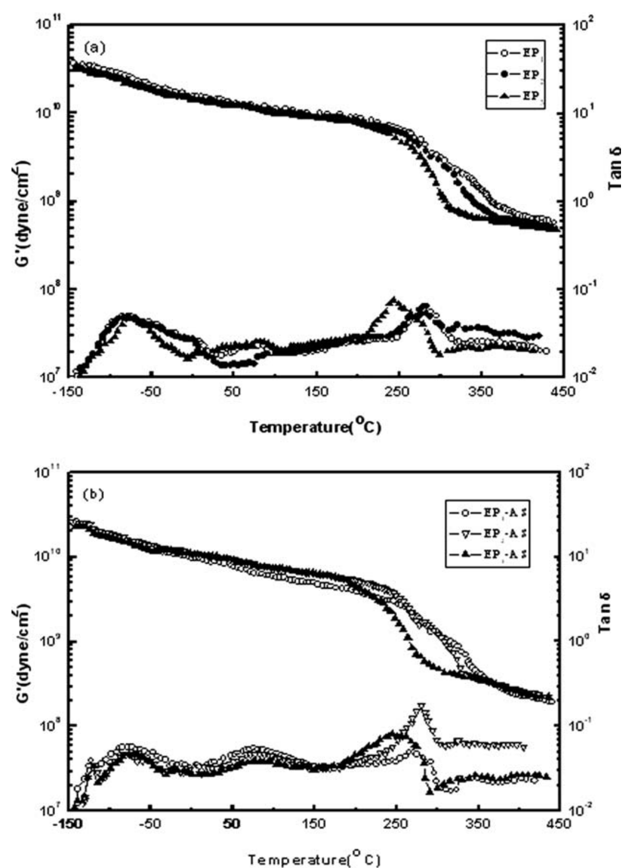


Figure 6 Dynamic viscoelastic analysis for the cured (a) neat EP and (b) EP-AS resins.

phases of silicone rubber.[14] Values of T_g and G' of cured EP and EP-AS resins are summarized in Table II. Based on the assumption of rubbery theory,[24,25] above T_g, G' is directly related to the crosslink density of the epoxy systems and can be represented as[26]

$$\chi = G'/RT, \tag{9}$$

where χ is the crosslinking density defined with numbers of crosslinked mole at unit volume and G' is the shear modulus at $T_g + 40°C$. Figure 6(a,b) showed that G' curves of EP or EP-AS resins display a clear rubbery plateau characteristics in the temperature range of 300–450°C. For a better comparison, the G' is taken here at 400°C, the χ of epoxy resins is thus obtained by eq. (9), which are listed in the Table II. It is observed from Table II, the EP_3 resin shows the lowest χ, while the EP_1 displays the highest. It means that the softer aliphatic group in backbone of epoxy resin provides a poor development of epoxy networks, leading to a lower crosslinking density. As compared to the EP resins, χ value of EP-AS resin is lower than that of neat EP resin, which is originated from the plasticization effect of the dispersed PMDS phase.

The relationship between cure kinetics and epoxy network

Despite that the viscoleastic technique can be used to clarify the effects of backbone structure and rubber-modified phase morphology on the cure characteristics of cured EP and EP-AS resins. It does not properly describe the developing of epoxy networks during cure. Based on the cure kinetic results, the inspection of all kinetic parameters (such as, E_a, α_m, A_1, A_2, m and n), the α_m seems more suitable as an index for describing the development of networks due to its directly monitoring the cure reaction and

TABLE II
Dynamic Vicoelastic Properties of Cured Epoxy Resin Systems

Sample	T_g (°C)[a] matrix	T_g (°C)[b] rubber	Shear modulus[c] ($\times 10^8$ dyne/cm^2)	χ ($\times 10^{-5}$ mole/cm^3)
EP_1	282	–	6.89	1.22
EP_2	279	–	5.86	1.08
EP_3	243	–	5.30	0.96
EP_1-AS	265	−120	3.14	0.56
EP_2-AS	270	−120	2.91	0.52
EP_3-AS	240	−119	2.69	0.48

[a] Peak of tan δ at higher temperature.[14]
[b] Peak of tan δ at lower temperature.[14]
[c] Obtained from RDA-II at 400°C.[14]

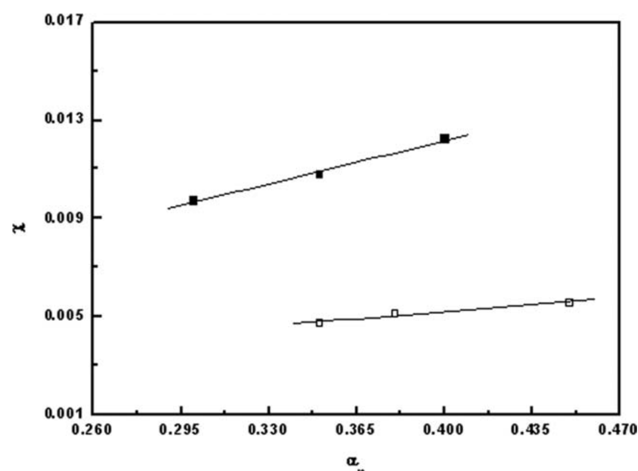


Figure 7 α_m vs. χ for (■) EP and (□) EP-AS resins.

the formation of networks during the course of cure. The relationship between α_m and χ for EP and EP-AS resins is shown in Figure 7. It can be seen that a good linear relationship between χ and α_m is observed, indicating the χ of EP or EP-**AS** resins increases with increasing α_m. This suggests that α_m increases with the depressing backbone flexibility, leading to better development of epoxy networks, the χ is hence increased. It demonstrates that the presence of a more flexible group in backbone of epoxy resin with lower α_m value can easily induce the occurrence of crosslinking, the M_c of epoxy networks is increased,[14,27] leading to the incompletely development of epoxy networks, the χ is hence depressed. As compared to the EP resins, the χ of EP-As resin is lower than that of EP resin due to the plasticization effect of PDMS. As for EP-AS resins, it is worthy of noting that the increasing tendency (slope) of α_m vs. χ is weaker than those of EP resins, suggesting the increase in crosslinking density depends on both the backbone structure and dispersed morphology. It demonstrates that the α_m can be effectively used as the precursor for describing the developing of epoxy networks during the course of cure.

CONCLUSIONS

The EP and their EP-AS resins obeyed the autocatalytic reaction mechanism and followed a reaction order of about 3. The softer aliphatic backbone of epoxy resin provided higher cure reactivity and stronger tendency towards autocatalysis; the crosslinking was being easier to occur, leading to the lower crosslinking density. The PDMS-modified epoxy resins showed higher initial cure reactivity due to the plasticization effect of the presence of the dispersed PDMS phase, after plasticization point, the developing of epoxy networks was apparently restricted by

the dispersed PDMS phase, the crosslinking density was hence depressed. In combination with cure kinetics and dynamic viscoelastic results, the α_m can effectively used as the precursor for describing the developing of epoxy networks during the course of cure.

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