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Thermal stabilities and dynamic mechanical properties of sulfone-containing epoxy resin cured with anhydride

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Abstract

A sulfone-containing epoxy resin, the diglycidylether of bisphenol-*S* (DGEBS), was obtained and its structure was confirmed by means of FT-IR, ^{1}H NMR, ^{13}C NMR spectra, and elemental analysis. Curing behaviours, thermal stabilities, and dynamic mechanical properties of the DGEBS resin cured with phthalic anhydride (PA) and tetrahydrophthalic anhydride (THPA) as curing agents were studied using dynamic differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), and dynamic mechanical analysis (DMA). The cure reaction of the DGEBS/anhydride systems was initiated at a relatively low temperature in the presence of tertiary amine. The DGEBS/THPA/DMBA system showed higher glass transition temperature, initial decomposition temperature, and activation energy for decomposition than those of the DGEBS/PA/DMBA system, which was attributed to the higher cross-linking density of the DGEBS/THPA/DMBA system.

Keywords: Synthesis; Bisphenol-*S*; Epoxy resin; Thermal properties; Glass transition temperature

1. Introduction

Epoxy resins, one of the most important thermosetting polymers, are currently used in advanced composites, coatings, structural adhesives, and microelectronics, due to their high stiffness, high strength, good chemical resistance, and dimensional stability [1,2]. However, the epoxy resins have major drawbacks of lack of toughness and their brittleness reduces many end-use applications.

Recently, many attempts have been used to improve the toughness of epoxy resins. Thus, various types of high-performance thermosetting resins, such as sulfone-containing epoxy, phosphorus-containing epoxy, polyimide-containing epoxy, and polyester-containing epoxy have been explored [3–6]. Among the thermosetting resins, the diglycidylether of bisphenol-*S* (DGEBS) containing a sulfone group in the backbone, exhibits excellent properties, e.g., good thermal stability, chemical resistance, mechanical properties, and so on [7,8].

Polymerisation of the epoxy resins to form cross-linked polymer can be accomplished by using curing agents, such as amines, carboxylic acid anhydrides, and thermally latent catalysts. The anhydride cured resins are preferred for electrical and electronic applications, due to their higher thermal stability and transparency [9,10].

In this study, the sulfone group-containing epoxy resin, diglycidylether of bisphenol-*S* (DGEBS), was synthesized and the chemical structure of the resin

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characterized by FT-IR, ^{1}H NMR, ^{13}C NMR, and elemental analysis. The thermal properties of both DGEBS/phthalic anhydride (PA) and DGEBS/tetrahydrophthalic anhydride (THPA) systems were investigated using dynamic differential scanning calorimetry (DSC), dynamic mechanical analysis (DMA), and thermogravimetric analysis (TGA) measurements.

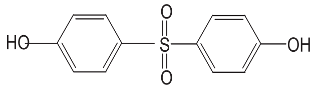
2. Experimental

2.1. Materials

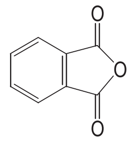
Bisphenol-*S* (BPS) was supplied by Aldrich. Epichlorohydrin (ECH), NaOH, and isobutyl methyl ketone (MIBK) were purchased from Junsei Chem. Phthalic anhydride (PA, Aldrich, equivalent weight 148 g eq^{-1}) and tetraphthalic anhydryde (THPA, Aldrich, equivalent weight 155 g eq^{-1}) were selected as curing agents and *N*,*N*-dimethylbenzylamine (DMBA, Aldrich Chem.) was used as accelerator. The chemical structures of the BPS, PA, and THPA are shown in Fig. 1.

2.2. Synthesis of the epoxy resin

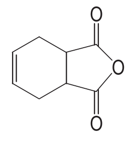
A solution of BPS (200.2 g, 0.8 mol), ECH (370.1 g, 4 mol), and 40% NaOH aqueous solution (80 g, 0.8 mol) were placed in a round, four-necked 1000 mL flask equipped with a mechanical stirrer, thermometer sensor, and reflux condenser. The mixtures were heated to 100 °C and reacted for 7 h. After the reaction was completed, the crude product was filtered and dissolved in MIBK. The mixture was stirred for 30 min and then filtered. Finally, the MIBK and ECH were removed in a vacuum oven at 100 °C. The obtained DGEBS epoxy resin was a viscous liquid, and yield was 80%. The epoxy equivalent weight (EEW) of the DGEBS epoxy resin was found to be 236 g eq^{-1}.



Bisphenol-S (BPS)



Phthalic anhydride (PA)



Tetraphthalic anhydride (THPA)

Fig. 1. Chemical structures of BPS, PA, and THPA.

IR (KBr): $\nu = 1295$ (SO$_2$ stretching), 3074 cm^{-1} (CH stretching), 1593 cm^{-1} (aromatic C=C), 1151 cm^{-1} (C–O stretching), 913 cm^{-1} (epoxide C–O–C).

^{1}H NMR (acetone-d_6): $\delta = 6.8-7.2$ (4H, aromatic ring), 2.67–2.86 (2H, epoxide CH–CH_2–O), 3.3 (m, 1H, epoxide CH–CH$_2$–O).

^{13}C NMR (acetone-d_6): $\delta = 163-115$ (aromatic ring), 68.7, 51.9, 43.9 (epoxide ring).

Elemental analysis: C, 55.74%; H, 5.30%; S, 7.75%.

2.3. Sample preparation

Epoxy resins were preheated to 100 °C for 30 min and then the stoichiometric amount of the curing agent and 1 wt% DMBA were added. The mixtures were fully stirred by a mechanical stirrer and then degassed in a vacuum oven to eliminate air bubbles before pouring into a mould. The mixtures were cured at 150 °C for 2 h and at 180 °C for 2 h in a convection oven.

2.4. Characterization and measurements

Fourier transform infrared (FT-IR) spectra were recorded with a Digilab FTS-165 spectrometer (Bio-Rad Co.) by using KBr pellets. ^{1}H NMR and ^{13}C NMR spectra were performed on a DRX300 spectrometer (BRUKER Co.) operation at 300 MHz using acetone-d_6 as a solvent. Elemental Analyser (CE EA-1110) was used for elemental analyses (C, H, O) of the epoxy resin. The EEW of the epoxy resin was determined by the pyridinium chloride titration method.

The cure behaviours of the epoxy resin were investigated with a differential scanning calorimeter (Perkin Elmer, DSC6) in the temperature range from 30 to 300 °C under a nitrogen flow of 30 mL min^{-1}.

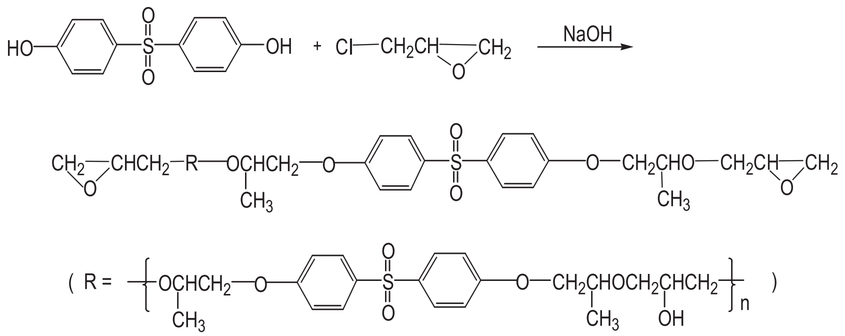
Glass transition temperature and storage modulus were measured by using a dynamic mechanical analyser (RDS-II, Rheometrics Co.) at a frequency of 1 Hz and a temperature range from 30 to 250 °C at a scan rate of 5 °C min^{-1}.

Thermogravimetric analysis (TGA) was performed with a DuPont TGA-2950 analyser to investigate the thermal stabilities of the cured epoxy specimens from 30 to 850 °C at a heating rate of 10 °C min^{-1} in a nitrogen atmosphere.

3. Results and discussion

3.1. Synthesis of the epoxy resin

The sulfone-containing epoxy resin, the diglycidylether of bisphenol-*S* (DGEBS), was obtained by



Scheme 1. Synthetic route for the DGEBS epoxy resin.

alkaline condensation of BPS with ECH using NaOH as catalyst at 100 °C for 7 h. The synthetic route for the DGEBS epoxy resin is shown in Scheme 1. The structure of the synthesized resin was characterized by means of FT-IR, ^{1}H NMR, ^{13}C NMR spectra, and elemental analysis.

Fig. 2 shows the IR spectrum of the resulting DGEBS epoxy resin, which are characterized by absorption band of the sulfone groups ($-SO_2-$) at 1295 cm^{-1}. The characteristic absorption band at 913 cm^{-1} is attributed to the epoxide ring. And both bands at 3074 and 1593 cm^{-1} show the aromatic ring [11].

For ^{1}H NMR spectra (acetone-d_6), the corresponding proton signals at 6.8–7.2 are due to the aromatic ring and the chemical shift at 2.67–3.3 ppm corresponds to the protons of the epoxide groups. For ^{13}C NMR spectrum (acetone-d_6), chemical shift at 163–115 ppm belongs to the aromatic ring and chemical shift at 68.7, 51.9, and 43.9 ppm corresponds to the epoxide groups [12].

For elemental analysis: Calculated for $(C_{20}H_{25}O_7S)_n$: C, 58.68%; H, 6.11%; S, 7.82%. Found: C, 55.74%; H, 5.30%; S, 7.75%. FT-IR, ^{1}H NMR, ^{13}C NMR spectra, and elemental analysis clearly confirmed the chemical structure of the DGEBS epoxy resin.

3.2. Cure behaviours

The cure behaviours of the DGEBS epoxy resin cured with phthalic anhydride (PA) and tetrahydrophthalic anhydride (THPA) as curing agents and DMBA as accelerator were evaluated using DSC. Fig. 3 shows typical DSC thermograms of the DGEBS/anhydride systems at a heating rate of 10 °C min^{-1}. These thermograms provide information for determining the condition of cure reactions. Fractional conversion as a function of temperature for DGEBS/anhydride systems from the DSC thermograms is shown in Fig. 4. Curing characteristics, such as temperature of cure initiation, peak maximum temperature, final cure temperature, and enthalpy of cure reaction (ΔH), of the DGEBS/anhydride systems are summarized in Table 1. The ΔH values obtained by the integration of areas under the curve, indicate that the reaction enthalpies of

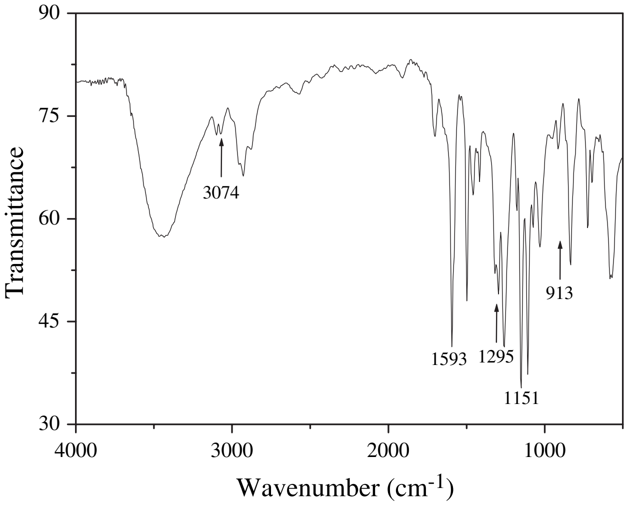


Fig. 2. FT-IR spectra of the DGEBS epoxy resin.

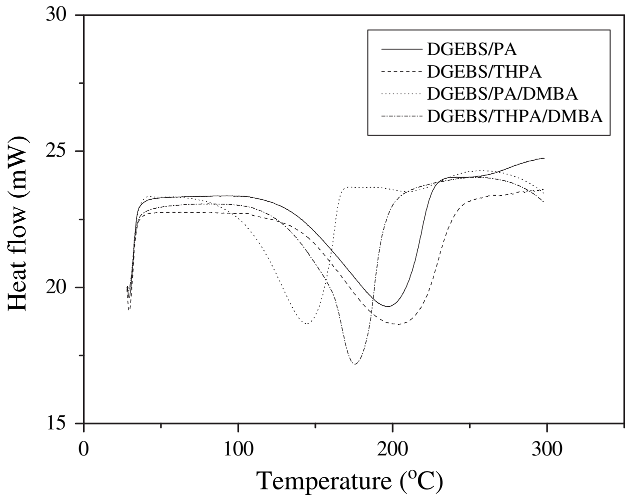


Fig. 3. Dynamic DSC thermograms of the DGEBS/anhydride systems.

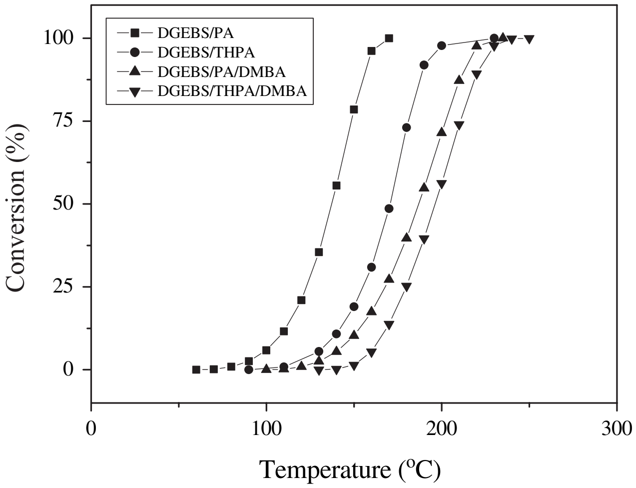
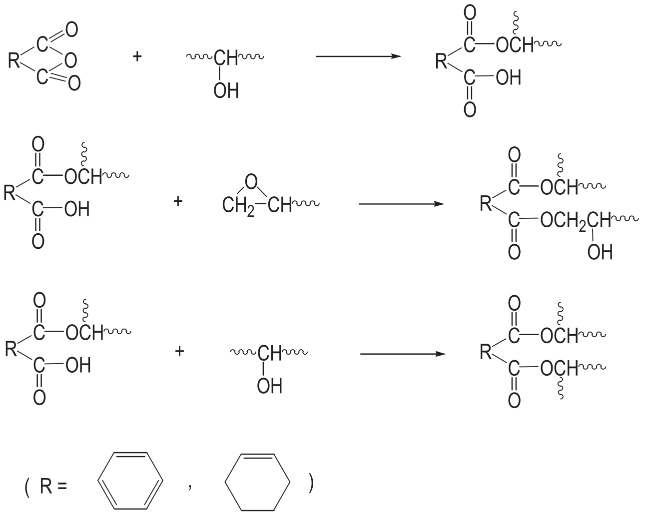


Fig. 4. Conversion vs. temperature of the DGEBS/anhydride systems.



Scheme 2. Cure reaction mechanism of the anhydride and epoxide.

DGEBS/PA, DGEBS/THPA, DGEBS/PA/DMBA, and DGEBS/THPA/DMBA systems are 118, 132, 102, 123 J g^{-1}, respectively.

From Table 1, it is clear that the cure reaction of the DGEBS/anhydride systems is carried out at relative low temperature in the presence of tertiary amine. This result can be explained by the cure mechanism between the epoxy and the anhydride. Scheme 2 shows the cure reaction mechanism of the epoxide with anhydride. Anhydride reacts first with the secondary hydroxyl groups of the resins to produce monoester, and then the newly formed carboxyl groups react with the epoxide groups to give a diester. In contrast, the reaction catalysed by tertiary amines is initiated by the activation of the anhydride with amine, as shown in Scheme 3. Thus, the cure reaction is initiated at relative low temperature in the presence of tertiary amine [13]. The DSC result also indicates that the maximum temperature and ΔH of the DGEBS/THPA system are higher than those of the DGEBS/PA system. Thus, it is expected that the DGEBS/THPA system can lead to an excellent network structure [14].

Table 1
DSC thermogram data of the DGEBS/anhydride systems (heating rate: 10 °C min^{-1})

System	Initiation of cure temperature (°C)	Peak maximum temperature (°C)	Final cure temperature (°C)	ΔH (J g^{-1})
DGEBS/PA	110	196	235	118
DGEBS/THPA	140	203	250	131
DGEBS/PA/DMBA	70	144	170	102
DGEBS/THPA/DMBA	100	176	230	123

3.3. Dynamic mechanical properties

One of the most important characteristics of the amorphous state is the behaviour of a polymer during its transition from solid to liquid [15]. The tan δ and storage modulus of the cured DGEBS/anhydride/DMBA specimens were measured in a wide temperature range 30–250 °C at a heating rate of 5 °C min^{-1}, as shown in Fig. 5. From the results, the DGEBS/THPA/DMBA system shows a relatively higher glass transition temperature and storage modulus than those of the DGEBS/PA/DMBA system.

The cross-linking density (ρ) of the cured specimens was calculated from the equilibrium storage modulus in the rubber region over the α-relaxation temperature according to the rubber elasticity theory [16], as follows:

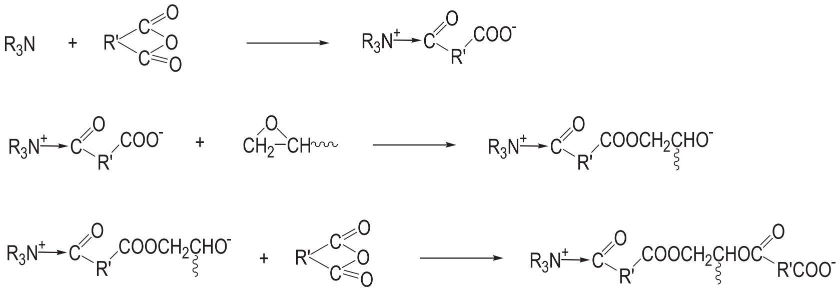
$$\rho = G'/\phi \mathrm{R} T \qquad (1)$$

where T_α is the α-relaxation temperature, G' the storage modulus at $T_\alpha + 30$ °C, ϕ the front factor, R the gas constant, and T the absolute temperature at $T_\alpha + 30$ °C.

The obtained glass transition temperature (T_g), storage modulus (G'), and cross-linking density (ρ) are summarized in Table 2. The results indicate that the ρ of cured DGEBS/PA/DMBA and DGEBS/THPA/DMBA specimens is 0.32×10^{-3} and 0.42×10^{-3} mol cm^{-3}, respectively. Differences in cross-linking density of the cured resins can be attributed to the different activities of the anhydride.

3.4. Thermal stabilities

TGA traces of the cured epoxy samples provide their thermal stability and thermal degradation behaviours. Fig. 6 shows the TGA thermograms of the cured



Scheme 3. Cure reaction mechanism of the anhydride and epoxide in the presence of tertiary amine.

DGEBS/anhydride/DMBA systems in a nitrogen atmosphere. The degradation of the anhydride cured DGEBS epoxy resin exhibits a two-stage process. A relatively short stage of two cured systems with 5% weight loss is happened at 294 and 324 °C, respectively, which is attributed to the breaking of unreacted epoxy or other impurity traces apart from the cured DGEBS. Above 410 °C, the main process is a much higher thermal-resistance stage, and this is caused by thermal degradation of the cured DGEBS network [17].

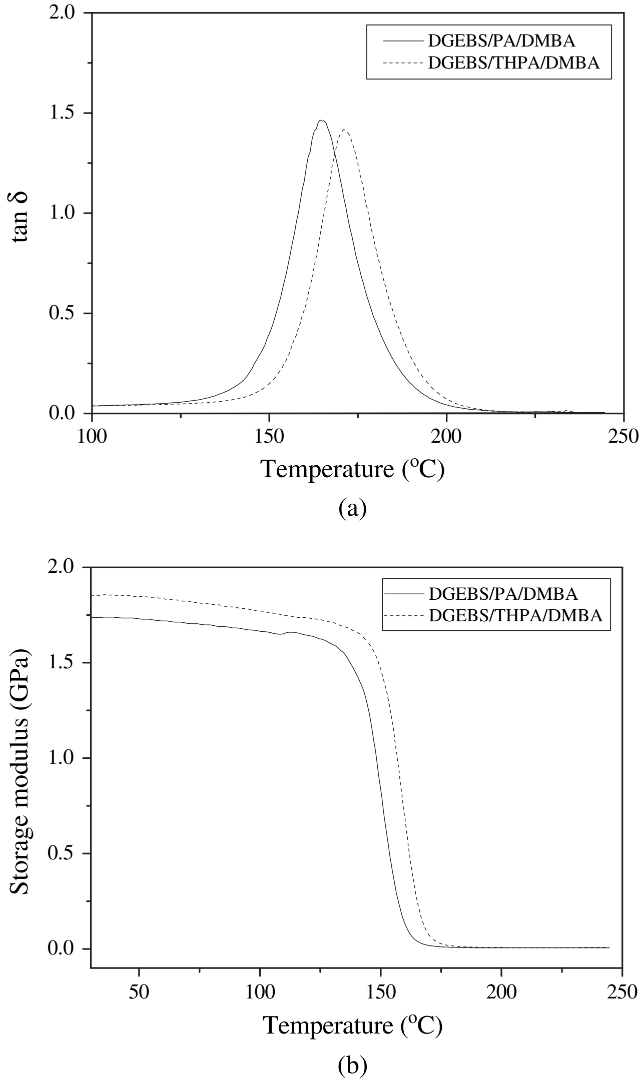


Fig. 5. The tan δ (a) and storage modulus of the DGEBS/anhydride/DMBA systems (b) as a function of temperature.

Generally, it is accepted that the reliable degradation temperature and kinetic parameters, such as the initial decomposed temperature (IDT), the temperatures of the maximum rate of degradation (T_{max}), and the activation energies for decomposition (E_t), can be used to assess a material's lifetime [18,19]. The obtained IDT and T_{max} values are summarized in Table 3. The DGEBS/THPA/DMBA system shows higher IDT than that of the DGEBS/PA/DMBA system, which can be attributed to the relative high cross-linking density of the DGEBS/THPA system [20].

The activation energy for decomposition of the cured resin was calculated from the TGA curves by the integral method of Horowitz and Metzger according to the following equation [21].

$$\ln[\ln(1-\alpha)^{-1}] = \frac{E_t\theta}{RT_{max}^2} \tag{2}$$

where α is the decomposed fraction, T_{max} the temperature at the maximum rate of weight loss, $\theta = T - T_{max}$, and R the gas constant.

The plots of $\ln[\ln(1-\alpha)^{-1}]$ vs. θ are shown in Fig. 7. The E_t of the systems were calculated from the slope of the straight lines using Eq. (1) and listed in Table 3. The E_t of the DGEBS/PA/DMBA and DGEBS/THPA/DMBA systems is 96 and 130 kJ/mol, respectively. This result can be attributed to the higher cross-linking

Table 2
Dynamic mechanical analysis of the cured DGEBS/anhydride/DMBA systems

System	T_g (°C)	Storage modulus (GPa)		ρ (10^{-3} mol cm^{-3})
		Glassy region[a]	Rubbery region[b]	
DGEBS/PA/DMBA	164	1.74	0.006	0.32
DGEBS/THPA/DMBA	171	1.85	0.008	0.42

[a] Storage modulus at 30 °C.
[b] Storage modulus at T_g + 30 °C.

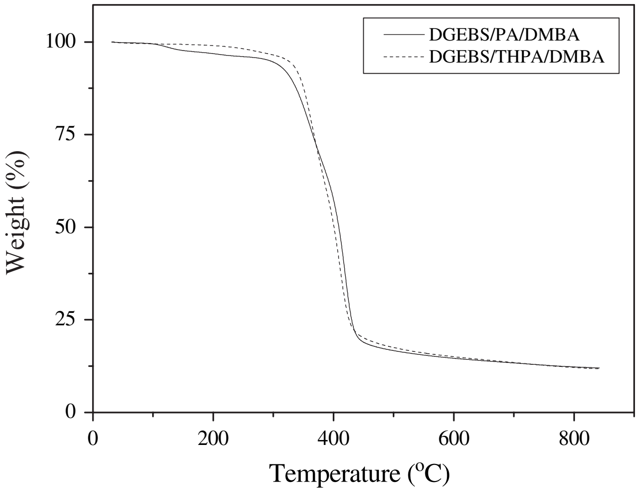


Fig. 6. TGA thermograms of the DGEBS/anhydride/DMBA systems.

Table 3
Thermal properties of the cured DGEBS/anhydride/DMBA systems

System	IDT (°C)	T_{max} (°C)	E_t (kJ/mol)	Char (%)[a]
DGEBS/PA/DMBA	294	415	96	13.4
DGEBS/THPA/DMBA	324	413	130	13.5

[a] Char at 700 °C.

density in the DGEBS/THPA/DMBA system, as mentioned in the result of IDT [20]. The char yields of the DGEBS/PA/DMBA and DGEBS/THPA/DMBA systems at 700 °C are 13.4 and 13.5%, respectively. The relative high char yields can be attributed to the sulfone linkage in the epoxy resin, which may provide the better thermal stability in the degradation of the cured DGEBS/anhydride systems.

4. Conclusions

In this work, a sulfone-containing epoxy resin was obtained and characterized in terms of the cure behaviours, the glass transition temperatures, and thermal stabilities. The network structure of the DGEBS/THPA/DMBA system was formed at relatively higher temperature than that of the DGEBS/PA/DMBA system and the DGEBS/THPA/DMBA system showed better thermal properties, including glass transition temperature, initial decomposition temperature, and activation energy for decomposition than those of the DGEBS/PA/DMBA system. This could be attributed to the higher cross-linking density of the DGEBS/THPA/DMBA system.

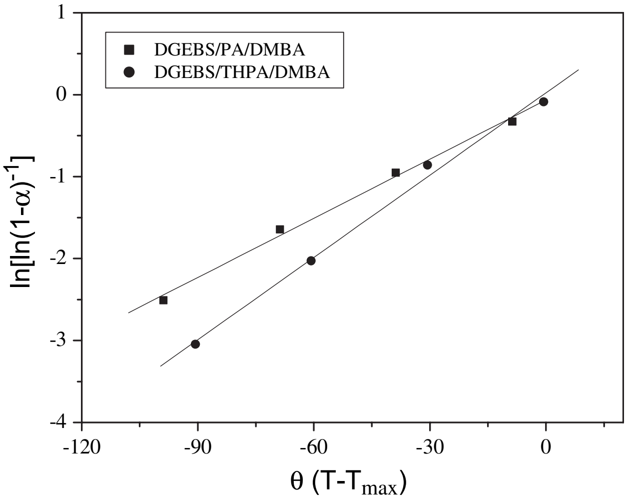


Fig. 7. Plots of $\ln[\ln(1-\alpha)^{-1}]$ vs. θ for the DGEBS/anhydride/DMBA systems.

References

[1] May CA. Epoxy resins, chemistry and technology. New York: Marcel Dekker; 1988 p. 1.
[2] Park SJ, Jin FL, Lee JR. Mater Sci Eng A 2004;374:109.
[3] Grubbs RB, Dean JM, Bates FS. Macromolecules 2001;34:8593.
[4] Wang CS, Lin CH. J Polym Sci Polym Chem 1999;37:3903.
[5] Zuo M, Takeichi T. J Polym Sci Polym Chem 1997;35:3745.
[6] Fomine S, Posada I, Ogawa T. Macromol Chem Phys 1995;196:3723.
[7] Li YF, Shen SG, Liu YF, Gao JG. J Appl Polym Sci 1999;73:1799.
[8] Lin JF, Ho CF, Huang SK. Polym Degrad Stab 2000;67:137.
[9] Guerrero P, De Caba K, Valea A, Corcuera MA, Mondragon I. Polymer 1996;37:2195.
[10] Hakala K, Vatanparast R, Li SY, Peinado C, Bosch P, Catalina F, et al. Macromolecules 2000;33:5954.
[11] Parekh JK, Patel RG. Angew Makromol Chem 1995;227:1.
[12] Liaw DJ, Shen WC. Angew Makromol Chem 1992;199:171.
[13] Matějka L, Lövy J, Pokorný S, Bouchal K, Dušek K. J Polym Sci Polym Chem Ed 1983;21:2873.
[14] Park SJ, Kim TJ, Lee JR. J Polym Sci Polym Phys 2000;38:2114.
[15] Stevens MP. Polymer chemistry. New York: Oxford University Press; 1999 p. 70.
[16] Iijima T, Yoshioka N, Tomoi M. Eur Polym J 1992;28:573.
[17] Liu YL, Wu CS, Chiu YS, Ho WH. J Polym Sci Polym Chem 2003;41:2354.
[18] Park SJ, Kim HC, Lee HL, Suh DH. Macromolecules 2001;34:7573.
[19] Park SJ, Jin FL, Lee JR. Macromol Rapid Commun 2004;25:724.
[20] Park SJ, Seo MK, Lee JR, Lee DR. J Polym Sci Polym Chem 2001;39:187.
[21] Horowitz HH, Metzger G. Anal Chem 1963;35:1464.