

Cure Kinetics and Properties of Blends of Epoxy Resins with Polyethersulfone

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Abstract

In this article, polyethersulfone and flourene-coating epoxy resin were utilized to modify both the toughness and the mechanical properties of traditional epoxy resins. The cure kinetics and the thermal stability of the resulted blends were tested by differential scanning calorimetry technology and thermogravimetric analysis, respectively. Additionally, the mechanical properties of resulted thermosets were discussed after tested by Dynamic Thermomechanical Analyzer. When compared to the traditional epoxides, the obtained blends exhibit much better heat resistance, thermal stability and mechanical properties.

Keywords: *Epoxy resins, mechanical properties, curing behavior*

I. Introduction

Epoxy resins are attractive thermosets because of their excellent properties, for example, high mechanical properties and good insulation performance. Thus, they are widely used in forming copper clad laminate, producing molded product, and taking as the matrix resin for advanced composite materials and so on. However, the brittleness has limited their applications in forming films. Nowadays, many engineering thermoplastics are preferable materials as modifiers due to their high modulus, good toughness, and better heat resistance. A series of high-ductile thermoplastics, for example, poly (ether ether ketone), polysulfone and polyethersulfone, have been utilized in modification of epoxy resins [1-5].

Recently, a novel high performance epoxide, diglycidyl ether of 9, 9-bis (4-hydroxyphenyl)-flourene (DFE) has drawn a widely public attention since the incorporation of fluorene moieties endow its cured resin many excellent properties, for example, high thermal stability and good moisture resistance. According to the literature, DFE was obtained by 9, 9-bis (4-hydroxyphenyl)-flourene and chloroepoxy propane with the addition of sodium hydroxide [6]. However, the superiority compared to conventional resins can't cater to all the needs of high-performance resins and the high cost of raw materials has restricted the use of DFE.

In order to obtain a series of high performance thermosets, both polysulfone and DFE were used as modifiers to improve the properties to traditional epoxy (E-51) in this article. The curing behavior, cure kinetics, thermal and mechanical properties of the resulted epoxides were also discussed.

II. Experimental

2.1 Materials

The DFE with an epoxy value of 0.40 and a melting point of 133-135 °C was synthesized by 9, 9-bis (4-hydroxyphenyl)-fluorene and chloroepoxy propane as reported [6]. The engineering plastic, polyethersulfone (PES) was used as one of the modifiers. The structures of PES and DFE were shown in Figure 1. In addition, 4, 4'-diamino-diphenyl-sulfone (DDS) was taking as curing agent. In this paper, PES, DDS, E-51 and other reagents and solvents were purchased from Aladdin Company and used without further purification.

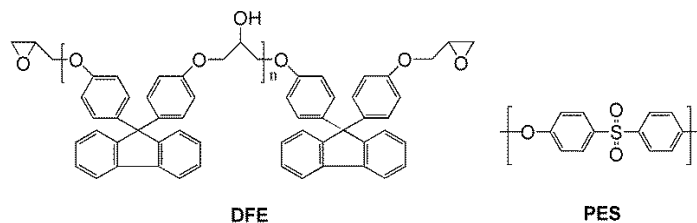


Figure 1: The structures of DFE and PES

2.2 Blend preparation

The mixtures were blending on a melting-point apparatus. Due to the melting point of DFE is 132 °C, the pure DFE mixed with PES is hard to operate with a high mixing temperature of 220 °C. Some paper advanced to use methylene dichloride to dissolve resin and curing agent, but the solvent cannot be lustrated in the vacuum since the film above the surface which is formed by the mixture can prevent methylene dichloride evaporating. In this study, E-51, DFE, PES and DDS were blending together at 160 °C with a constant stirring since the traditional epoxy resin can depress the mixed temperature. The mixtures were transparent and uniform without phase separation. The obtained samples were listed in Table 1.

Table 1. The formulation of samples

Samples	DFE	E-51	PES
A0	100	0	0
A1	100	0	10
A2	80	20	10
A3	60	40	10
A4	40	60	10

2.3 Characterizations

Differential scanning calorimetry technology (DSC, TA Q200), differential scanning calorimetry technology (DMA, TA Q50) and thermogravimetric analysis (TGA, TA Q50) were used to discuss the curing behavior, cure kinetics, thermal and mechanical performance of resulted epoxy blends.

III. Results and Discussion

3.1 Melting temperature

The result is showed in Table 2.

Table 2. The relationship between mixed temperature and content of E-51

Sample Name	Mixed tempetature/°C
DFE/DDS	180
DFE/PES ₁₀ /DDS	220
DFE ₈₀ E-51 ₂₀ /PES ₁₀ /DDS	180
DFE ₆₀ E-51 ₄₀ /PES ₁₀ /DDS	150

From the Table 2, we can obtain that E-51 can drastically decrease the mixed temperature. The reason can be explained that E-51 is a liquid resin and it can solve DFE and PES acutely. Whereas, the mixed temperature reduce was at the expense of increase in the E-51 content. In addition, the mixed temperature do not greatly reduced any more when the E-51 content rise to 60 wt%.

3.2 DSC studies

Dynamic non-isothermal DSC studies were done for the DFE +PES+DDS mixture with various heating rates of 20, 15, 10 and 5 °C /min. The obtained curves are exhibited in Figure 2. From Figure 2, we can find that the peak temperature decreased as the heating rate lowered. In addition, the curing temperature from the DSC curves of the samples can be deduced. The curing temperature of mixtures was 150°C/1h+190 °C/2h+240°C/1h.

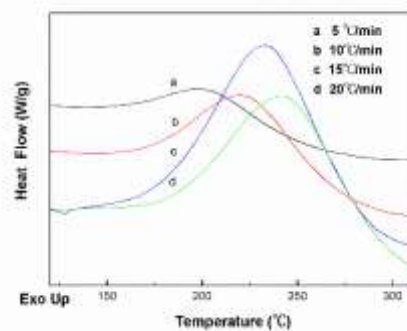


Figure 2: Dynamic non-isothermal DSC curves

As reported, the curing reactions reflected the apparent activation energy ΔE was deduced by the Kissinger equation [5].

$$\frac{d[\ln(\beta / T_p^2)]}{d[1/T_p]} = -\frac{\Delta E}{R} \quad (1)$$

β : the heating rate (°C/min);

ΔE : the apparent activation energy (kJ/mol);

T_p : the peak temperature (K);

R : a gas constant, 8.1314 J/mol·K.

According to the different heating rate of value from $\ln(\beta/T_p^2)$ against $1/T_p$ plot for samples A0~A4, some straight lines can be obtained. What's more, the slopes of these curves were concluded to calculate ΔE .

The reaction order of curing chemical reaction can be deduced from Crane equation.

$$\Delta \ln \beta / \Delta \left(\frac{1}{T_p} \right) = - \left(\frac{\Delta E}{nR} + 2T_p \right) \quad (2)$$

$$\frac{\Delta E}{nR} \gg 2T_p$$

$$\Delta \ln \beta / \Delta \left(\frac{1}{T_p} \right) = - \left(\frac{\Delta E}{nR} + 2T_p \right) \approx - \frac{\Delta E}{nR} \quad (3)$$

The calculated kinetic parameters were summarized in Table 3. The results show that ΔE increased about $1\text{kJ}\cdot\text{mol}^{-1}$, and the reaction order of curing chemical reaction n is about 0.9.

Table 3 The calculated kinetic parameters

Sample NO.	$-\ln\beta/T_p^2 - 1/T_p$	$\Delta E/\text{kJ}\cdot\text{mol}^{-1}$	$\ln\beta - 1/T_p$	n	Kinetic equation
A0	7.049	58.605	-8.059	0.875	$-\frac{d\alpha}{dt} = \kappa(1-\alpha)^{0.875}$
A1	7.159	59.520	-8.149	0.879	$-\frac{d\alpha}{dt} = \kappa(1-\alpha)^{0.879}$
A2	9.975	82.932	-10.988	0.908	$-\frac{d\alpha}{dt} = \kappa(1-\alpha)^{0.879}$
A3	8.462	70.353	-9.479	0.893	$-\frac{d\alpha}{dt} = \kappa(1-\alpha)^{0.879}$
A4	7.685	63.893	-8.681	0.885	$-\frac{d\alpha}{dt} = \kappa(1-\alpha)^{0.879}$

3.3. Dynamic mechanical thermal analysis studies

The heat resistance and mechanical properties were tested by DMA. The $\tan\delta$ versus temperature plots are shown in Figure 3(b). From Figure 3(b), we can see only one $\tan\delta$ peak appears at 200~300 °C, meaning that there was no phase separation occurs in the mixture. In addition, the glass transition temperature (T_g) of mixtures hold the line of 260 °C with the increase of PES, which means that the addition of PES has little influence on the heat resistance of obtained resins.

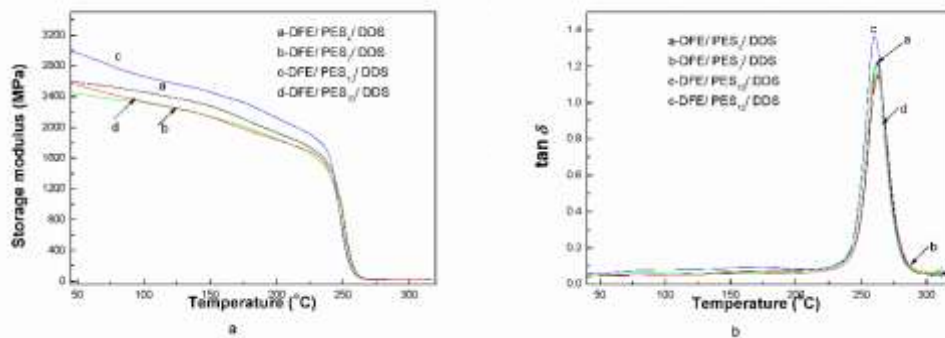


Figure 3: a: Storage modulus versus temperature plot for 4, 7, 10, 13wt% PES modified neat DFE
b: $\tan\delta$ versus temperature plot for 4, 7, 10, 13wt% PES modified neat DFE

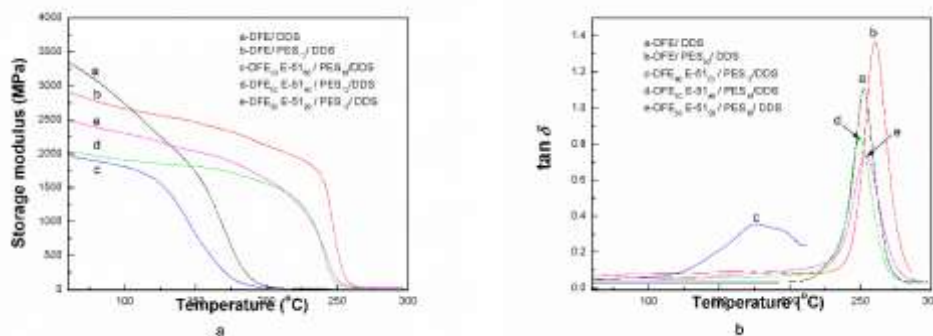


Figure 4: a: Storage modulus versus temperature plot for neat resin, content of 0,20,40,60 wt% E-51 cured with DDS
b: $Tan\delta$ versus temperature plot for neat resin, content of 0,20,40,60 wt% E-51 cured with DDS

When the E-51 added in 20, 40 wt%, the T_g cut down about 10 °C, compared to neat DFE mixed PES. And it did not lower than nonmodified resin. But it had an enormous loss when the content of E-51 reached to 60 wt%. All of it can achieve visually from Fig 4(b).

The storage modulus of resin matrixes decrease, compared to neat DFE cured with DDS. From Fig 3(a), the relationship between the storage modulus and content of PES is without rules. But the downtrend of it is in a line. The storage modulus of resin matrix mixed with E-51 appeared excellent rules. From Fig 4(a), we can obtained that the neat resin cured with DDS is maximum. The storage modulus decrease with the content of E-51 increased.

3.4 Thermogravimetry analysis studies

In order to investigated the heat resistance of mixture, we carried out the experiment in four heat rate (5, 10, 15, 20 °C/min), the results showed in Fig 5(a). The formulation of thermal degradation has been discussed in the paper of Sunnan Tiptakorn [7] and the thermal degradation energy of mixture was calculated by the Kissinger method.

From Kissinger method, Eq. (4) is used to determine the thermal degradation energy of solid state reactions.

$$\ln\left(\frac{\beta}{T_p^2}\right) = \ln\left(\frac{AR}{Ea}\right) + \ln[n(1-\alpha_p)^{n-1}] - \frac{Ea}{RT_p} \quad (4)$$

Where T_p is the absolute temperature, α_p is the weight loss at maximum weight-loss rate $(da/dt)_p$, and n is the reaction order, respectively.

From the slope of the straight line $\ln(\beta/T_p^2)$ divided $1/T_p$, the thermal degradation energy can be obtained. The data were summarized in Table 4. The thermal degradation energy (E_a) reached to 141.18 kJ/mol. It has preferable thermal stability.

Table 4. Thermal degradation data of 10wt% PES modified DFE cured with DDS

$\beta/^\circ\text{C}\cdot\text{min}^{-1}$	T_p/K	$\alpha_p/\text{g}\cdot\text{min}^{-1}$	$\ln(\beta/T_p^2)$	$1000/T_p$	$E_a/\text{kJ}\cdot\text{mol}^{-1}$
5	652.247	61.571	-11.351	1.533	141.18
10	667.905	33.321	-10.706	1.499	
15	676.042	22.446	-10.324	1.479	
20	686.941	18.071	-10.069	1.456	

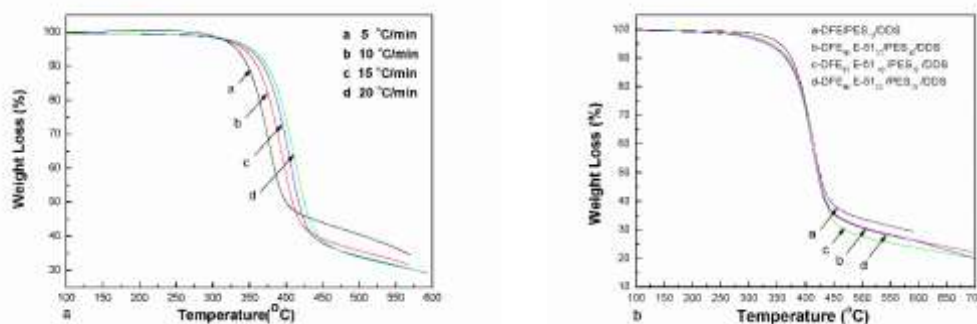


Figure 5: a: TGA thermograms of 10wt% PES modified with DFE at different heat rate.
b: TGA thermograms of the relationship between the content of E-51 and the anaerobic char yields.

The results of added E-51 was showed in Fig 5(b). The anaerobic char yields at 580 °C have little decline with the increase of E-51. But the extent is not obviously when the content reached to 60 wt%.

IV. Conclusion

In the blending systems of PES modified DFE cured with DDS, the content of PES has little effect to the T_g . And neat DFE blended with PES is hard to operating, the mixture temperature as high as 220 °C. With E-51 adding, it has acutely decline. When added about 40 wt% E-51, the operation temperature cut down about 70 °C. But the T_g only declined about 2.5 °C, compared with neat resin.

Acknowledgements

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