

Thermal properties of a series of liquid crystal epoxy resins modified with PES

Tiantian Feng¹, Xin Li^{2,*}

¹ Faculty of Intelligent Manufacturing Engineering, Guangdong Baiyun University, Guangzhou, Guangdong, China

² College of Architecture and Engineering, Guangdong Baiyun University, Guangzhou, Guangdong, China

Abstract. Polyether sulfone (PES) was mixed into liquid crystal epoxy resin (LCER) in order to improve the thermal performance and reduce the cost of curing epoxy resin. The thermal effects of the obtained composites during curing were studied by differential scanning calorimetry (DSC), and their thermal stability was evaluated by thermogravimetric analysis (TGA). The dynamic mechanical properties were measured by dynamic thermodynamics analyzer (DMA). The addition of 10 wt% PES resulted in a significant increase in glass transition temperature (T_g) of approximately 50°C compared to the unmodified liquid crystal epoxy resin. At the same time, the addition of cheap, high-performance commercial resin E-44 to the resin matrix significantly reduces costs at the expense of reducing thermal performance.

1. Introduction

The diglycidyl ether of 9,9-bis(4-hydroxyphenyl)-fluorene (LCER) was synthesized from 4,4'-di(2,3-epoxyhexyloxy) biphenyl and 3-chloroperoxybenzoic acid in the presence of dichloromethane [1]. The addition of liquid crystal units makes LCER have the advantages of high thermal stability and excellent thermal conductivity [2-11]. Therefore, LCER is widely used in the formation of interlayer insulating films, the production of molded products, and the adhesive component of anti-flux in the manufacture of printed circuit boards. However, although LCER has advantages over conventional resins, it may not fully meet the requirements of high-performance resins, thus limiting its application. Therefore, modified LCER is the key to obtain epoxides with better performance. Engineering thermoplastics are attractive modifiers for epoxy resins due to their good toughness, high modulus, and enhanced heat resistance. In recent years, various types of high ductility thermoplastics have been used to modify epoxy resins, such as polysulfone (PSF), polyether ether ketone (PEEK), and polyether sulfone (PES)[8]. In this paper, PES was used as modifier to improve the thermal properties of 4,4'-diamino-diphenyl sulfone (DDS) cured LCER. In addition, a cost-effective and high-performance commercial resin E-44 was added to the liquid crystal epoxy resin matrix to reduce the overall cost. The effects of PES and E-44 on the thermal stability and heat resistance of cured epoxy resin were also investigated.

2. Experimental

2.1. Materials

The LCER was prepared in accordance with the procedure proposed by Zhang[1]. The engineering plastic, Poly(oxy-1,4-phenylenesulfonyl-1,4-phenylene) (PES, (C₁₂H₈O₃S)_n), was utilized as a modifier. The structural representation is provided below. Their chemical structure are depicted in Fig.1. In addition, the polyethersulfone (PES), 4,4'-diamino-diphenyl-sulfone (DDS), and other chemical reagents were purchased from commercial sources and utilized without any additional purification in this study.

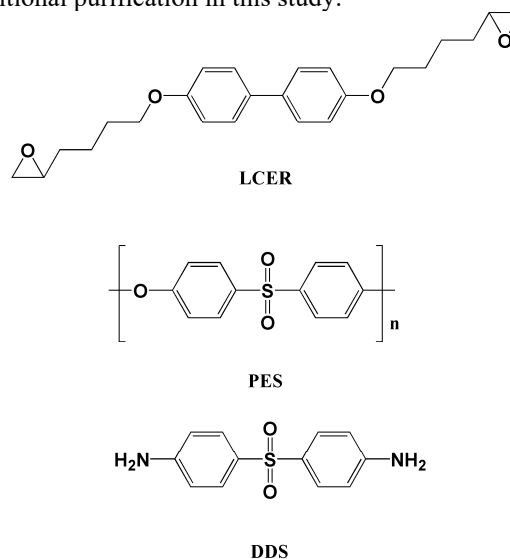


Fig. 1. The chemical structure of LCER, PES and DDS

* Corresponding author: lixin@baiyunu.edu.cn

2.2. Blending preparation

The PES was carefully incorporated into the LCER at 120 °C while maintaining constant stirring. To minimize any premature curing reaction during mixing, the curing agent was swiftly dissolved in the blend at 120 °C within a time frame of less than 40 seconds. Meanwhile, the high cost restricts the practical application of LCER. Therefore, we introduced common resins as additives to address this issue. In this study, E-44 resin was selected specifically for lowering the required mixing temperature. The formulation details of samples are provided in Table 1. According to the literature, LCER was cured with DDS at 160 °C for 4 h and 195 °C for 1 h.

Table 1. The formulation details of samples

Samples	LCER	PES	E-44
LCER	100	0	0
LCES1	100	10	0
LCES2	80	10	20
LCES3	60	10	40
LCES4	40	10	60

3. Results and discussion

3.1. DSC study of LCES

A power-compensated differential scanning calorimeter (DSC, TA Instruments Q200) was employed for conducting dynamic non-isothermal DSC measurements. Prior to commencing the experiments, the instrument underwent calibration using indium, tin, and benzophenone standards [3]. Nitrogen gas was used as the purge gas while samples weighing 4-8 mg were utilized for the measurements. Dynamic DSC measurements were performed on the LCER + PES + DDS mixture at heating rates of 20, 15, 10, and 5 °C/min. The resulting dynamic heating curves obtained at different heating rates are presented in Figure 1. It was observed that a decrease in heating rate resulted in a shift of the peak maximum towards lower temperatures. By analyzing the DSC curves of the samples, we can extrapolate their curing temperature which was determined as follows: 120 °C/1h+160 °C/2h+190 °C/1h.

3.2. DMA study of LCES

No visual evidence of phase separation was observed, as all mixtures exhibited transparency. The temperature-dependent $\tan\delta$ plots are presented in Fig.3b. As depicted in Fig.3b, following the addition and curing of PES, only one peak is evident at high temperatures, corresponding to the epoxy-rich phase. This behavior does not provide any indication of phase separation, suggesting a potential miscibility between the cured matrix and the modifier. When E-44 was added at 20% and 40% by weight, the T_g decreased by approximately 10 °C compared to neat LCER mixed with PES; however, it did not decrease

below that of the unmodified resin. A significant reduction in T_g was observed when the content of E-44 reached 60 wt%. These observations can be visually confirmed from Fig.3b. The storage moduli of resin matrices decreased compared to neat LCER cured with DDS. From Fig.2a, there appears to be no clear relationship between storage modulus and PES content; however, a general decreasing trend can be observed. On the other hand, excellent trends were observed for storage modulus when E-44 was incorporated into the resin matrix Fig.3a. Neat resin cured with DDS exhibited maximum storage modulus values which decreased as E-44 content increased.

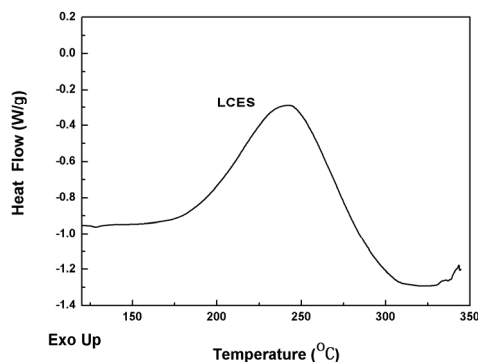
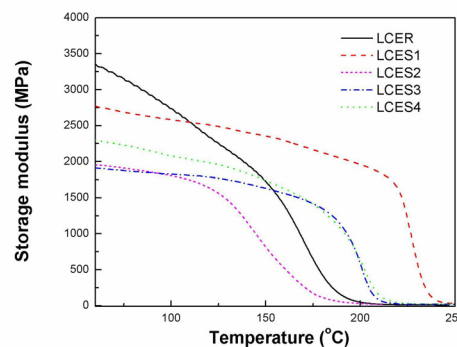
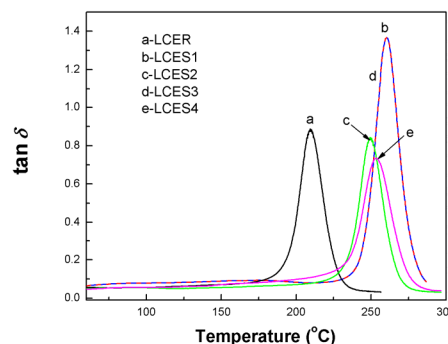


Fig. 2. Dynamic DSC curve of LCER



(a)



(b)

Fig. 3. a. Storage modulus curves of LCER and LCES
b. $\tan\delta$ curves of LCER and LCES

3.3. TGA study of LCES

In order to investigate the thermal stability of LCES, thermo gravimetry analysis were tested at four different

heating rates (5, 10, 15, and 20 °C/min). The results are presented in Fig.4. The formulation of thermal degradation has been extensively discussed by Sunnan Tiptipakorn [7], and here we will provide a concise overview of the fundamental concepts underlying the Kissinger method. This method utilizes equation (1) to determine the activation energy (Ea) for solid-state reactions.

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

Where:

β ---heating rate (°C/min);

T_p ---absolute temperature (K);

α_p ---weight loss at maximum weight-loss rate;

n --- reaction order;

Ea --- activation energy(KJ·mol⁻¹);

R ---gas constant , 8.1314 J/mol·K.

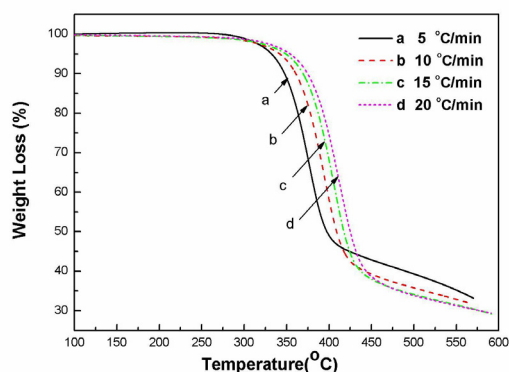


Fig. 4. TGA curves of LCES at different heating rate

The activation energy (Ea) can be determined by analyzing the slope of the linear relationship between $\ln(\beta/T_p^2)$ and $1/T_p$. The corresponding data is presented in Table 2.

Table 2. Thermal degradation data of LCES

β (°C·min ⁻¹)	T_p (K)	α_p (g·min ⁻¹)	$\ln(\beta/T_p^2)$	Ea (KJ·mol ⁻¹)
5	653	62.556	-12.432	143.28
10	669	34.568	-11.731	
15	677	23.673	-10.315	
20	689	19.112	-10.211	

The calculated value for the thermal degradation energy is 143.28 KJ/mol, indicating a high level of thermal stability.

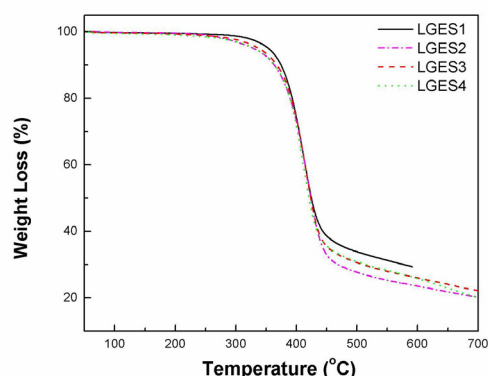


Fig. 5. TGA curves of LCES1, LCES2, LCES3 and LCES4

The effect of E-44 on the thermal stability of LCES is shown in Fig.5. It can be seen from the figure that LGES1 without adding E-44 has good thermal stability, and the char yield at 600°C exceeds 30%. With the increase of the content of E-44, the temperature of thermal weight loss of LGES at 5% and the char yields at 600°C gradually decreased. However, when the content of E44 was higher than 40%, the thermal stability gradually became stable, and the impact is not significant.

4. Conclusions

In this paper, PES was used to modify the liquid crystal epoxy resin LCER. At the same time, different contents of E-44 were added to the resin matrix to reduce the cost. The thermal effects during curing were studied by DSC, and their thermal stability was evaluated by TGA. Furthermore, the dynamic mechanical properties were measured by DMA. It was found that the addition of PES can improve the toughness, mechanical properties, thermal stability and heat resistance of LCER, while the addition of E-44 can reduce the thermal stability and of heat resistance LCER.

Acknowledgments

The present research is financially supported by the Guangzhou Basic Research Plan and Applied Basic Research Project (Grant No. 202201011510).

References

1. Q. Zhang, G. L. Chen, K. Wu, et al, J. Appl. Poly. Sci, 10, 49413 (2020)
2. A. Motahari, A. A. Rostami, A. Omrani, et al, J. Macro. Sci. Part. B, 54, 517 (2015).
3. K. P. Ruan, X. Zhong, X. Shi, et al, J. Mtphys, 20, 100456(2021).
4. K. Maciej, M. L Beata, Polym, 16, 857(2014).
5. X. R. Fan, Z Liu, S. S. Wang, J. W. Gu, Sus, 3, 877(2023).
6. L.Y. Zhong, Y.X. Hao, Macromol, 55, 595(2022).
7. S. Tiptipakorn, S. Ande, S. J. Ando, et al, Poly. Degra. Sta, 92, 1265(2007).
8. K. Mimura, H. Ito, H. Fujioka, Polym, 41, 4451 (2000).
9. C. Chen, S. Qin, X. Wang, Polym. Bul, 80, 6385(2023).
10. J. Li, H. H. Aung, B. Du, Molecules, 28, 547(2023).
11. X. Wu, W. Liu, F. Shi, L. Yang, C. Zhang, Polym Cop, 43, 1711(2022).