

Study of a novel kind of thermoresist bismaleimide resin

Feng liu, Liuyang Dong, Heng Zhou, Tong Zhao*
Institute of Chemistry, Chinese Academy of Sciences, Beijing, 100190

Abstract

A novel kind of bismaleimide resin modified by active diluent was synthesized. The bismaleimide resin presented good processability, such as low cure temperature and melting viscosity. The thermal property of the cured resin was characterized by TGA and DMA. The result indicated that the glass transition temperature of the cured resin was 372°C, and the 5% mass loss temperature reached 407°C.

Keyword : Bismaleimide, Active diluent, Matrix resin

1. Introduction

Thermosetting bismaleimide (BMI) resins are used as matrices for advanced composites in aerospace and electronic industries. They possess excellent thermal and oxidative stability, flame retardation and low propensity to moisture absorption. However, the BMI resins are brittle as a result of the aromatic nature and the high crosslink density of the network¹.

To overcome the brittleness, many toughened resins have been blended with the BMI resins, such as cyanate ester, aromatic diamines, polysiloxanes etc²⁻⁴. Especially, when allyl derivatives of phenols are blended with BMI resins, the brittleness of BMI resins is substantially reduced and their high heat resistance is still retained. In the literature, a series of allylic derivatives of phenols have been used to toughen BMI resins, such as 2, 2'-diallyl-bisphenol A (DABPA), 2,2'-diallyl-bisphenol F, allyl phenolic resin etc⁵⁻⁹, which led to the commercialization of new resins systems based on BMI chemistry. The XU292, blend resin of DABPA with 4,4'-bismaleimido diphenyl methane (BDM), has been developed by Ciba-Geigy Co, and show better toughness and higher heat resistance¹⁰. Recently, the propargyl derivatives of phenols have been developed as high performance resins and they possess good thermal stability and moisture resistance^{11, 12}. Bis propargyl ether bisphenol A (PBPA) has been investigated in blends with BMI resins by our group and a highly thermal stable resins system is obtained, indicating that the propargyl ether phenol are also a good modifier as allyl ether phenols to toughen the BMI resins¹³.

However, some adverse properties of the modified BMI resins should be noticed. First, most of the modified BMI resins are solids at room temperature, the prepreg is stiff, and it is very difficult to produce the composite with complex structure. Second, the cure temperature of the modified BMI resins is higher, and the post-cure temperature of the resin often reaches 250°C. In addition, the thermal properties of the modified BMI resins should be improved to meet the developing of the composite.

In this paper, a novel modified BMI resin was prepared via 3-aminophenylacetylene reacting with bismaleimide. The curing behavior and the thermal properties were studied.

2. Experimental

2.1. Materials and instruments

3-aminophenylacetylene (C.P, Jiao Zhou Fine Chemical Corporation) was distilled before use, and 4, 4'-Bismaleimide diphenyl methane (BDM) (Feng Guang Chemical Co. Honghu, China) was used as

received. Other reagents were used without further purification.

The cure characteristics of the resins were studied by Differential Scanning Calorimetry (DSC) using a Mettler thermal analysis DSC-822e at a heating rate of 10°C/min under nitrogen atmosphere. Thermal gravimetric analysis (TGA) was performed by a Netzch STA 409PC at a heating rate of 10°C/min under nitrogen atmosphere. Dynamic mechanical analysis (DMA) was carried out on Netch DMA242 under nitrogen atmosphere at a heating rate of 3°C/min, and the test frequency was 1 Hz.

2.2. Preparation of the novel modified BMI resin (JM-1)

The novel modified BMI resin (JM-1) was prepared via 3-aminophenylacetylene reacting with BDM at high temperature. First, in a 250ml flask, 58.5g (0.5mol) 3-nitrophenolacetylene was added. The flask was heated to about 120°C, and 179g (0.5mol) BMD was added. The mixture was kept reacting about 60 minutes at 120°C, then the mixture was poured out and the JM-1 resin was obtained. The prepared JM-1 resin was copper colored sticky liquid.

2.3. Thermal curing of the JM-1resin

The cure behavior of JM-1 resin was characterized by DSC and FT-IR spectra. The monomers were cured as per the following procedure: 170°C/2h+200°C/2h to obtain cured resins. The thermal stabilities of the cured resins were evaluated by TGA, and dynamic mechanical properties of them were characterized by DMA.

3. Results and Discussion

The novel modified BMI resin (JM-1) was prepared via 3-aminophenylacetylene reacting with BDM at high temperature. The prepared JM-1resin presented very good solubility in acetone.

In this section, DSC was applied to evaluate the cure behavior and give cure kinetic parameters of the monomers, and the DSC curve of JM-1 resin was shown in Fig 1.

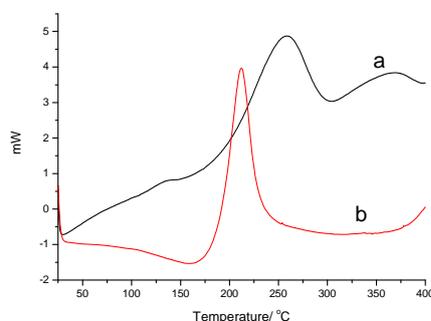


Fig 1 DSC curve of the JM-1 resin

(a) allyl bispheno A modified BMI resin; (b) JM-1 resin

For JM-1 resin, the exotherm was attributed to the cure reaction of the JM-1, and the onset cure temperatures was about 160°C, the peak cure temperature was about 210°C. On the other hand, the cure temperature of bisphenol A modified BMI resin was higher than that of JM-1resin. The onset temperature of it was about 190°C, and the peak cure temperature was about 255°C. Therefore, the DCS result indicated that the JM-1 resin could cured at lower temperature than traditional modified BMI resin.

The viscosity of JM-1resin at different temperature was characterized, and the data was shown in Table 1. The JM-1 resin displayed very low viscosity when the temperature was up to 70°C. Therefore, the JM-1 resin could be fit for resin transfer molding(RTM) processing between 70~100°C.

Table the viscosity of JM-1 resin at different temperature

Temperature, oC	70	80	90	100	110	120	130
Viscosity (mPa.S)	400	180	60	39	31	33	53

The JM-1 resin was cured at 170 °C/2h+200 °C/2h to obtain brown compact cured resin. The thermal stabilities of the cured resin was characterized by TGA and the profile was shown in Figure 2. The 5% mass loss temperatures of the cured JM-1 resin was as high as 405 °C, which indicated the cured resin possessed excellent thermal stability.

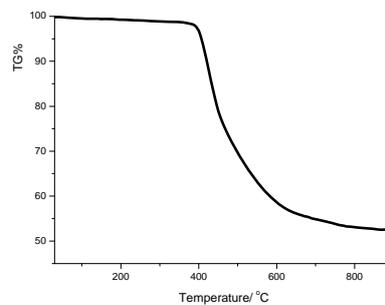


Fig 2 the TGA curve of the cured JM-1 resin

Dynamic mechanical analysis (DMA) was an efficient tool to measure the dynamic mechanical properties of cured resins. The storage modulus (E') and the loss factor ($\tan\delta$) for cured JM-1 was shown as a function of temperature in Figure 3. It could be seen that the retention rate of storage modulus at 350 °C of the cured JM-1 resin was 89%, which was much higher than that of traditional modified BMI resins. In addition, the peak of curves of $\tan\delta$ was attributed to the glass transition of the cured resin, and the glass transition temperature (T_g) was defined as the peak temperature. The T_g of the cured JM-1 resin was about 372°C, and it was much higher than that of the typical commercial BMI resins.

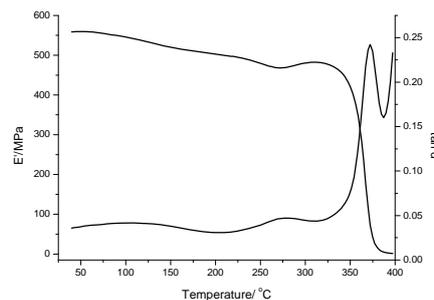


Fig 3 DMA curve of the cured JM-1 resin

4. Conclusions

A novel kind of modified BMI resin(JM-1) successfully synthesized via 3-aminophenylacetylene reacting with BDM. DSC study showed that JM-1 resin exhibited lower cure temperature than traditional modified BMI resin. TGA results indicated the cured resin presented excellent thermal stabilities because their 5% mass loss temperatures were high about 400 °C. DMA study suggested that T_g of the cured resin was about 372°C, which were much higher than the typical modified BMI resins. Owing to the excellent process and thermal properties, the novel modified BMI resin could be

candidate for the high performance composite matrices.

References

1. HD, S., High Performance Polymers Advances in Polymer Science 117, 165 1994.
2. KN Ninan, K. K., Thermochemica Acta 134, 5 1988.
3. Hamerton, I.; Herman, H.; Mudhar, A. K.; Chaplin, A.; Shaw, S. J., Polymer 43, 3381 2002.
4. Chun-Shan, W.; Tsu-Shang, L., Polymer 40, 5407 1999.
5. Gouri, C.; Nair, C. P. R.; Ramaswamy, R.; Ninan, K. N., European Polymer Journal 38, 503 2002.
6. Gouri, C.; Nair, C. R.; Ramaswamy, R., Polymer International 50, 403 2001.
7. ZhongMing, L.; Ming, X.; Ai, L.; MeiDong, Z.; Rui, H., Journal of Applied Polymer Science 74, 1649 1999.
8. IK Varma, S. G., DS Varma, Angewandte Makromolekulare Chemie 184, 12 1991.
9. Yao, Y.; Zhao, T.; Yu, Y., Journal of Applied Polymer Science 97, 443 2005.
10. Zhao, Q., Handbook of Advanced Composites; China Medicine Press: beijing, 2003.
11. Nair, C. P. R.; Bindu, R. L.; Ninan, K. N., Journal of Macromolecular Science-Pure and Applied Chemistry A40, 357 2003.
12. Nair, C. P. R.; Bindu, R. L.; Krishnan, K.; Ninan, K. N., European Polymer Journal 35, 235 1999.
13. Feng Liu, W. L. L. W. T. Z., Journal of Applied Polymer Science 102, 3610 2006.