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STUDY ON HOT-MELTING RESIN BASED ON BMDPM/DABAP

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Abstract

This paper introduced a hot-melting resin system based on 4, 4'—bismaleimidodiphenyl methane (BMDPM) and o,o'—diallylbisphenol A (DABPA). To improve its processibility and toughness, several reactive diluents and toughness modifiers were incorporated. The results show that the optimized resin has good processibility and much improved toughness, as well as good heat-resistant property, and the resin/carbon cloth composite has excellent mechanical properties.

Key words: hot-melting bismaleimide resin

Introduction

The last three decades have seen a constant development in the area of temperature resistant thermosets, especially thermosetting polyimides which are gaining wide acceptance by both the aerospace and electric/electronics industries because they combine a series of unique features such as excellent physical property retention at elevated temperature and in wet environments, almost constant electrical properties over a wide range of temperatures and low flammability properties.

The two families of curable polyimide resin which are finding numerous applications and have reached a level of industrial maturity are the nadimides and bismaleimides. In particular, the bismaleimides have developed to combine the good processibility of epoxies with the excellent heat resistance of polyimides, and they have been modified to meet the composite processing requirements for low pressure autoclave molding, high pressure platen press molding, wet and tow pre-preg filament winding and resin transfer molding.

The most commonly used monomer is BMDPM which has a high melting point (161~163°C). When homopolymerized, highly brittle networks are usually formed. To improve its processibility and toughness, we introduced toughening comonomers and reactive diluents.

Experiments and Characterizations

1. Preparation and curing of the hot-melting resin

The hot-melting resin was synthesized by introducing toughening comonomers and diluents step by step to BMDPM/DABPA system at 120~130°C owing to different reactivities of reactants. The obtained resin can slowly flow at room temperature.

All the hot-melting resin was poured into open casting molds and cured by the following schedule: 2 hours/110°C(vacuum), 2 hours/130°C, 2 hours/ 150°C, and 2 hours / 195°C. Then the post curing at 220°C for 4 hours followed. Mechanical test samples were obtained from these cured plaques.

2. Preparation of the resin composite reinforced by T300 carbon cloth

After resin dissolved in acetone with the resin/acetone weight ratio 0.82, the sized carbon cloth was brushed with the resin solution. After the cloth soaked with the resin was heated at 100~120°C for about 1 hour, the pre-pregs were obtained. At about 190°C the laminates was produced under the pressure 200kgf/cm^2, then post curing was carried out at 220°C for 8 hours.

3. Viscosity determination of the hot-melting resin

Viscosity isotherms at 85°C, 90°C and 95°C were obtained by a Rotatory Viscometer NDJ-I with the third rotator.

4. Gelation time determination

Gelation time was investigated by the method of little knife. About one gram of resin was placed on the thermoplate with the stable corresponding temperature.

5. Thermal analysis

Differential Scanning Calorimetry (DSC) was used to characterize the relative reactivities. By means of a Dupont 2100 Differential Scanning Calorimeter, the samples were heated from 25°C to 500°C at 5°C /min under nitrogen.

Thermomechanical Analysis (TMA) was made using a Dupont 2100 Thermomechanical Analyzer. Sample diameter was approximately 4.6mm with the thickness 0.73mm. The cured sample was heated from 25°C to 350°C at 10°C/min under nitrogen.

Thermal Gravimetric Analysis (TGA) was carried out on a Dupont 2100 Thermal Gravimetric Analyzer at 10°C/min under nitrogen. The range of temperature was from room temperature to 750°C.

6. Mechanical properties

Flexural and tensile properties were obtained with an Instron 4505 Mechanical Tester. Impact property was tested with a Impact Elasticity Tester.

Results and Discussion

1. Processibility

Processing characteristics of the hot-melting resin were determined by viscosity and reactivity measurements.

The viscosity isotherms at 85°C, 90°C and 95°C are presented in Figure 1. The viscosity at 85°C, 90°C and 95°C are 340cp, 240cp and 220cp, respectively, and after 6 hours they are still less than 650cp, but the viscosity rising speed increases with the increase of the investigated temperature. So at these temperatures the resin has good flowability and long pot-life.

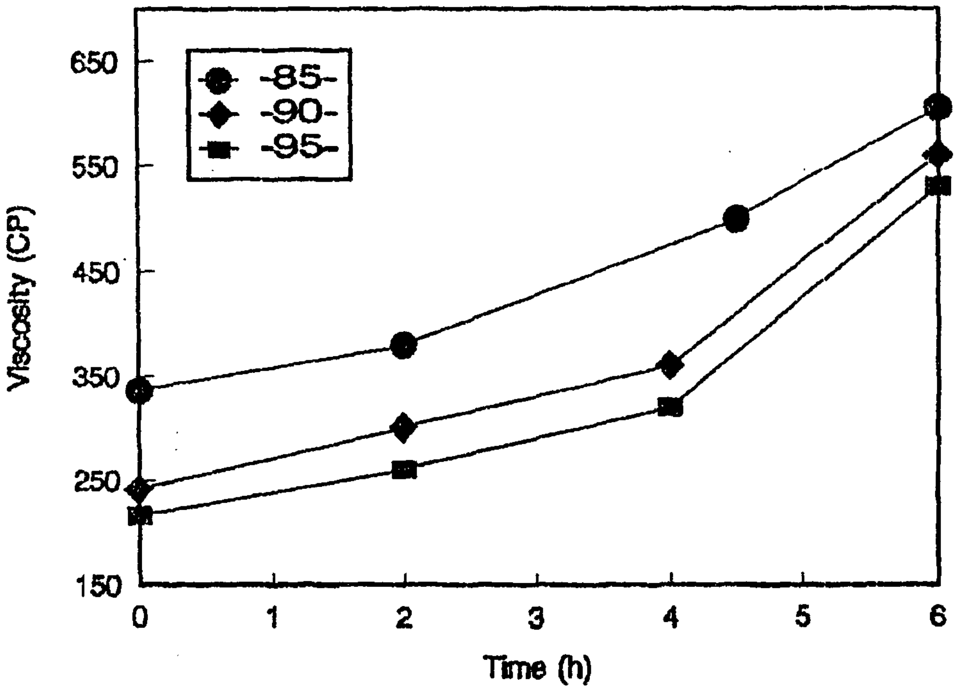

Fig 1 Relationship of viscosity vs time at 85°C, 90°C and 95°C

Through the method of little knife, the gelation times of the resin was investigated. The gelation time at 195°C is 3.7min, and at 150°C is 42.3min, while at 90°C is over 24 hours. That is to say, the resin has long pot-life at processing temperature while can be fast cured at shaping temperature.

For BMDPM, the gelation time at 180°C is as long as about 2 hours and the melting point is 162°C. For the optimized BMDPM/DABPA system, the viscosity at 100°C is 420cp and reaches 800cp after 6 hours.

So the hot-melting resin has improved BMDPM processibility a lot, which was identified by the DSC data in Table 1 obtained from Fig 2 and Fig 3.

Table 1 DSC data of the hot-melting resin and BMDPM

System	Hot-melting resin	BMDPM
Range of melting temperature, °C	50~120	161~163
Peak of curing temperature, °C	175.6	254.0

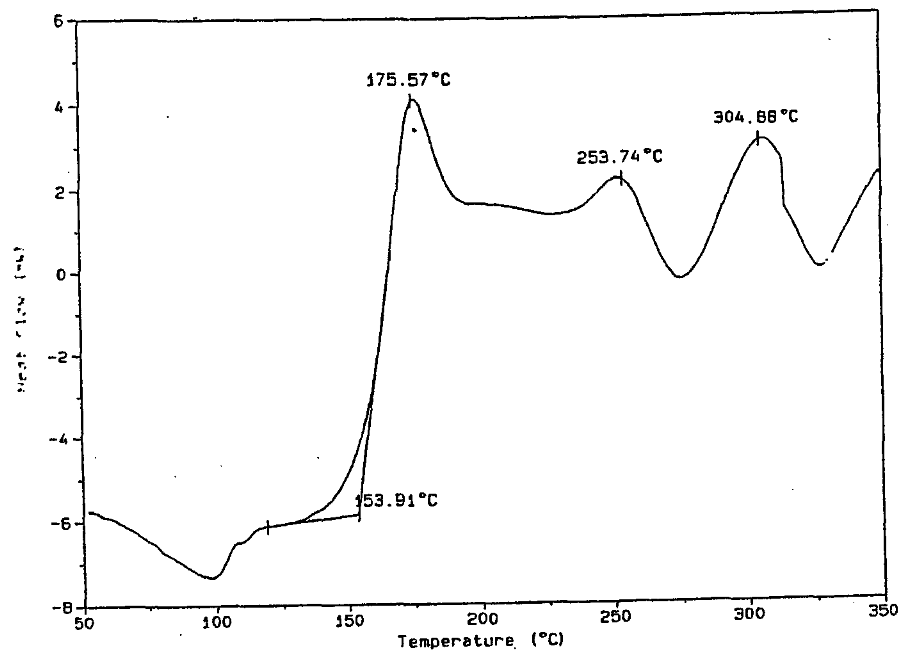

Fig 2 DSC curve of the hot-melting resin

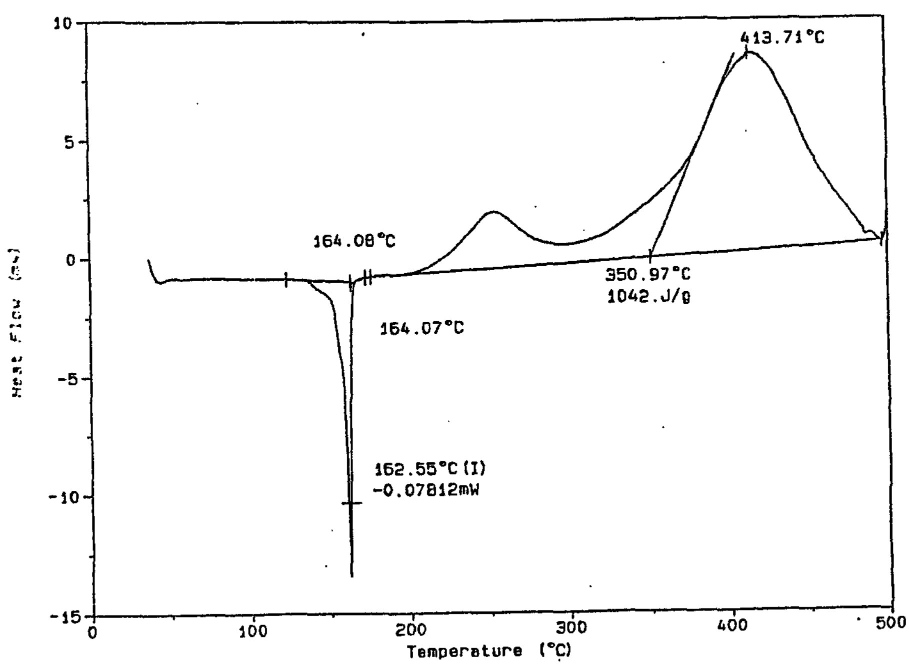

Fig 3 DSC curve of BMDPM

2. Mechanical properties

Table 2 shows the room temperature flexural, tensile, and impact properties of cast articles of the hot-melting resin.

Table 2 Mechanical properties of the cured resin

Items	Values
Tensile strength, MPa	55.2
Tensile modulus, GPa	3.15
Tensile elongation, %	2.3
Flexural strength, MPa	102
Impact strength, KJ/m^2	10.4

As we know, the toughness of a kind of materials can be effectively characterized by the value of tensile elongation. According to previous experiments, the tensile elongation for cured BMDPM is less than 1%, and for optimized BMDPM/DABPA system is still less than 1.8%, while for the hot-melting resin is 2.3%. It is obvious the toughening agents used to synthesize the hot-melting resin do improve the toughness of the BMDPM/DABPA system. Furthermore, other mechanical properties are also good.

Mechanical properties of the composite reinforced by T300 carbon cloth are shown in Table 3.

Table 3 Mechanical properties of the composite

Items		Values
Flexural strength, Mpa	25°C	797
	150°C	418
Flexural modulus, Gpa	25°C	61.0
	150°C	49.5
Tensile strength, Mpa	25°C	652
	150°C	537
Tensile modulus, Gpa	25°C	73.8
	150°C	63
Compress strength, Mpa	25°C	609

From Table 3 it can be concluded that the composite has high strength and modulus.

3. Thermal performance

From DSC curves of Fig 2 and Fig 3, we can know the temperature peaks of decomposing for the cured hot-melting resin and BMDPM are 304°C and 413°C, respectively. Furthermore we made the TGA of the cured resin, and the result is shown in Table 4.

Table 4 TGA data of the cured resin

Itcms	Valucs
Temperature of initial decomposing, °C	294
Peak temperature of decomposing, °C	433
Endpoint temperature of decomposing, °C	716

At the same time, we investigated Glass Transition Temperature (Tg) of the cured resin. It was confirmed by TMA shown in Fig 4 that the Tg of thc curcd rcsin is as high as 298.2°C.

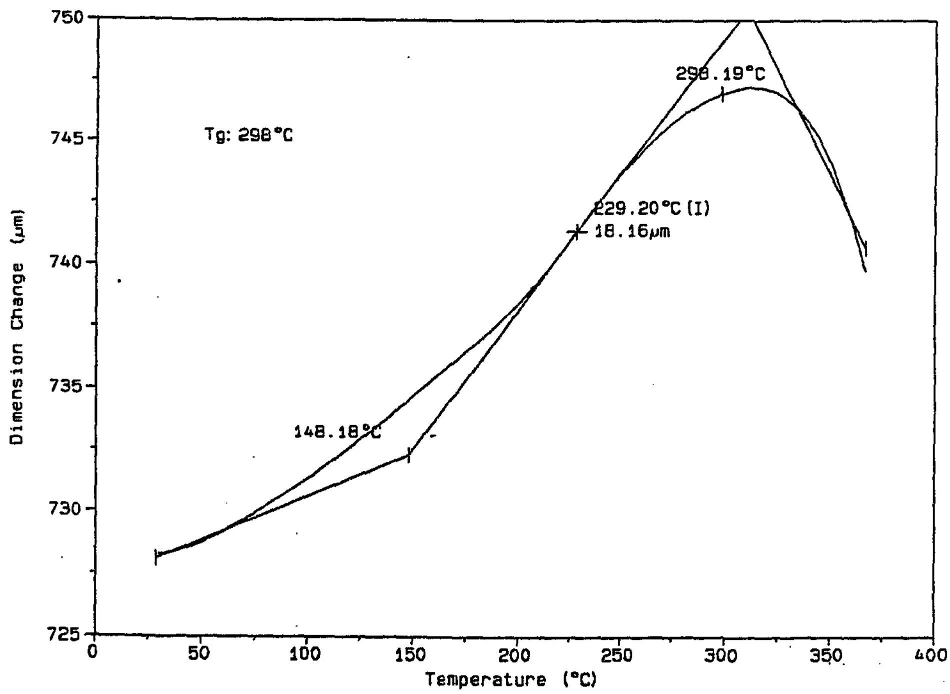

Fig 4 TMA curve of the cured resin

Conclusions

This study has demonstrated that the poor processing flowability and brittle property of BMDPM can be effectively improved by the reactive diluents and toughening comonomers with little sacrifice to heat resistant performance. The hot-melting resin synthesized has good processibility and comprehensive mechanical properties. Mechanical properties of the corresponding composite reinforced by T300 carbon cloth are also desirable.

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