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Study on Properties of Low Dielectric loss Resin Matrix

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Summary

One new high performance modified BMI resin matrix with enhanced processing characteristics, made from 4,4-bismaleimidodiphenyl methane (BDM) and allyl phenyl compounds, allyl epoxy resins and epoxy acrylate resins, were developed. Solubility, differential scanning calorimetry (DSC), gel time, and Fourier transform infrared (FTIR) spectroscopy were used to detect the structure and processing characteristics of the modified BMI resin and neat BDM. Results show that the new modified BMI resin systems have enhanced processability compared with neat BDM, especially improved solubility and faster thermal polymerization rate. In addition, the new cured systems have more than two times improved impact strength without a great decrease in excellent dielectric properties or thermal and hot–wet resistance of neat BDM resin.

Introduction

The search for advanced, high performance, high temperature resistant polymer is on the rise in view of the growing demand for polymer matrix composites that are to meet stringent functional requirements for use in the rapidly evolving high-tech areas. High performance resin matrix composites possess low weight, easy adjustment of structural design, high specific strength and toughness as well as heat resistance and fatigue resistance properties. The preparation of the high performance resin matrix composites contains resin matrix and reinforcement. The properties of advanced resin matrix composites mainly depend on the properties of resin matrix because the properties of reinforced fabric are relative stability. At present, there are many resins such as epoxy (EP), bismaleimide (BMI), polyimide (PI), and Cyanate ester resin (CE), which are usually adopted to prepare the advanced resin matrix composites, especially for EP and BMI [1]. Because of poor hot-wet resistance and high dielectric loss of epoxy, it cannot satisfy some special requirements such as electronic encapsulant and high performance printed circuit board. Although BMI possesses high temperature resistance, hot-wet resistance and dielectric properties, it cannot be applied because of the poor dissolvability, high reaction temperature and brittleness [2-4]. BMI can be used for these high performance areas only if its toughness and processing properties are improved and could keep its dielectric properties and heat resistance [5-7]. In this paper, allyl phenyl compounds and epoxy acrylate resins are adopted to cure with bismaleimide (BMI) resins to improve the properties of bismaleimide. Processing properties of the modified system are studied in detail.

Experimental

Materials

4,4'-bismaleimidodiphenyl methane (BDM), was industrial grade, supplied by Northwestern Chemical Institute and recrystallized from the chloroform/methanol mixture (volume ratio 1:1). O,O'-diallylbisphenol A (BA), epoxy acrylate and allyl epoxy resins were self-synthesized.

Preparation of Modified BMI Resin

O,O'-diallylbisphenol A (BA), epoxy acrylate and allyl epoxy were placed into a three-necked flask equipped with a mechanical stirring device and a thermometer. The contents were heated with stirring, BDM was added to the stirring solution at 100°C; then the temperature was maintained between 130 and 150°C until the solution was transparent; while being continuous stirred, the transparent solution was prepolymerized for 30-60min, stopped and poured onto film with release agent to obtain the modified BMI resin.

Properties Tests of Modified BMI Resin

The curing reaction pathway of modified BMI resin system was recorded by a Necolet-550 FTIR spectrometer. Resins were analyzed in the form of a film between two KBr disks placed in a thermally regulated cell. FTIR spectra were measured at 5min intervals during the cure cycle. The spectral width was $4000\pm400\text{cm}^{-1}$ with a 4 cm^{-1} spectral resolution.

Differential scanning calorimetry (DSC) was carried out using Perkin-Elmer thermal analyzer unit in a nitrogen atmosphere at a heating rate of 10°C /min.

Dissolvability: 10g resin was added to a stirred beaker, dissolved in 15~20g acetone and heated to a transparent solution. The reaction mixture was cooled to room temperature, airproofed for 48h and observed. It must be transparent without crystallization and muddiness.

Gel time: The gel time of resins was determined with a standard hot-plate with a temperature controller. The resins were spread over hot plates heated to different temperatures. The time required for the resin to stop legging and become elastic is called the gel time. Viscosity properties: That were done using MODEL DV-1 rheometer according to the guide book.

Softening point was measured by round-the-world method according to GB12007.6. Heat deflection temperature (HDT) was obtained by GB1634-1679.

The thermal stability of cured resins was obtained with a Perkin-Elmer thermogravimetric analyzer (TGA) with a heating rate of 10°C/min in a nitrogen atmosphere. Glass transition temperature (Tg) was obtained with a Perkin-Elmer DSC-7 in a nitrogen atmosphere at a heating rate of 10°C/min.

The dielectric properties were measured according to GB1409-78.

The hot–wet resistance of cured resins and composite was determined by placing samples into boiling distilled water for various lengths of time, removing and wiping off the sample with a dry cloth, and weighing the sample to the nearest 0.001 g immediately. Then, the value of water absorption was calculated according to ASTM D 570-81, and the value of HDT was tested.

Results and discussion

Physical Properties of Modified Resin

BDM is a yellow powder at room temperature with a melting point (m.p) of 120°C. BA, epoxy acrylate and allyl epoxy resin are all brown transparent viscous liquids and can be easily dissolved into common solvents such as acetone and alcohol. The physical properties of modified BMI resin are shown in Table 1. It could be found that modified BMI is a light brown transparent solid and with low softening point of 45~55°C. In addition, modified BMI have excellent dissolvability in common solvents and could dissolve in acetone and methylbenzene with any ratio. The viscosity of modified BMI resin at 120°C is 0.98 Pa·s and the gel time at 150°C is 20~40 minutes. That is to say, modified BMI resin system possesses wide processing windows. After storage at room temperature for 6 months, their color and solubility don't change, indicating that modified BMI resin systems have good storage stability.

Table 1 Physical properties of modified BMI

properties	value
Surface appearance	Light brown transparent solid
Dissolvability	Dissolved in acetone and methylbenzene
Softening point, °C	45~55
Gel time (150°C), min	20~40
Viscosity (120°C), Pa·s	0.98
Storing time (room temperature), month	6

Reactivity of Modified BMI Resin System

The relationships between temperature and gel time of modified BMI resin system and pure BDM resin are shown in Figure 1. The gel time of modified BMI decreases with the increasing of temperature. The reaction is accelerated obviously when the temperature is above 150°C. Furthermore, the gel time is shortened to 4min at 200°C. Compared with neat BDM, the gel time of modified BMI resin system is much shorter. At 150°C, the gel time of modified BMI resin system is only 26min, however the gel time of neat BDM resin is more than 1h, indicating that the curing reaction of modified BMI resin system is faster than that of neat BDM.

The DSC analysis of thermal polymerization behavior of modified BMI resin system and neat BDM resin at a scan rate of 10°C/min was investigated, and the results are depicted in Figure 2. Neat BDM resin has an onset of exothermic polymerization reaction temperature at ~256°C, with a processing window of 211~301°C. The DSC scans of curing process of modified BMI resin system exhibit the initial reaction temperature (T_i) and the final reaction temperature (T_f) is 164°C and 247°C, respectively, with each exothermic peak maximum shifting from ~256 to 201°C.

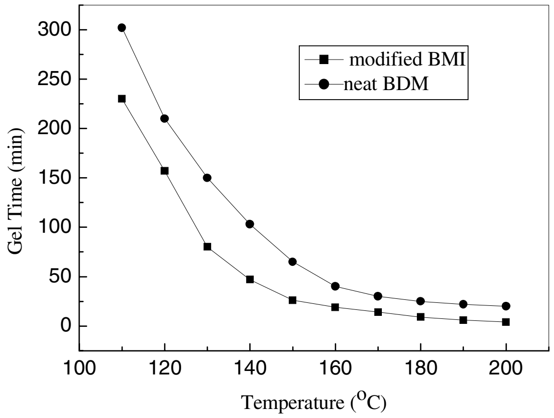


Figure 1 Temperature vs. gel time curves of modified BMI and neat BDM

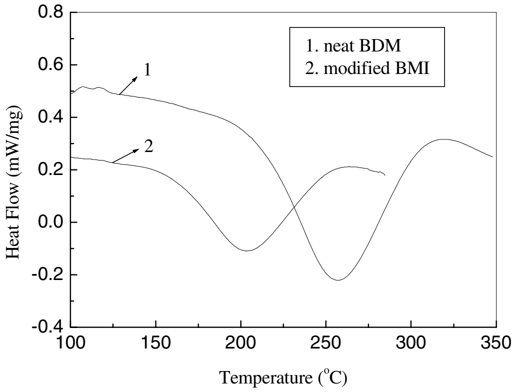


Figure 2 DSC curve of neat BDM and modified BMI

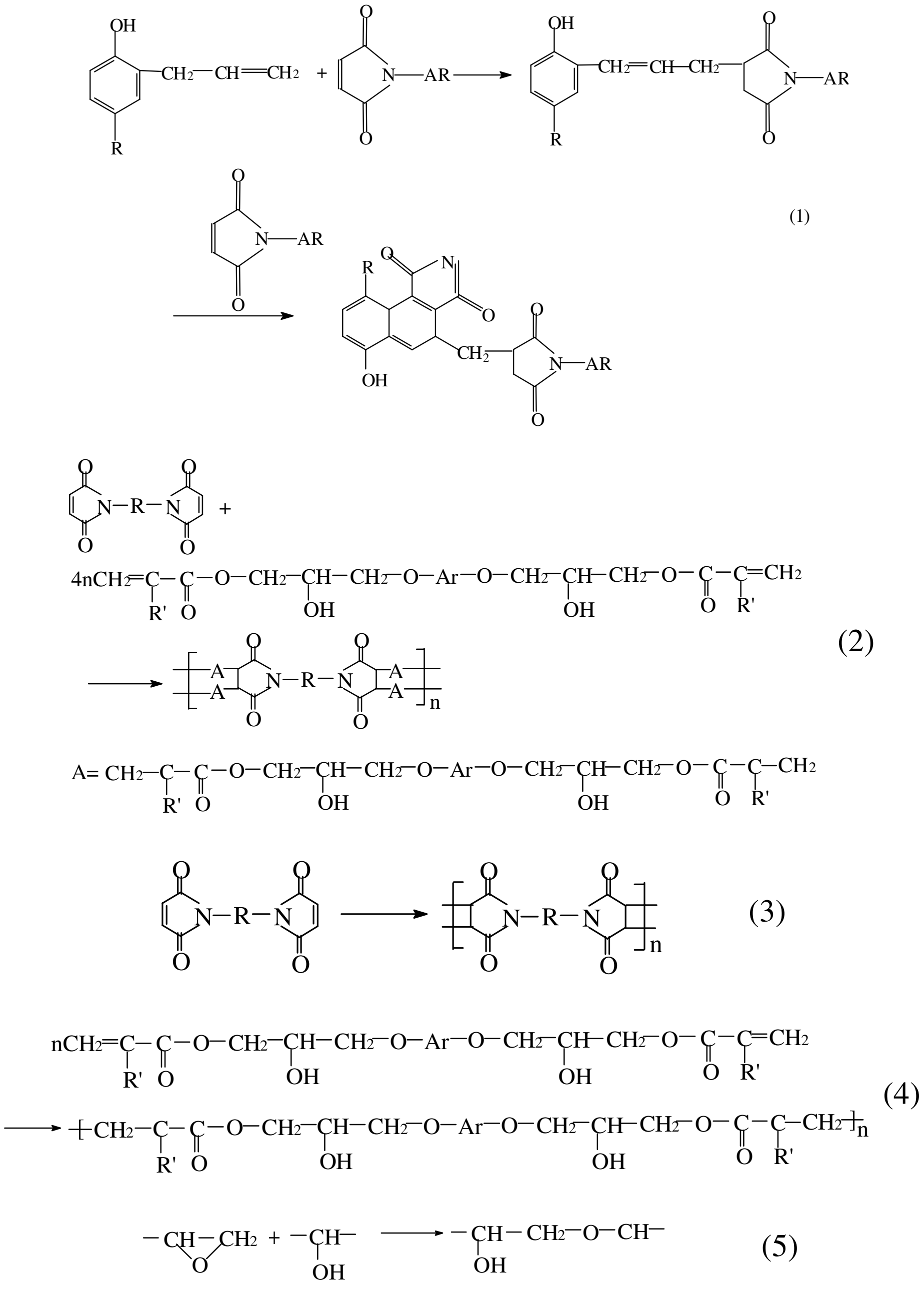
By this token, the reactivity of modified BMI resin system was much higher than reaction activity of neat BMI resin. The temperatures of co-curing reaction between allylbisphenol A (BA) resin, VE resin and BDM resin are both lower than the curing reaction temperature of neat BDM resin. Therefore, the co-curing could increase the reaction activity of modified BMI resin system.

Reaction Mechanism of Modified BMI Resin System

There are several reaction mechanism of allyl epoxy resin and epoxy acrylate resin co-curing with bismaleimide resin: a) the copolymerizes reaction between allyl and bismaleimide, b) the co-curing reaction between VE resin and bismaleimide resin, c) the curing reaction of bismaleimide resin, d) the curing reaction of VE resin, e) the reaction of remnant VE resin with hydroxy (—OH). The reaction mechanisms are all shown in Scheme 1.

Figure 3 presents typical IR spectrum of modified BMI resin system. The absorption at 1750cm^{-1} and 1770cm^{-1} are the outside and inside flexural vibrant absorption of C=O, respectively. The absorption at 3038 cm^{-1}, 603 cm^{-1}, 1510 cm^{-1} and 1010 cm^{-1}

are the typical absorption of phenyl. The absorption at 690 cm^{-1} and 830 cm^{-1} are the distorting vibrant absorption of C—H about —C=C—H. The absorption at 3100 cm^{-1}, 1640 cm^{-1} and 3500 cm^{-1} are the flexural vibrant absorption of C—H about —C=CH, —C=C—, and —OH, respectively.



Scheme 1 The cure reaction mechanism of modified BMI resin system

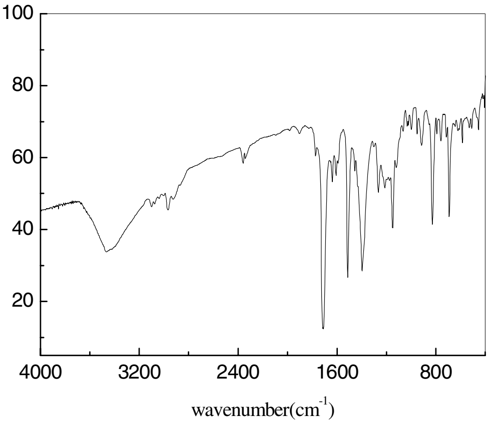


Figure 3 Typical FTIR spectrum of modified BMI

Viscosity of Modified Resin

The resin matrix that possesses lower softening point and viscosity change can be defined as a good matrix. Consequently, viscosity is an important standard to characterize the processing of resin. Figure 4 shows the viscosity and temperature curve of modified BMI. It can be seen that the viscosity of modified BMI decreases before 150°C and then slightly increases with the temperature prolonging. The viscosity is minimized to 0.30Pa·s at 150°C. When the temperature is less than 150°C, the resin softens and melts so as to reduce the viscosity and improve the processing properties. The resin has its lowest viscosity about 0.3 Pa·s at 150°C. However, when the temperature increases from 150°C, the viscosity increases because of increasing short-chain prepolymers induced by further reactions.

Figure 5 presents the dependence of viscosity on time at 110°C, 120°C and 130°C. It can be seen that the viscosity of modified BMI increases with an increasing time. After aging for 90min at 110°C, 120°C and 130°C, the resins have increasing viscosities of 3.07Pa·s from 1.78Pa·s, 4.70Pa·s from 1.78Pa·s and 5.20Pa·s from 0.52Pa·s, respectively. That indicates that the viscosity have low variety due to the

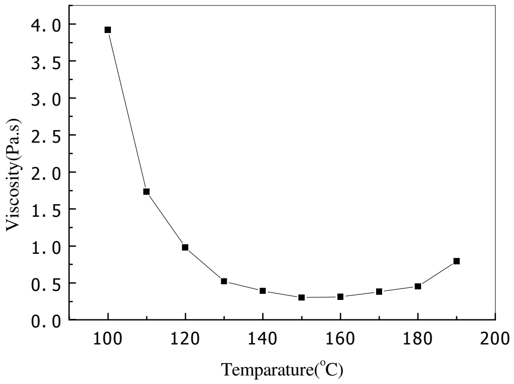


Figure 4 Viscosity vs. temperature curve of the modified BMI

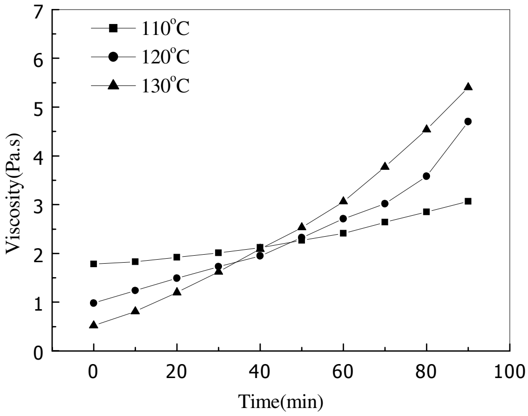


Figure 5 Dependence of viscosity on time at 110°C, 120°C and 130°C

gradual reaction from 110°C to 130°C. Hence, the composites possess wide range of processing time and temperature, which is quite convenient to pressing molding.

Storing Time of Modified Resin

Storing time is also an important standard to characterize the processing of resin. Figure 6 shows the relationship of gel time and softening point with storing time. From Figure 6 we can see that the gel time and softening point without much variety after aging 6 months at 150°C are 20min and 54°C, respectively. In addition, after aging 12 and 18 months at 150°C, the gel times and softening points are 8min, 69°C and 4min, 77°C, respectively. The resin can be reused when the time is properly adjusted on pressure at processing parameter of composites.

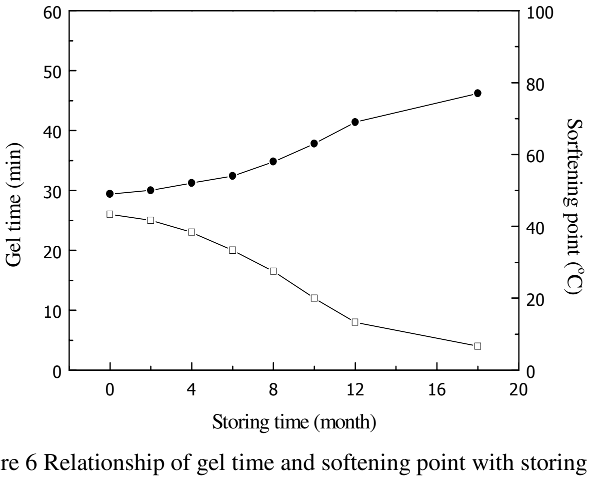


Figure 6 Relationship of gel time and softening point with storing time

Properties of Cured Modified Resin

Both processing characteristics and ultimate properties of a resin are very important for developing a new system. The previous sections give information on whether the resin can be processed via conventional industrial methods, and the section determines whether the resin has the potential to be used widely. These investigations prove that the addition of modifying agent in BDM can greatly enhance the processing properties, so it is necessary to study the ultimate properties of modified BMI resin and the effect of the addition of modifying agent on the properties of neat BDM resin. The properties of BDM resin and modified BMI systems are listed in Table 2.

The modified BMI resin systems have good mechanical properties. In particular, the impact strengths of modified BMI resin system is 2.6 times than that of neat BDM resin, which may be due to the existence of many soft linkages in the networks. This improvement may be also reflected by the increase of the tensile elongation with the addition of modifying agent.

Heat deflection temperature (HDT), glass transition temperature (*T*g), and the typical temperatures obtained from thermogravimetric analysis (TGA) are used to reflect the thermal stability of cured resins. Cured neat BDM resin shows better thermal stability, which may be attributed to its thermally resistant crosslinked structure. The thermal stability of the modified BMI resin systems decreases slightly because the addition of modified agent reduces the crosslinking density of BDM resin. However, the reduced range of thermal stability of modified BMI resin is very limited, and the modified BMI resins still possess excellent thermal resistance.

Table 2 Physical properties of cured modified BMI resin

Properties		Modified BMI resin	Neat BDM resin
Tensile strength, MPa		78	55
Tensile modulus, GPa		3.6	3.8
Tensile elongation, %		2.3	1.6
Flexural strength, MPa		108	100
Flexural moudulus, GPa		3.7	3.9
Impact strength, kJ/m^2		15.2	5.83
HDT	Dry	265	283
	Wet (aged 100h in boiling water)	231	234
T_g (DSC), °C		274	293
T_d, °C		424	438
Water absorption		2.3	2.0
tanδ(10 GHz)		0.012	0.013
ε(10 GHz)		3.14	3.09

A resin with poor hot–wet resistance usually has high moisture absorption, causing a lowering of thermal stability and associated reliability problems. Therefore, hot–wet resistance is very important for developing a new resin. After aging for 100 h in boiling distilled water, modified BMI systems and neat BDM resin have water absorptions of 2.0 and 2.3%, respectively, their HDT values decrease from 265 to 231°C and 283 to 244°C, respectively. Both of these changes are higher than 85% retention of their original values, indicating that modified BMI resin systems have good hot–wet resistance.

From the results in Table 2, it can be seen that the dielectric properties of the modified BMI resin system is almost as good as that of neat BDM resin, which are generally considered to be good dielectric materials.

Conclusion

To improve the processing properties of bismaleimide resin, allyl phenyl compounds, allyl epoxy resins and epoxy acrylate resins are adopted to co-cure with bismaleimide (BDM) resin. Investigations show that the reactivity of BMI is increased because of the addition of modifying agent. Modified BMI resins could dissolve well in the general solvent such as acetone and possess wide processing temperature and lifetime. In addition, the cured resins retain the positive characteristics of neat BDM, such as excellent dielectric properties, good thermal and hot-wet resistance properties, as well as improved impact strength.

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