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Studies of Silicon-Containing Bismaleimide Resins – Preparation and Characteristics of Reactive Blends of Silicon-Containing Bismaleimide and Epoxy

Three kinds of silicon-containing bismaleimide (4,4'-Bismaleimido phenoxy silane) monomers were synthesized and added through blending to general epoxy system for the study of their applications as reactive flame retardants. The thermal analysis of the BMI monomers in bisphenol type epoxy system had been discussed. An increase in the BMI contents decreased the storage modulus and glass-transition temperature and slightly reduced the mechanical strength of the epoxy blends. Although the initial pyrolysis temperatures of all the blending systems gradually decreased as the silicon-content increased, all the silicon-containing epoxy systems still had good thermal stability and the flame retardancy was promoted significantly by increasing contents of BMI. The LOI values of all the blend types were increased to about 30 as the BMI concentration reached 20%.

1 Introduction

Bismaleimide (BMI) resins are an important type of thermoset polymeric materials characterized by their high glass transition temperatures and high modulus (Pater, 1994; Mison and Sillion, 1999). Besides, they have a wide range of service temperatures between epoxy and polyimide. However, poor solubility of BMI monomers and BMI resins in common organic solvents, high melting and curing temperatures, high brittleness, low adhesiveness, and high cost limits to a great extent their wide applications (Hummel, 1974; Iwata, 1976). To overcome these problems, novel BMI monomers containing flexible units and BMI resins modified by using comonomers, such as the copolymerization of BMI monomers with diamines via the Michael addition reaction, so as to decrease the crosslinking density has been developed (White, 1986; Loustalot, 1998; Shu et al., 2002)

Epoxy resins can be introduced as plasticizers to improve the stiffness and processing of BMI resins, and the thermal sta-

bility and hygroscopic characteristics of epoxy can be improved via BMI resins. However, aromatic diamines, usually used as chain-extension agents of BMI, can also be curing agents of epoxy. Thus, BMI/epoxy/diamine resins, exhibiting, like BMI, high glass-transition temperatures (T_g), hygroscopic characteristics, and dimensional stability, can be improved in other characteristics, such as poor adhesiveness, high brittleness, and high cost. Blends of BMI with epoxy have become one of the main streams of research on BMI modification (Mikroyannidis and Kourtides, 1984; Wang et al., 1996; Shu et al., 2004).

In recent years, many kinds of BMI resins blended with epoxy have been widely studied. Some flexible segments, for example, have been introduced to promote the processing of BMI (Gu et al., 1996). Fluorine-containing segments have been introduced to reduce the dielectric constant of BMI resins (JP Patent, Kawai, 1993). BMI resins with higher thermal stability (Kim et al., 1994) or amine-terminated BMI that can be directly used as a curing agent in epoxy system (Shah and Partch, 1998) have been developed so as to modify the heat or solder resistance. For the modification of flame retardancy, phosphorous-containing BMI (Varma et al., 1983; Wang and Lin, 1999; Lin and Wang, 2000), blends of BMI with halogen-type epoxies (Nakamura, 1993), general epoxies with the addition of a general flame retardant (e.g., graphite) (Sorathia et al., 1992; Enoki et al., 1995) or a phosphorous-containing flame retardant (e.g., triphenylphosphate) (Yorisue and Katayori, 2000; Ito et al., 1999), and BMI/epoxy blends with a phosphorous-containing curing agent (Hitachi, 1984) have been widely studied. However, there are rare literature references for dealing with halogen or phosphorous-free bismaleimide resins (Varma and Chander, 1989; Hao and Jiang, 1996).

Silicon-containing polymers have been developed for various applications in the past 20 years because of their good solubility, high thermal and thermo-oxidative stability, good flame retardancy, high moisture resistance, and good adhesion with semiconducting substrates (Wang and Kaafarani, 2003; Zhang and Horrocks, 2003; Guenther and Yandek, 2006). All of these polymers show improved processability and thermal stability and are promising candidates for wide applications ranging from aerospace to electronics. Introduction of silicon atoms into BMI resins may lead to a new type of high

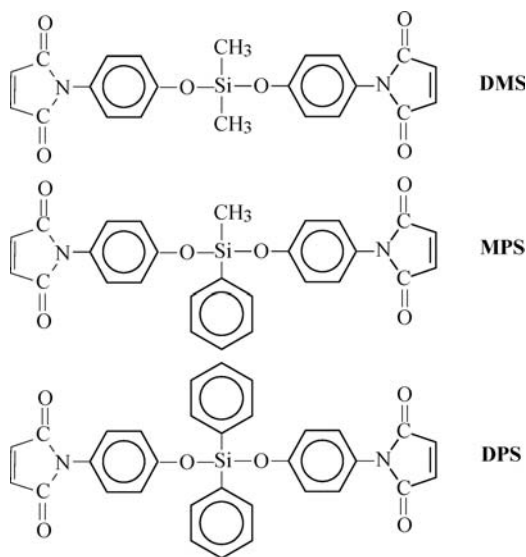
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performance polymeric materials. However, there are only a few literature references studying with silicon-containing BMI resins (Mikroyannidis and Melissaris, 1990; Hao et al., 1999; Tang et al., 2008). We have synthesized 3 kinds of silicon-containing BMI monomers and their derivatives that exhibit good flame resistance (Shu et al., 2003; 2009). This research mainly concerns these novel silicon-containing BMI monomers blended with phenol-type of epoxy resins, examining the influence of the maleimide segments on the physical properties of general epoxy resins. The promoting effect of silicon-containing segments in flame retardancy has also been analyzed to confirm its practical value.

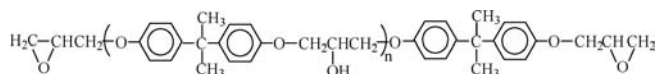
2 Experimental

2.1 Materials

Three silicon-containing BMI monomers, Dimethyl(4,4'-bismaleimido phenoxy)silane (DMS), Methylphenyl(4,4'-bismaleimido phenoxy)silane (MPS), and Diphenyl(4,4'-bismaleimido phenoxy)silane (DPS) were synthesized by a two-step reaction (Shu et al., 2003; 2009):



Two epoxy resins were used. Epon 828 (diglycidyl ether of bisphenol A with an epoxy equivalent of 190) was obtained from Shell Chemical Co. (Akron, OH):



Diaminodiphenyl sulfone (DDS) was obtained from TCI (Tokyo, Japan).

2.2 Preparation of Blending System

For the comparison of different epoxy equivalents, the synthesized BMI monomers were mixed with epoxy and the curing agent DDS. DDS theoretically opened all the double bonds of BMI and the epoxy groups. The mixture was then blended

homogeneously at 160°C. Bubbles in the blends were drawn out in a vacuum oven. Then, the blends were introduced into the molding device. The hardening periods of all the BMI epoxy blend systems were determined with differential scanning calorimetry (DSC).

2.3 Instrumentation

The scanning curves of the BMI and related blending resins were determined with a TA Instruments DSC10 instrument (New Castle, DE) at a heating rate of 10°C/min in N₂ for the analysis of the melting temperatures, curing parameters, and T_g. The T_g values of the blends were also measured with a TA Instruments DMA2980 instrument at a frequency of 1 Hz. The thermal stability and flame-retarding properties of these resins were analyzed with a TA Instruments TGA 51 instrument at a heating rate of 20°C/min in air or N₂. The flame retardancy was also studied by the limiting oxygen index (LOI) with an oxygen index analyzer (Stanton Redcraft; Atlas Equipment Corp., Taipei, Taiwan) at an O₂/N₂ flow rate of 20 L/min. The mechanical properties of the cured blends were measured with an Instron 4469 universal testing instrument (Canton, MA) by the ASTM D 412-75 tensile method.

3 Results and Discussion

3.1 Thermal Reaction of BMI with a Diamine

The BMI monomer can react with a diamine via nucleophilic addition (Michael addition) to synthesize a polyaspartimide copolymer (Crivello, 1973; Varma et al., 1982). The reaction of Si-BMI with diamine had also been discussed in our previous paper (Shu, et al., 2009). Figs. 1 and 2 show the DSC traces of the BMI/DDS systems. In the DMS/DDS system, as shown in Fig. 1, the melting and curing temperature of DMS were promoting as mixing with DDS. Besides, there was a eutectic phenomenon between the BMI monomer and DDS: the melting point decreased as the DDS content increased. Because the secondary hydrogen within the amine groups of DDS could not re-

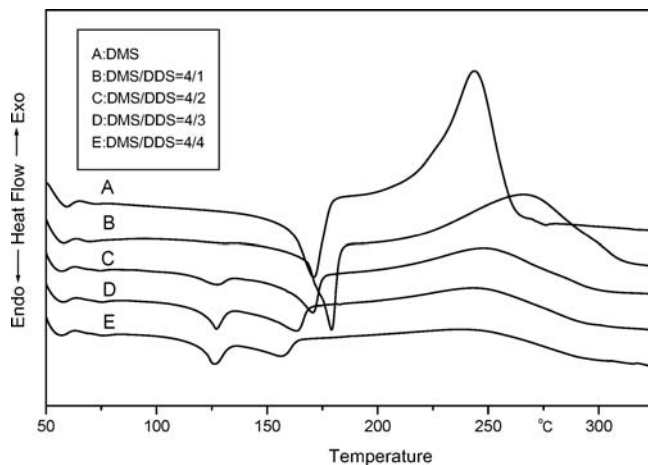


Fig. 1. DSC traces of DMS cured with various equivalent ratios of DDS in nitrogen gas

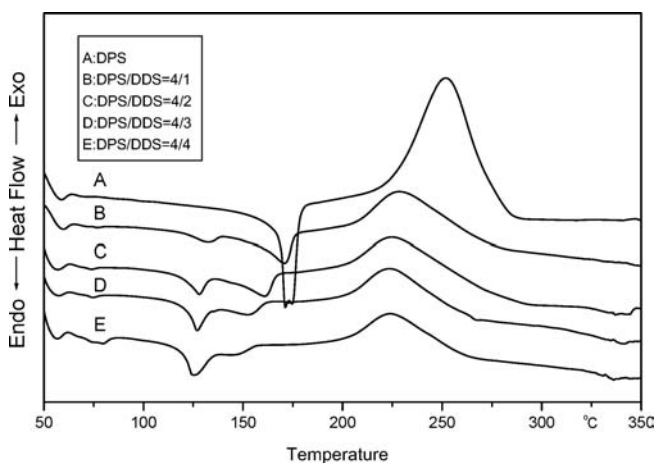


Fig. 2. DSC traces of DPS cured with various equivalent ratios of DDS in nitrogen gas

act with BMI easily, there was an exothermic peak around 270 °C due to the Michael addition of the secondary hydrogen of the amine groups with BMI which was followed by the primary addition and the self-polymerization of DMS when the DDS content was lower to 25%. For the eutectic effect, the self-polymerization temperature of the DMS monomer was shifted lower with increasing DDS content.

Fig. 2 shows DSC traces of the DPS/DDS systems. The eutectic phenomenon between the EBMPP monomer and DDS was more obvious because their melting points were close. When the equivalent ratio of BMI to DDS was 4/4, it exhibited a near eutectic state, with a eutectic point around 125 °C. For the eutectic effect, the exothermic peak due to the Michael addition of the primary hydrogen of the amine groups with BMI and the self-polymerization of DPS was obviously shifted to a lower point. The exothermic peak due to the Michael addition of the secondary hydrogen of the amine groups with BMI appeared around 300 °C when the DDS content was higher.

3.2 Curing Reaction of the BMI/Epoxy/DDS Blends

Excess BMI monomer can react with a diamine to produce a crosslinking resin (Tung et al., 1985), furthermore, the reaction system of BMI/epoxy/DDS blends would be more complicated (Tung, 1987; Park and Jang, 1992). The BMI/epoxy/DDS blends were prepared through the mixing of BMI monomers with various ratios of epoxy and the curing agent DDS. Fig. 3 shows the DSC trace of the DMS/Epon 828/DDS blending system. There were two exothermic peaks: 152 °C ($T_{\max 1}$) due to the Michael addition of BMI with DDS and the self-polymerization of DMS, and 225 °C ($T_{\max 2}$) due to the ring-opening reaction of the epoxy. $T_{\max 2}$ increased as the epoxy content increased, and this indicated that more of the secondary amine joined the ring-opening reaction of the epoxy. Besides, the secondary amine reacted with DMS via Michael addition at a higher temperature only when the epoxy content was lower. The Michael addition of the blend with 20% BMI, for example, appeared around 320 °C ($T_{\max 3}$). The thermal reactions of the other 2 BMI monomers (MPS, DPS) with epoxy are quite

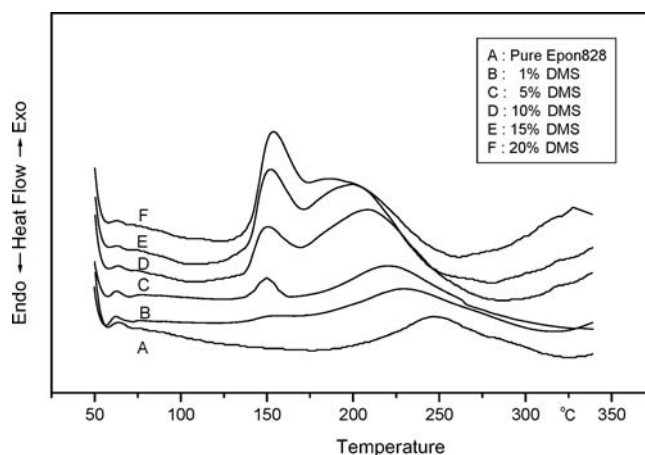


Fig. 3. DSC traces of the DMS/Epon828/DDS blending system in nitrogen gas

alike and all the data for the thermal reactions of these blending systems are listed in Table 1.

3.3 Characteristics of the BMI/Epoxy/DDS Blends

3.3.1 Dynamic Mechanical Properties

The dynamic mechanical properties of all the slices molded from the BMI/epoxy/DDS blends were measured under an air pressure. The dynamic mechanical analysis (DMA) traces of the BMI/Epon 828 blends are shown in Figs. 4 and 5. The T_g 's of the BMI/epoxy/DDS systems measured by DSC and the DMA method according to the maximum of loss modulus (G'') are also listed in Table 1. The storage modulus (G') and T_g of the Epon 828 system were decreased by the blending of the BMI monomer. This was attributed to the lower T_g of the BMI segments (138 °C for DMS, 142 °C for MPS, and 146 °C for DPS) (Shu, et al., 2009). Because the addition-reaction temperature of the BMI monomer with DDS was lower, the blends were expected to undergo the Michael addition reaction more easily when the BMI contents were increased. This could also reduce the crosslink density and T_g of the blend system. Besides, the DPS system which had a higher phenyl density also exhibited a lower value of G' because of the state of phase separation. Therefore, there was a trend of the second peak developing at a lower temperature, as shown in the $\tan \delta$ curve of Fig. 5. The incorporation of Si-containing BMI into epoxy had decreased the $\tan \delta$ maximum and storage modulus due to the increased crosslink density.

3.3.2 Mechanical Properties

The mechanical properties of the curing samples, such as the yield strength, Young's modulus, and breaking strength, were measured with the ASTM D 412-75 method. Table 2 shows the mechanical properties of all the BMI/epoxy/DDS blends. The mechanical strength of all the curing blends slightly decreased as the BMI contents increased. This was primarily re-

BMI type	Epoxy eq.%	BMI ^a eq.%	BMI wt.%	Si ^b wt.%	T _{max1} °C	T _{max2} °C	T _c °C	T _g °C
	100	0	0	0	247	–	235	204.4
DMS	99	1	2.3	0.15	150	227	215	202.5
DMS	95	5	10.7	0.69	152	222	210	187.1
DMS	90	10	20.2	1.31	153	207	200	182.3
DMS	85	15	28.6	1.86	155	203	195	160.4
DMS	80	20	36.2	2.35	157	200	190	154.7
MPS	99	1	2.6	0.15	151	230	220	203.1
MPS	95	5	12.0	0.68	152	226	215	191.8
MPS	90	10	22.4	1.27	154	221	210	185.2
MPS	85	15	31.5	1.78	156	218	210	173.5
MPS	80	20	39.4	2.23	158	212	205	167.2
DPS	99	1	2.9	0.14	155	232	220	204.1
DPS	95	5	13.4	0.67	157	227	220	195.1
DPS	90	10	24.5	1.23	159	224	215	187.3
DPS	85	15	34.1	1.71	162	221	210	175.9
DPS	80	20	42.3	2.13	165	218	210	171.3

T_{maxi} = exothermic peak temperature in the *i*th stage as measured by DSC at a heating rate of 10 °C/min;

T_c = temperature selected for the blends to cure;

T_g = glass transition temperature analyzed by DMA at a heating rate of 5 °C/min in air and DSC at a heating rate of 10 °C/min in N₂.

a: equality ratio of BMI and epoxy as they were cured with equality ratio of DDS.

b: theoretical calculation weight ratio of Si composition in blends.

Table 1. Compositions and thermal reaction temperatures of the BMI/epoxy/DDS blending system

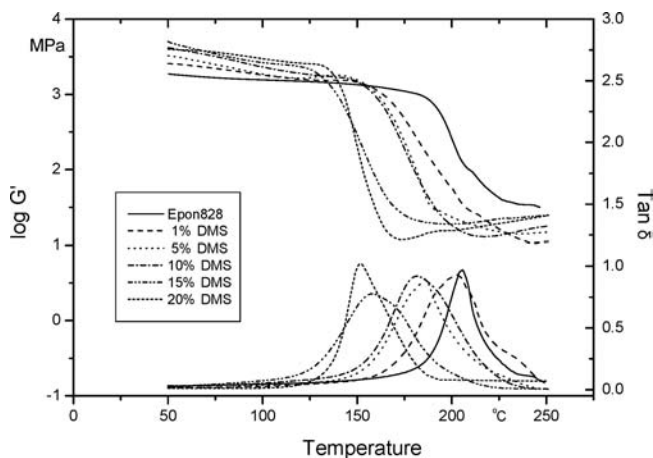


Fig. 4. DMA traces of the DMS/Epon828/DDS blending system

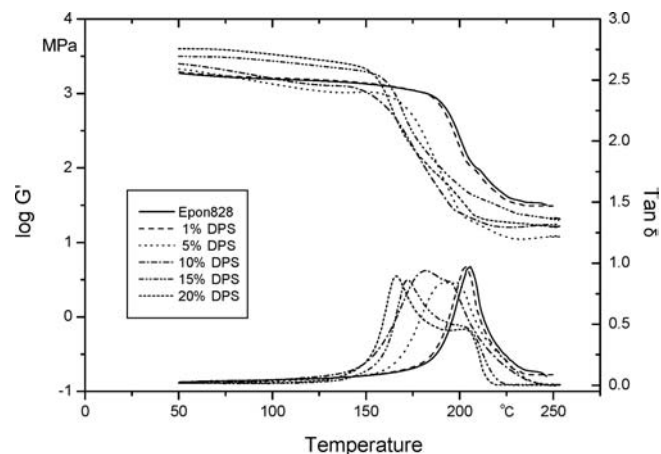


Fig. 5. DMA traces of the DPS/Epon828/DDS blending system

lated to the brittleness of BMI and the addition of BMI/DDS segments, which reduced the crosslink density of the epoxy system. On the contrary, the stiffness of BMI could be promoted efficiently with increases in the epoxy contents.

3.3.3 Thermal Properties

Fig. 6 shows the decomposition traces of the DMS/Epon828/DDS blending system analyzed by thermogravimetric analysis (TGA). The onset temperature (T_{5%}) of the blending system decreased as the contents of silicon increased under nitrogen or air pressure. This was primarily attributed to the lower chain energy of the silicon-containing segments. Also, Fig. 6A shows that all the cracking curves of the blends in N₂ were one-stage

pyrolysis curves and that the pyrolysis rate slowed as the adding ratio of DMS was gradually increased. The cracking curves of the blends in air, as shown in Fig. 6B, were two-stage pyrolysis curves. The first stage was due to the pyrolysis of the unstable silicon-containing segments and diamine segments, especially for the secondary amine groups (HN-C). The second stage was the pyrolysis of the stable five-member ring and imide groups, which could also be catalyzed by oxygen in air (Liu et al., 1996).

The TGA traces of the DPS/Epon828/DDS blending system are shown in Fig. 7. All the data for the thermal properties of these blends are also listed in Table 3. The pyrolysis conditions of the MPS or DPS blends were mostly like those of the DMS system. The T_{5%} values of the blends decreased as the silicon contents increased. Because the phenyl density of the DPS sys-

BMI type	Epoxy eq.%	BMI eq.%	Breaking stress N/mm ²	Breaking strain %	Yield stress N/mm ²	Modulus kN/mm ²
	100	0	52.9	5.2	52.0	2.63
DMS	99	1	52.0	5.1	51.0	2.57
DMS	95	5	49.0	4.8	49.0	2.43
DMS	90	10	47.1	4.7	47.1	2.36
DMS	85	15	46.1	4.5	46.1	2.30
DMS	80	20	45.1	4.4	45.2	2.26
MPS	99	1	51.0	5.0	49.0	2.56
MPS	95	5	47.1	4.7	47.1	2.37
MPS	90	10	46.2	4.6	46.2	2.26
MPS	85	15	45.1	4.5	44.1	2.25
MPS	80	20	43.1	4.2	43.1	2.22
DPS	99	1	51.0	5.0	48.0	2.55
DPS	95	5	46.1	4.6	46.1	2.33
DPS	90	10	44.1	4.4	44.1	2.24
DPS	85	15	43.2	4.2	43.1	2.22
DPS	80	20	42.2	4.0	42.2	2.20

a: According to the test method of ASTM-D412-75 with a sample size 50×12.7×1.25 mm

Table 2. Mechanical properties^a of the BMI/epoxy/DDS blending system

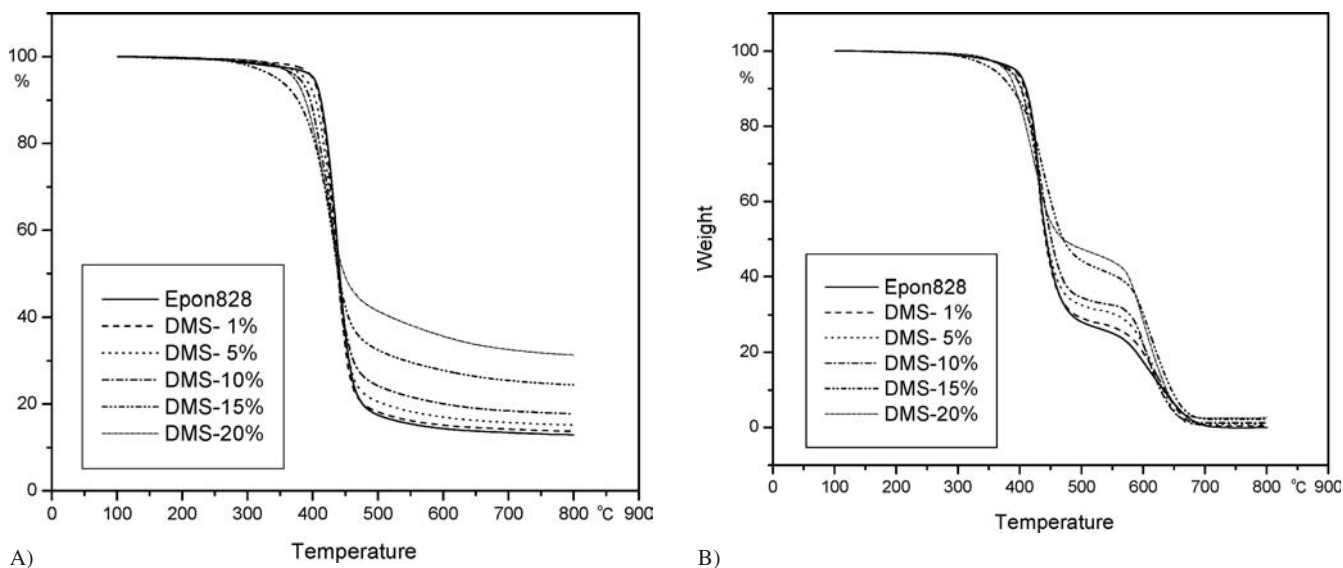


Fig. 6. TGA traces of the DMS/Epon828/DDS blending system: (A) in nitrogen gas and (B) in air

tem was higher, these blends exhibited better thermal stability. The DPS system exhibited a higher $T_{5\%}$ value than the DMS or MPS system as the data listed in Tables 3.

3.3.4 Flame Retardancy

The flame retardancy of all the curing blends was probably improved as the BMI contents increased. The decomposition reactions of all the silicon-containing blends were initialized mainly by the scission of silane segments with lower bond energy, and they produced further scission of the maleimide main chain along with carbonization, forming high char yields of solid residues. This was confirmed by the TGA traces (Shu et al., 2005) and LOI data listed in Table 3. The pyrolysis rate

slowed as the adding ratio of BMI was gradually increased. The char yield also obviously increased under nitrogen or air pressure. The LOI values of all the blend types also increased gradually as the BMI contents increased, and the trend mostly agreed with the char yields measured by TGA (van Krevelen, 1975). The LOI values of all the blend types were increased to about 30 as the BMI concentration reached 20%. The LOI of the DMS system with a higher percentage of silicon was higher than the LOI of the MPS or DPS system.

4 Conclusions

Three kinds of silicon-containing BMI monomers were applied to an epoxy blending system. Although the mechanical

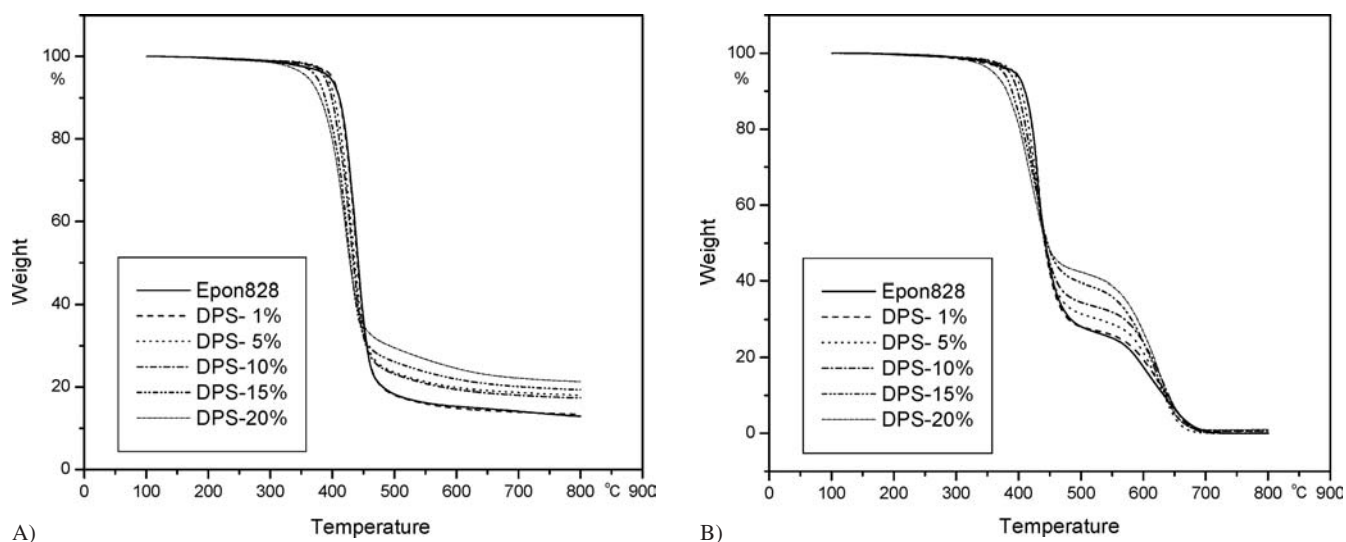


Fig. 7. TGA traces of the DPS/Epon828/DDS blending system: (A) in nitrogen gas and (B) in air

BMI type	Epoxy eq.%	BMI eq.%	Si wt.%	T _{5%} °C		Char at 800 °C wt.%		LOI ^b
				N ₂	Air	N ₂	Air	
	100	0	0	399	394	12.9	0.0	25
DMS	99	1	0.15	396	390	14.9	1.5	27
DMS	95	5	0.69	384	384	17.2	1.9	28
DMS	90	10	1.31	375	382	18.8	1.3	29
DMS	85	15	1.86	373	372	24.4	2.2	31
DMS	80	20	2.35	368	368	31.3	2.6	33
MPS	99	1	0.15	398	394	13.9	0.6	26
MPS	95	5	0.68	389	392	16.3	0.7	27
MPS	90	10	1.27	379	384	18.0	1.1	28
MPS	85	15	1.78	374	376	19.3	1.3	29
MPS	80	20	2.23	370	372	21.3	1.8	30
DPS	99	1	0.14	400	404	13.4	0.5	26
DPS	95	5	0.67	392	392	16.0	0.6	27
DPS	90	10	1.23	388	386	17.2	0.6	28
DPS	85	15	1.71	375	379	18.1	0.7	28
DPS	80	20	2.13	372	375	19.6	1.0	29

a: thermal properties were analyzed by TGA at a heating rate of 20 °C in N₂ or in air.

b: LOI was analyzed with an LOI chamber at an O₂/N₂ flow rate of 20 L/min.

Table 3. Thermal properties^a of the BMI/epoxy/DDS blending system

strength of the BMI/epoxy blends was slightly reduced, they still had good thermal stability and exhibited very good flame resistance. The conditions of the thermal reactions and the blend formulations of these systems can be used as a reference for the blending of normal resins in industry.

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