

# Studies on Fluorine-Containing Bismaleimide Resins Part II: Preparation and Characteristics of Reactive Blends of Fluorine-Containing Bismaleimide and Epoxy

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## ABSTRACT

*A series of fluorine-containing bismaleimide (FBMI) monomers were synthesized and added through blending to general epoxy system for application of low-dielectric content ( $D_k$ ) materials. The thermal analysis and dielectric property of the FBMI monomers in bisphenol-type epoxy system has been discussed. An increase in the FBMI contents decreases the glass-transition temperature ( $T_g$ ) and slightly reduces the mechanical strength of the epoxy blends. Although the initial pyrolysis temperature of all the blending systems gradually decreases as the fluorine-content increased, all the fluorine-containing epoxy systems still had good thermal stability. The FBMI-blends exhibit improved dielectric properties as compared with commercial epoxies with the dielectric constants ( $D_k$ ) lower than 3.07.*

*KEYWORDS: Dielectric property, Blends, Fluorine-containing bismaleimide, Thermal stability, Epoxy.*

## INTRODUCTION

Bismaleimide (BMI) resins are an important type of thermoset polymeric materials characterized by their high glass transition temperatures and high modulus.<sup>[1,2]</sup> 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.<sup>[3,4]</sup> 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<sup>[5-7]</sup>.

Epoxy resins can be introduced as plasticizers to improve the stiffness and processing of BMI resins, and the thermal stability 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, epoxy/BMI/diamine resins, exhibiting, like BMI, high glass-transition temperatures ( $T_g$ 's), hygroscopic characteristics, and dimensional stability, can be improved in other characteristics, such as poor adhesiveness, high brittleness, and high cost<sup>[8-10]</sup>. Besides, there are many reports on BMI-epoxy blend mediated by allylphenol derivatives in similar lines<sup>[11-14]</sup>. Blends of BMI with epoxy have become one of the main streams of research on BMI modification.

In recent years, many kinds of BMI resins blended with epoxy have been widely studied. Some fluorine-containing segments, for example, have been introduced to reduce the dielectric constant of BMI resins<sup>[15]</sup>. The low materials are generally defined as a material with dielectric constant ( $D_k$ ) below 3.9. The  $D_k$  of commercial epoxies, for example, are about 3.3-3.5. It is well known that incorporation of fluorinated groups into polymer's structure could effectively improve the dielectric property for applications in PCB substrates and electronic packaging technology. The  $D_k$  of polymer materials could be decreased sufficiently, which is related to the low polarizability of the carbon-fluorine (C-F) bond as well as the large molecular free volume in opposition to other atoms<sup>[16]</sup>. Besides, the hydrophobic and

oleophobic nature of perfluorinated alkyl groups could reduce  $T_g$  of materials and further decrease the dielectric constants<sup>[17]</sup>. The incorporation of fluorinated substituents in the network structure of epoxies will improve the resins durability in moist environments and lower their moisture adsorption<sup>[18]</sup>. Sasaki<sup>[19]</sup> incorporated perfluorobutenyloxy groups into the chain of epoxy resins and found that dielectric constant of the materials decreased to 2.7-2.8. Nakamura et al.<sup>[20]</sup> reported that fluorine modified bisphenol-A type epoxy could reduce the water adsorption by 75%. Maruno et al.<sup>[21]</sup> developed a novel fluorinated epoxy resin with alicyclic segments, which had improved optical transparency and low refractive index properties. Further, many high functional fluorinated epoxy resins, such as fluorinated epoxy acrylate for optical communication devices<sup>[22]</sup>, fluorinated resins for surface modifier or high-performance elastomers in UV-curing system<sup>[23-25]</sup>, and many studies based on blends of epoxy resins and versatile type resins had been explored<sup>[26-28]</sup>. On the other hand, recently, fluorinated polyimides have received much attention on optoelectronics industry because of their thermal properties and low dielectric constants for intermetal dielectric materials (IMD)<sup>[17]</sup>. Many studies demonstrate the synthesis of fluorine-containing polyimides by the incorporation of trifluoro-methyl groups and perfluoroalkyl groups, etc in order to reduce  $D_k$  and moisture adsorption and improve optical properties<sup>[29,30]</sup>. A problem often encountered with low  $T_g$  by introduction of perfluorinated alkyl group. Therefore, novel fluorinated polyimides with improving  $T_g$  were synthesized and characterized<sup>[31,32]</sup>.

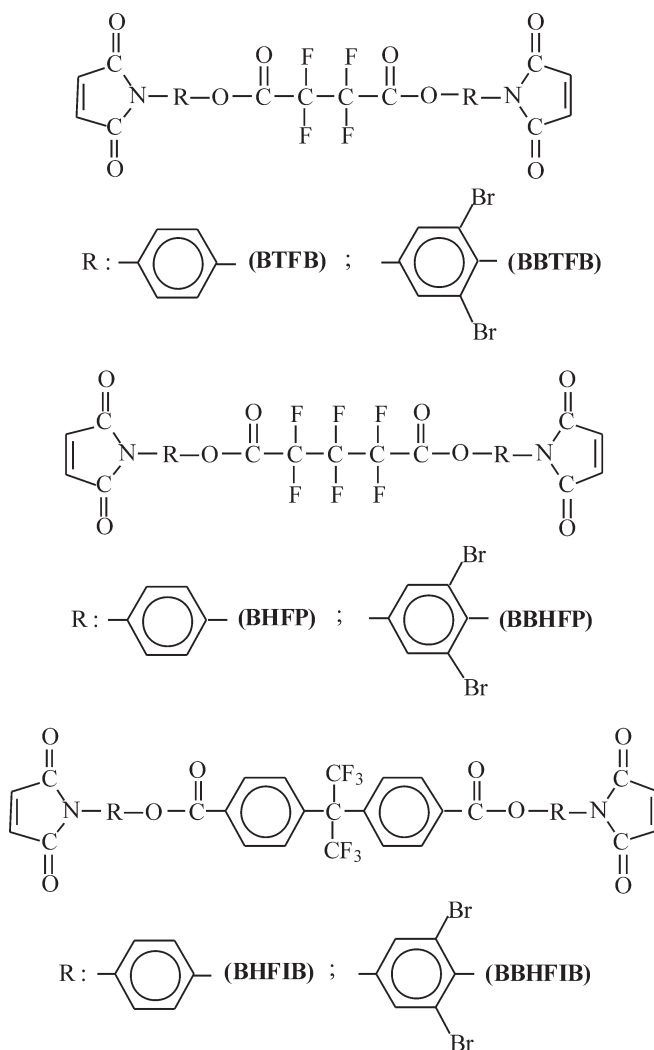
We have synthesized a series of fluorine-containing BMI monomers and their derivatives that exhibit low  $D_k$  and good flame resistance<sup>[33]</sup>. This research mainly concerns these novel F-containing BMI monomers blended with bisphenol-type of epoxy resins, examining the influence of the maleimide segments on the physical properties of general epoxy resins. The promoting effect of F-containing segments

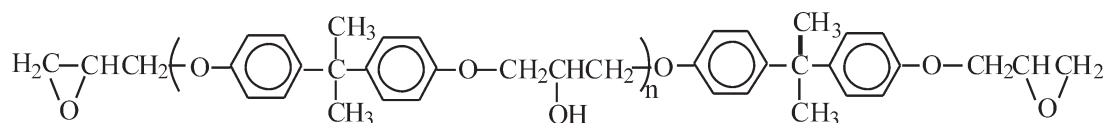
in dielectric property and Br-containing segments in flame retardancy has also been analyzed to confirm its practical value.

## EXPERIMENTAL

### Materials

A series of fluorine-containing bismaleimide (FBMI) monomers, Bis(4,4'-maleimidophenyl) tetra-fluoro-





butanedioate (BTFB), Bis(4,4'-maleimidophenyl) hexafluoropantanedioate (BHFP), Bis(4,4'-maleimidophenyl) hexafluoroisopropylidene bisbenzoate (BHFIB), Bis(2,6-dibromo-1-(N-maleimido)phenyl) tetrafluorobutanedioate (BBTFB), Bis(2,6-dibromo-1-(N-maleimido)phenyl) hexafluoropantanedioate (BBHFP) and Bis(2,6-dibromo-1-(N-maleimido)phenyl) hexafluoroisopropylidene bisbenzoate (BBHFIB) were synthesized by a 3-step reaction<sup>[33]</sup>.

The epoxy resin Epon 828 (Ep828, 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).

#### Preparation of Blending System

For the comparison of different epoxy equivalents, the synthesized FBMI monomers were mixed with epoxy and the curing agent DDS. DDS theoretically opened all the double bonds of FBMI and the epoxy groups. The mixture was then blended homogeneously at about 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 epoxy-FBMI blend systems were determined with differential scanning calorimetry (DSC). The temperatures below the top and the end of the exothermal peak 10°C had been taken as the temperature of the initial and post curing, respectively.

#### Instrumentation

The scanning curves of the FBMI and related blending resins were determined with a TA Instruments DSC10 instrument (New Castle, DE) at a heating rate of 10°C/min in N<sub>2</sub> for the analysis of the melting temperatures, curing parameters, and *T<sub>g</sub>*'s. The *T<sub>g</sub>* 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 N<sub>2</sub>. 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 O<sub>2</sub>/N<sub>2</sub> 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. The electrical properties are measured on a Precision Component Analyzer (Wayne Kerr 6440B).

## RESULTS AND DISCUSSION

### Thermal Reaction of FBMI with a Diamine

The FBMI monomer can react with a diamine via nucleophilic addition (Michael addition) to synthesize a polyaspartimide copolymer<sup>[34]</sup>. Such reaction of BMI with diamine had also been discussed in our previous paper<sup>[35]</sup>. Figures 1 and 2 show the DSC traces of the FBMI/DDS systems. In the BTFB/DDS system, as shown in Figure 1, the melting and curing temperature of BTFB were promoting as mixing with DDS. Besides, there was a eutectic phenomenon between the FBMI monomer and DDS: the melting point decreased as the DDS content increased. Because the secondary hydrogen within the amine groups of DDS could not react with FBMI easily, there was an exothermal peak around 260°C due to the Michael addition of the secondary hydrogen of the amine groups with FBMI which was followed by the primary addition and the self-polymerization of BTFB when the DDS content was lower to 25%. For the eutectic effect, the self-polymerization temperature of the BTFB monomer was shifted lower with increasing DDS content.

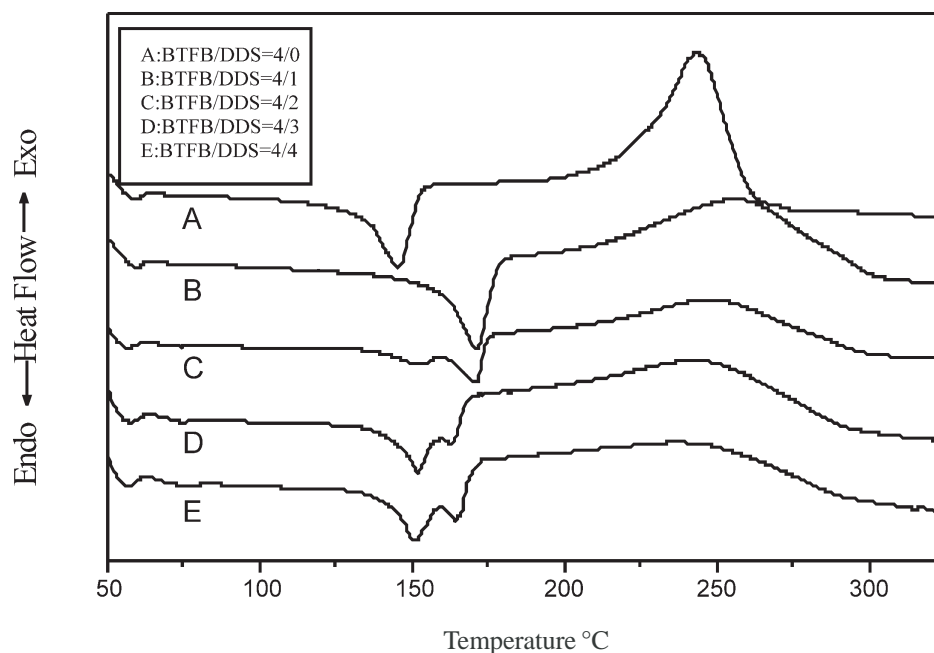


Figure 1. DSC traces of BTFB cured with various equivalent ratios of DDS in nitrogen gas.

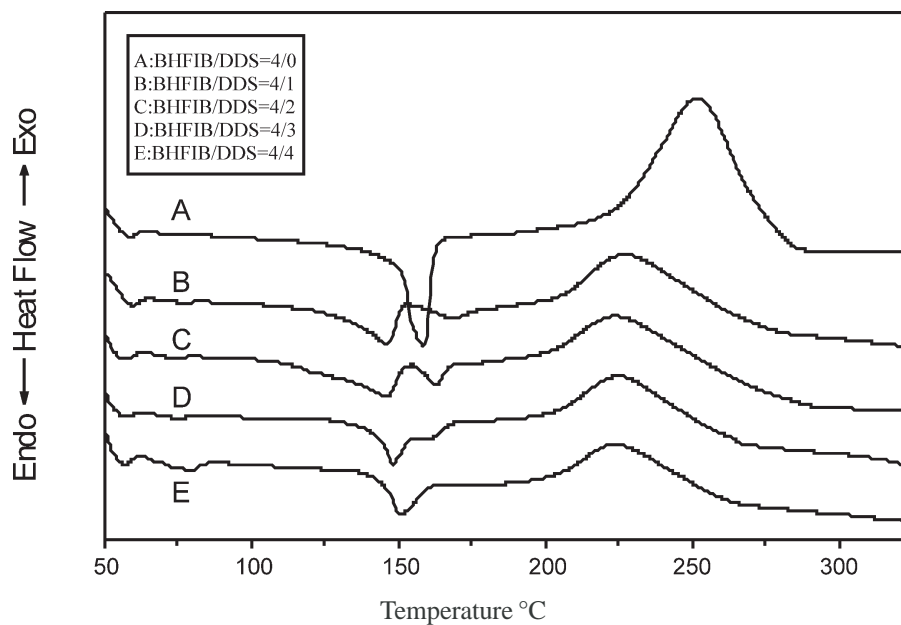


Figure 2. DSC traces of BHFIB cured with various equivalent ratios of DDS in nitrogen gas.

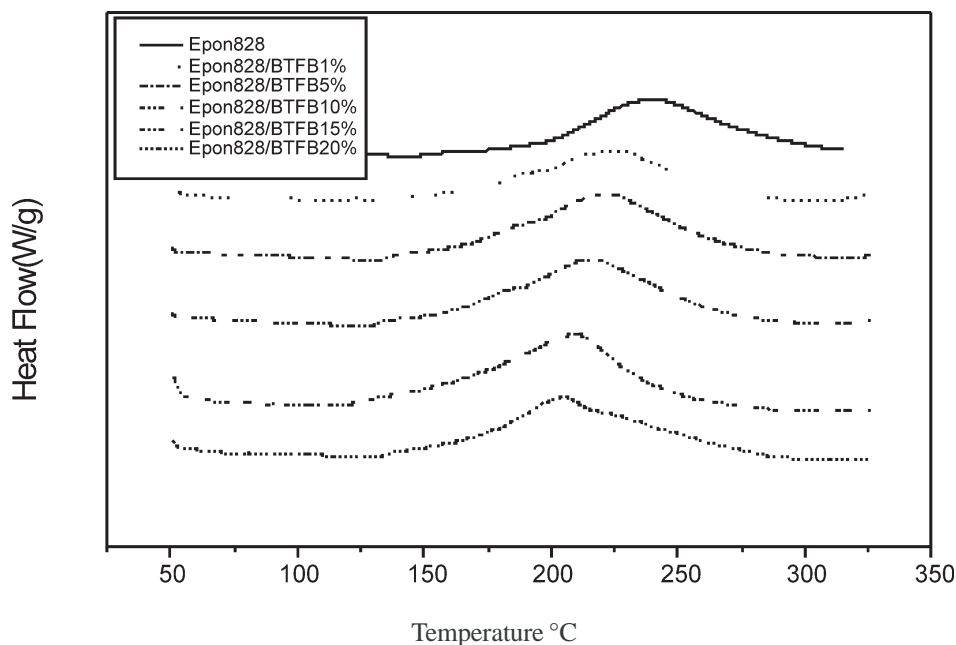


Figure 3. DSC traces of Epoxy/BTFB/DDS blending system

Figure 2 shows DSC traces of the BHFIB/DDS systems. The eutectic phenomenon between the BHFIB monomer and DDS was more obvious because their melting points were close. When the equivalent ratio of FBMI to DDS was 4/4, it exhibited a near eutectic state, with a eutectic point around 150°C. For the eutectic effect, the exothermal peak due to the Michael addition of the primary hydrogen of the amine groups with FBMI and the self-polymerization of BHFIB was obviously shifted to a lower point. The exothermal peak due to the Michael addition of the secondary hydrogen of the amine groups with FBMI appeared around 300°C when the DDS content was higher.

### Curing Reaction of the Epoxy/FBMI/DDS Blends

The Epoxy/FBMI/DDS blends were prepared through the mixing of FBMI monomers with various ratios of epoxy and the curing agent DDS. Figure 3 shows the DSC trace of the Epon 828/BTFB/DDS blending system. There was only one exothermal peaks: 205-225°C ( $T_{max}$ ) due to the Michael-addition of FBMI with DDS, the self-polymerization of FBMI, and the ring-opening reaction of the epoxy. The  $T_{max}$  decreased as the BTFB content increased, and this indicated that more of the amine reacted with FBMI via Michael-addition at a lower temperature. The thermal reactions of the other FBMI monomers (BBTFB, BHFP, BBHF, BHFIB, and BBHFIB) with epoxy are quite alike and all the data for the thermal reactions of these blending systems are listed in Table 1.

TABLE 1. Compositions and Thermal Reaction Temperatures of the Epoxy/BMI /DDS Blending System

BMI type	Epoxy <sup>a</sup> (eq.%)	BMI <sup>a</sup> (eq.%)	BMI (wt%)	T <sub>max</sub> (°C)	T <sub>c</sub> (°C)	T <sub>g</sub> (°C)
	100	0	0	240	230	205.5
BTFB	99	1	2.8	225	215	202.3
	95	5	12.8	222	210	192.5
	90	10	23.7	217	205	183.0
	85	15	33.1	210	200	175.6
	80	20	41.2	205	195	168.8
	0	100	100	210	200	128.0
BHFP	99	1	3.0	230	220	202.2
	95	5	13.9	227	215	193.2
	90	10	25.4	224	215	183.8
	85	15	35.1	221	210	176.0
	80	20	43.4	218	205	170.1
	0	100	100	215	205	132.0
BHFIB	99	1	3.8	235	225	202.1
	95	5	16.9	232	220	191.6
	90	10	30.0	228	215	182.2
	85	15	40.5	225	215	174.3
	80	20	49.1	223	215	168.9
	0	100	100	220	210	137.0
BBTFB	99	1	4.3	224	215	201.2
	95	5	19.0	220	210	188.8
	90	10	33.2	215	205	177.5
	85	15	44.1	207	200	169.0
	80	20	52.7	202	190	162.9
	0	100	100	200	190	131.0
BBHFP	99	1	4.6	229	220	201.4
	95	5	19.9	225	215	189.3
	90	10	34.4	222	210	178.5
	85	15	45.5	219	210	170.8
	80	20	54.2	216	205	164.6
	0	100	100	212	200	136.0
BBHFIB	99	1	5.3	234	225	201.0
	95	5	22.5	230	220	188.8
	90	10	38.0	225	215	178.1
	85	15	49.4	223	215	171.0
	80	20	58.0	221	210	165.1
	0	100	100	217	205	141.0

T<sub>max</sub>: exothermic peak temperature measured by DSC at a heating rate of 10°C/min; T<sub>c</sub>: temperature selected for the blends to cure; T<sub>g</sub>: 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 N<sub>2</sub>. a: Equality ratio of BMI and epoxy as they were cured with equality ratio of DDS.

## Characteristics of the Epoxy/FBMI/DDS Blends

### Glass-transition temperature

The  $T_g$ 's of the Epoxy/FBMI/DDS systems measured by DSC and the dynamic mechanical analysis (DMA) method according to the maximum of loss modulus ( $G''$ ) are listed in Table 1. The  $T_g$ 's of the Epon 828 system were decreased by the blending of the FBMI monomer. This was attributed to the lower  $T_g$  of the FBMI segments (such as 128°C for BTFB, 132°C for BHFP and 137°C for BHFIB)<sup>[33]</sup>. As the addition reaction temperature of the FBMI monomer with DDS was lower, the blends were expected to undergo the Michael-addition reaction more easily when the FBMI contents were increased. This could also reduce the crosslink density and  $T_g$  of the blend system. Besides, the  $T_g$  of BHFIB/BBHFIB system due to the high density of benzene ring is higher than the other series.

### 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 Epoxy/FBMI/DDS blends. The mechanical strength of all the curing blends slightly decreased as the FBMI contents increased. This was primarily related to the brittleness of FBMI and the addition of FBMI/DDS segments, which reduced the crosslink density of the epoxy system. On the contrary, the stiffness of FBMI could be promoted efficiently with increases in the epoxy contents.

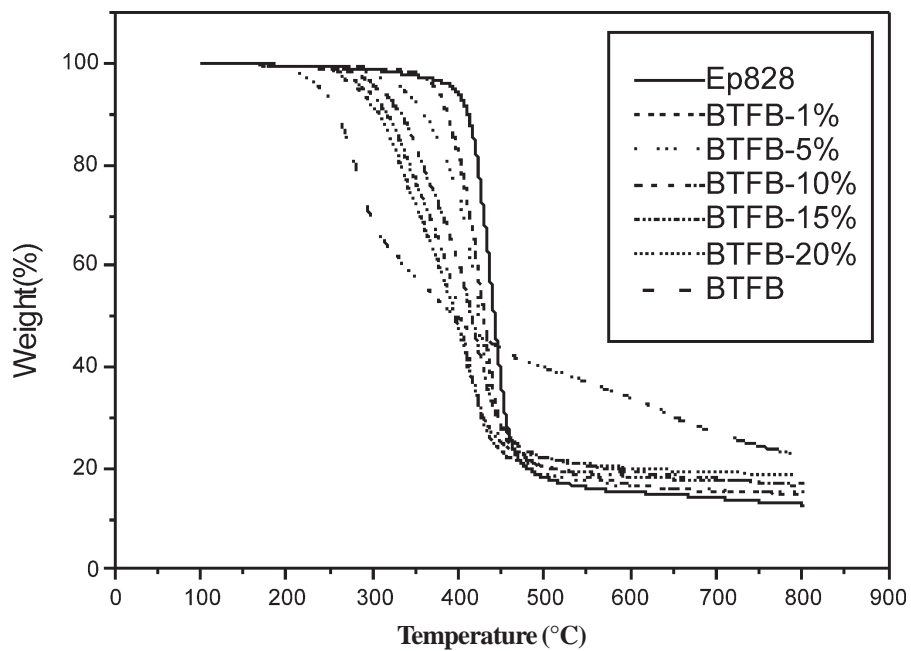
## Thermal Properties

Figure 4 shows the decomposition traces of the Epon828/BTFB/DDS blending system analyzed by thermogravimetric analysis (TGA). The onset temperature ( $T_{5\%}$ ) of the blending system decreased as the content of FBMI increased under nitrogen or air pressure. This was primarily attributed to the lower chain energy of the F-containing segments. Also, Figure 4(a) shows that all the cracking curves of the blends in  $N_2$  were one-stage pyrolysis curves. The pyrolysis rate slowed down as the adding ratio of BTFB was gradually increased.

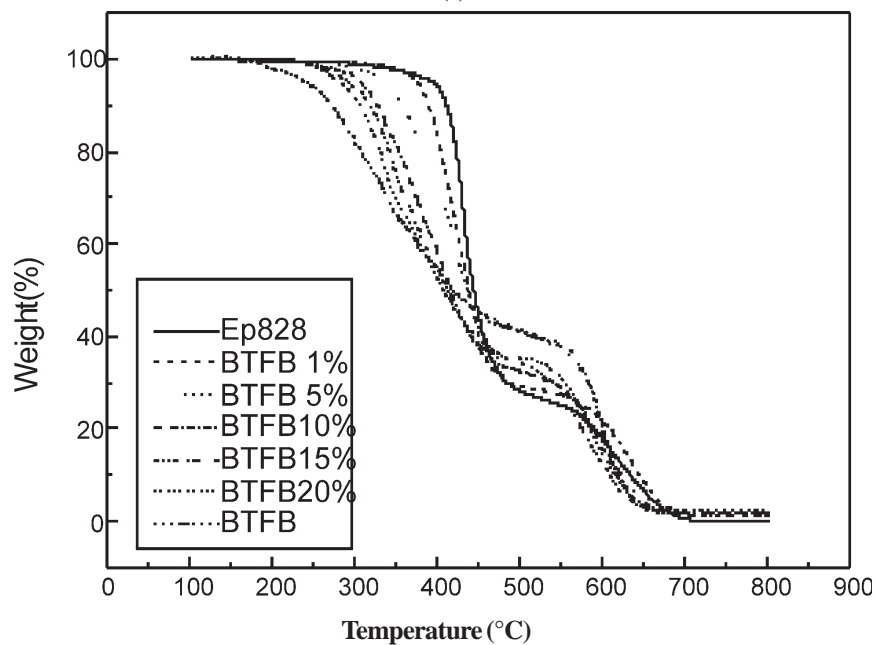
The cracking curves of the blends in air, as shown in Figure 4(b), were two-stage pyrolysis curves. The first stage was due to the pyrolysis of the unstable F-containing segments and diamine segments, especially for the secondary amine groups (HN-C). The second stage was the pyrolysis of the stable five-member ring and imide groups, which could also be catalyzed by oxygen in air<sup>36</sup>.

The TGA traces of the Epoxy/BBTFB/DDS blending system are shown in Figure 5. All the data for the thermal properties of these blends are also listed in Table 3. The pyrolysis conditions of the BHFP/BBHFIP or BHFIB/BBHFIB blends were mostly like those of the BTFB/BBTFB system. The  $T_{5\%}$  values of the blends decreased as the FBMI contents increased. Because the higher density of benzene ring within BHFIB/BBHFIB system, it exhibits better thermal stability, such as a higher  $T_{5\%}$  value, than the other systems as the data listed in Table 3.





(a)



(b)

Figure 4. TGA traces of the Epon828/BTFB/DDS blending system: (a) in nitrogen gas and (b) in air.

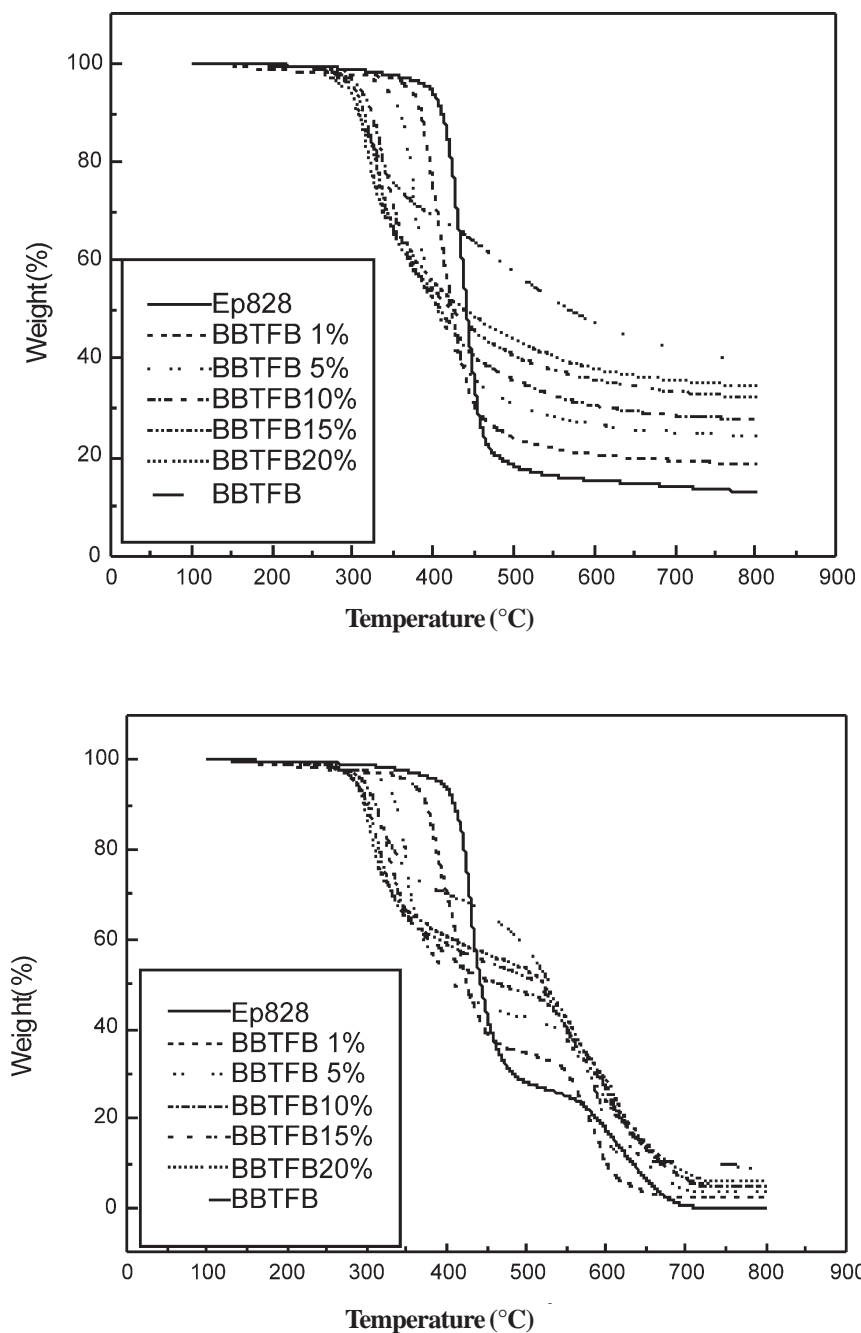


Figure 5. TGA traces of the Epon828/BBTFB/DDS blending system: (a) in nitrogen gas and (b) in air.

TABLE 2. Mechanical Properties<sup>a</sup> of the Epoxy/BMI/DDS Blending System

BMI type	Epoxy (eq.%)	BMI (eq.%)	Breaking Stress (N/mm <sup>2</sup> )	Breaking Strain (%)	Yield Stress (N/mm <sup>2</sup> )	Modulus (kN/mm <sup>2</sup> )
	100	0	52.9	5.2	52.0	2.63
BTFB	99	1	51.3	4.9	49.3	2.52
	95	5	48.8	4.6	47.4	2.37
	90	10	46.9	4.4	46.2	2.31
	85	15	45.6	4.3	44.0	2.29
	80	20	44.0	4.0	43.5	2.26
BHFP	99	1	52.0	5.0	49.8	2.59
	95	5	51.2	4.7	48.8	2.43
	90	10	48.5	4.5	48.2	2.37
	85	15	47.4	4.4	46.0	2.35
	80	20	45.9	4.2	45.7	2.32
BHFIB	99	1	52.4	4.7	51.1	2.61
	95	5	51.5	4.4	49.2	2.45
	90	10	48.7	4.2	48.4	2.39
	85	15	47.6	4.1	46.3	2.37
	80	20	46.1	3.9	46.9	2.35
BBTFB	99	1	51.2	5.0	49.1	2.51
	95	5	48.6	4.8	47.1	2.35
	90	10	46.8	4.5	46.0	2.30
	85	15	45.4	4.4	43.7	2.27
	80	20	43.7	4.2	43.2	2.23
BBHFP	99	1	51.9	5.2	49.6	2.58
	95	5	51.0	4.9	48.6	2.41
	90	10	48.4	4.8	48.0	2.35
	85	15	47.1	4.7	45.7	2.31
	80	20	45.7	4.4	45.4	2.30
BBHFIB	99	1	52.2	4.6	50.9	2.60
	95	5	51.3	4.2	49.1	2.43
	90	10	48.6	4.0	48.2	2.37
	85	15	47.4	3.9	46.0	2.34
	80	20	45.9	3.6	46.5	2.32

a: According to the test method of ASTM-D412-75 with a sample size 50x12.7x1.25mm

TABLE 3. Thermal Properties and Dk of the Epoxy/BMI/DDS Blending System

BMI type	Epoxy (eq.%)	BMI (eq.%)	F (wt%) <sup>a</sup>	Br (wt%) <sup>a</sup>	T <sub>5%</sub> at N <sub>2</sub> (°C) <sup>b</sup>	Char at 800 °C (wt%) <sup>b</sup>		LOI <sup>c</sup>	k <sup>d</sup>
						N <sub>2</sub>	Air		
	100	0	0	-	399	12.2	0.0	25	3.35
BTFB	99	1	0.39	-	374	14.9	1.2	26	3.07
	95	5	1.83	-	336	15.3	1.4	27	2.77
	90	10	3.39	-	307	16.6	1.7	28	2.49
	85	15	4.72	-	291	17.2	1.9	30	2.46
	80	20	5.88	-	282	18.8	2.1	31	2.33
	0	100	14.29	-	240	22.5	2.2	35	2.24
BHFP	99	1	0.59	-	372	15.9	1.4	27	2.98
	95	5	2.72	-	333	17.3	1.7	28	2.70
	90	10	4.97	-	305	19.9	2.0	29	2.43
	85	15	6.87	-	288	20.7	2.2	30	2.41
	80	20	8.49	-	280	23.1	2.5	32	2.31
	0	100	19.59	-	235	24.7	2.8	36	2.18
BHFIB	99	1	0.58	-	381	16.0	1.5	27	2.98
	95	5	2.62	-	366	18.2	1.9	28	2.72
	90	10	4.66	-	325	20.0	2.3	29	2.58
	85	15	6.30	-	310	21.3	2.6	30	2.45
	80	20	7.63	-	291	23.4	2.9	31	2.37
	0	100	15.53	-	251	25.4	3.2	35	2.20
BBTFB	99	1	0.38	1.63	372	18.4	2.2	28	3.07
	95	5	1.70	7.18	343	24.3	3.4	30	2.79
	90	10	2.97	12.51	309	27.6	4.7	32	2.68
	85	15	3.94	16.63	302	32.1	5.2	35	2.47
	80	20	4.73	19.90	296	34.3	6.1	38	2.45
	0	100	8.96	37.74	287	39.7	7.8	43	2.28
BBHFP	99	1	0.58	1.62	370	17.1	2.2	28	2.97
	95	5	2.53	7.10	341	24.0	3.1	30	2.73
	90	10	4.37	12.27	305	26.8	3.6	33	2.60
	85	15	5.77	16.21	288	29.7	4.1	36	2.45
	80	20	6.88	19.30	280	32.5	4.7	39	2.43
	0	100	12.69	35.63	265	36.0	5.2	43	2.26
BBHFIB	99	1	0.57	1.61	380	17.0	2.0	28	2.97
	95	5	2.45	6.87	362	23.2	2.8	30	2.74
	90	10	4.13	11.59	321	25.9	3.3	32	2.62
	85	15	5.36	15.05	313	27.1	3.7	34	2.48
	80	20	6.30	17.68	298	28.3	4.2	36	2.44
	0	100	10.86	30.48	293	30.0	4.6	41	2.28

a: To be the theoretical calculation values of F/Br composition ratio.

b: Analyzed by TGA at a heating rate of 20° in N<sub>2</sub> or in air: The T<sub>5%</sub> represents the onset temperature of 5% weight loss.

c: LOI was analyzed with an LOI chamber at an O<sub>2</sub>/N<sub>2</sub> flow rate of 20L/min.

d: Dielectric constants of FBMI blends(at 500MHz).

### Flame Retardancy

The flame retardancy of all the curing blends was probably improved as the FBMI contents increased. The decomposition reactions of all the F-containing blends were initialized mainly by the scission of C-F or C-Br 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 and LOI data listed in Table 3. The pyrolysis rate slowed as the adding ratio of FBMI 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 FBMI contents, especially the Br 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 31-39 as the FBMI concentration reached 20%.

### Electrical and dielectric properties

The electrical properties of the FBMI resins were studied by measuring the dielectric constant ( $D_k$ ). The  $D_k$  for the FBMI resins were measured by a dielectric spectrometer at 500MHz and ambient temperature. The dielectric constants of FBMI resins are listed in Table 3. The  $D_k$  of these blends decreases with the increase of the fluorine content. All the  $D_k$ 's of FBMI-blending resins are lower than 3.07. The BHFP/BBHFP system with the higher fluorine content exhibited the lower  $D_k$ . The decreased dielectric constants of the fluorinated resins can be interpreted by the low polarizability of the C-F bond and the large free volume of  $CF_3$  groups. These results suggested

that the C-F bond or  $CF_3$  groups in the network structure of FBMI resins play an important role in their electrical and dielectric performances.

### CONCLUSIONS

A series of fluorine-containing BMI monomers were blended with an epoxy resin system. Although the mechanical strength of the Epoxy/FBMI blends was slightly reduced, but they shown good thermal stability and improved dielectric properties as compared with commercial resins with the  $D_k$  lower than 3.07. Besides, the flame retardancy of all these blend system could be enhanced via the introduction of Br atom. 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. All the novel F-containing bismaleimide monomers can be applied as the low dielectric content materials or modifier in the blending systems of general resins.

### REFERENCES

1. R. H. Pater, *SAMPE J.* **30** (1994) 29.
2. P. Mison and B. Sillion, *Adv. Polym. Sci.* **140** (1999) 137.
3. D. O. Hummel, *J. Appl. Polym. Sci.* **18** (1974) 2015.
4. K. Iwata, *J. Polym. Sci. Polym. Chem. Ed.* **14** (1976) 2841.
5. J. E. White, *Ind. Eng. Chem. Prod. Res. Dev.* **25** (1986) 395.
6. M. F. Loustalot and L. D. Cunha, *Polymer*, **39** (1998) 1799.
7. W. J. Shu and R. S. Tsai, *Int. Polym. Pro.* **25** (2010) 125.

8. T. S. Wang, J. F. Yeh and M. D. Shau, *J. Appl. Polym. Sci.* **59** (1996) 215.
9. W. J. Shu, W. K. Chin, and H. J. Chiu, *J. Appl. Polym. Sci.* **92** (2004) 2375.
10. X. H. Xiong, P. Chen, J. X. Zhang, Q. Yu and B. C. Wang, *J. Appl. Polym. Sci.* **121** (2011) 3122.
11. C. P. Reghunadhan Nair, *Prog. Polym. Sci.* **29** (2004) 401.
12. D. Ambika, C. P. Reghunadhan Nair, R. Sadhana and K. N. Ninan, *Polym. Polym. Compos.* **16** (2008) 447.
13. K. A. Devi, C. P. Reghunadhan Nair and K. N. Ninan, *Polym. Polym. Compos.* **17** (2009) 141.
14. V. Gaina and C. Gaina, *Polym. Plast. Technol.* **48** (2009) 525.
15. Y. Kawai, S. Nishimura, A. Nagai, M. Suzuki, S. Amo and A. Takahashi, *Japan Pat.* (1993) JP05-140304.
16. D. W. Van Krevelen, "Properties of Polymers", 3<sup>rd</sup> ed. Amsterdam:Elsevier, (1990) p321.
17. G. Maier, *Prog. Polym. Sci.* **26** (2001) 3.
18. H. P. Hu, R. D. Gilbert and R. E. Fornes, *J. Polym. Sci. Part A: Polym. Chem.* **25** (1987) 1235.
19. S. Sasaki, *J. Polym. Sci. Part C: Polym. Lett.* **24** (1986) 249.
20. S. Sasaki and K. Nakamura, *J. Polym. Sci. Polym. Chem. Ed.* **22** (1984) 831.
21. T. Maruno, K. Nakamura and N. Murata, *Macromol.* **29** (1996) 2006.
22. T. Maruno and K. Nakamura, *J. Appl. Polym. Sci.* **42** (1991) 2141.
23. M. Sangermano, R. Bongiovanni, G. Malucelli, A. Priola, A. Policino and A. Recca, *J. Appl. Polym. Sci.* **89** (2003) 1524.
24. Z. K. Hu, L. M. Pitet, M. A. Hillmyer and J. M. DeSimone, *Macromol.* **43** (2010) 10397.
25. Z. Hu, J. A. Finlay, L. Chen, D. E. Betts, M. A. Hillmyer, M. E. Callow, J. A. Callow and J. M. DeSimone, *Macromol.* **42** (2009) 6999.
26. F. R. Dammont and T. K. Kwei, *J. Polym. Sci. Part A-2: Polym. Phys.* **5** (1967) 761.
27. T. E. Twardowski and P. H. Geil, *J. Appl. Polym. Sci.* **41** (1990) 1047.
28. J. R. Lee, F. L. Jin and S. J. Park, *J. Appl. Polym. Sci.* **98** (2005) 1860.
29. E. T. Ryan, A. J. McKerrow, *J. Leu and P. S. Ho, MRS Bull.* **22** (1997) 49.
30. F. W. Mercer and M. T. McKenzie, *High Perform. Polym.* **5** (1993) 97.
31. F. Li, S. Fang, J. Ge, P. S. Honigfort, J. C. Chen, F. W. Harris and S. Z. D. Chen, *Polymer* **40** (1999) 4571.
32. C. Y. Yang, S. L. C. Hsu and J. S. Chen, *J. Appl. Polym. Sci.* **98** (2005) 2064.
33. Z. Y. Wang, J. C. Ho and W. J. Shu, *J. Appl. Polym. Sci.* **123** (2012) 2977.
34. J. V. Crivello, *J. Polym. Sci. Polym. Chem. Ed.*, **11** (1973) 1185.
35. W. J. Shu and R. S. Tsai, *Des. Monomers Polym.* **13** (2010) 33.
36. Y. L. Liu, G. H. Hsiue, Y. S. Chiu, R. J. Jeng and C. Ma, *J. Appl. Polym. Sci.* **59** (1996) 1619.

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