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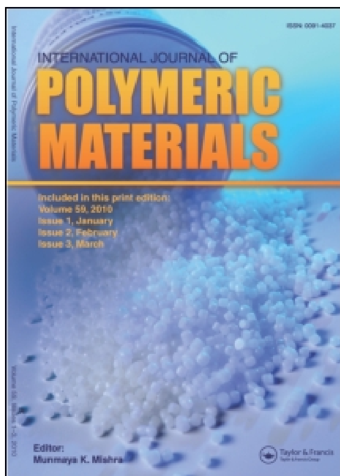

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Effects on Dielectric Properties of Modified Bismaleimide Resins

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Six modified bismaleimide (BMI) resin systems are developed. The modifier is diallyl bisphenol A, diallyl bisphenol A ether, TDE–85 epoxy/MNA anhydride, and styrene, respectively. In view of structure of those cured resins, relationships between structure and dielectric properties have been studied emphatically, while effects of postcure temperature and catalysts on dielectric properties were also shown. Results indicate that dielectric properties lie on structure of cured resin and postcure temperature; catalysts can strikingly improve the heat–resistance of materials, but has little effect on the dielectric properties. In addition, mechanical and thermal properties of neat resins were also shown.

Keywords: Dielectric properties; Bismaleimide; Catalysis; High performance radome

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1. INTRODUCTION

Worldwide research efforts have focused on development of new materials for high technology applications. One such application is the need for an improved material for advanced aircraft radomes. These radomes are required to have high temperature strength and thermal shock resistance, maintenance of a low dielectric constant (ε) and loss tangent (tgδ) and have improved rain erosion resistance. Radomes are usually made up of reinforcements and matrix resins, the usable reinforcements are high purity glass fibers (such as E–glass fiber, fused silica fiber, etc.), and organic fibers (such as kevelar, polyeneylene, etc.). After the reinforcements have been chosen, properties of radomes mainly depend on matrix resins.

For past decade, several high performance radome resins have been developed, such as polyester, polyimide, polybutadiene, etc. [1 ~ 2]. But

thermal abilities of polyester and polybutadiene do not meet the needs of modern aerospace industry. On the other hand, processing features of polyimide are poor.

Bismaleimide (BMI) belongs to addition–type polyimide, it has been widely used in aerospace industry because of its high temperature stability, good dielectric and mechanical properties, and fine environment resistance (in particular in hot/wet situation) [3 ~ 4]. However, the cured resin is brittle and the processing characteristics are not good. So numerous research approaches are being investigated in the search for new and improved materials. This paper introduces six modified BMI resins to be considered as future radome materials and discusses the relationship between formular, chemical structure and dielectric properties of the six systems.

2. EXPERIMENTAL

2.1 Starting Materials

4,4'–bismaleimidodiphenyl methane (MBMI), mp 156 ~ 158 °C, was obtained from HuBei Fengguang Chemicals, China and recrystallized from methylene chloride. Diallyl bisphenol A (DBA) and diallyl bisphenol A ether (DBAE) were supplied by Sicuan Jiangyou Insulation Factory, China. Commercial epoxy resin TDE—85 (epoxy content 8.5 equivalents/kg; viscosity 1.6 ~ 2.0 poise at 25 °C) and MNA anhydride were obtained from 637th Research Institute of Chinese Aviation Corporation. Styrene, imidazole and diisopropylbenzyl peroxide (DIPBP) were supplied by Xi' an Reagent Factory, China.

2.2 Preparation of Prepolymer and Neat Resin

Six modified bismaleimide resin system formulations were evaluated. They were:

System	Formulation
I	MBMI: DBA (100: 80 Weight Ratio)
II	MBMI: DBAE (100: 80 Weight Ratio)
III	System I: styrene (81: 20 Weight Ratio)
IV	System I: TDE—85 epoxy: MNA anhydride (70: 12: 18 Weight Ratio)

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V System I: imidazole : DIPBP
(100: 0.02: 0.5 Weight Ratio)
VI System II: imidazole: DIPBP
(100: 0.02: 0.5 Weight Ratio)

Appropriate quantities (depending on each system except V and VI) of all components were weighed in a three necked round bottom flask equipped with a mechanical stirrer and a thermometer. The reaction mixture was stirred at 110 ~ 150 °C for 0.5 ~ 1 hour to form a homogenous solution. The resultant liquid was prepolymer I, II, III and IV, respectively.

Prepolymer V and VI were prepared by adding appropriate quantities of imidazole and DIPBP in prepolymer I and II at 60 ~ 70°, respectively, stirring the mixture till a clear homogenous liquid was obtained.

Neat resin was prepared by degassing and casting the prepolymer into preheated glass moulds and cured. The following two cure and postcure cycles were used.

System I ~ IV:

120 °C/2hrs + 150 °C/2hrs + 180 °C/2hrs + 200 °C/2hrs + 220 °C/10hrs

System V ~ VI

120 °C/2hrs + 150 °C/2hrs + 180 °C/2hrs + 200 °C/12hrs

2.3 Measurement of Neat Resin

Tensile and flexural data were obtained according to GB1451–83 and GB3356–82, respectively. Impact strength was done by GB1451–83. In addition, Heat Deflection Temperature (HDT) and dielectric properties were measured by GB1634–79 and GB1409–78, respectively, and density by GB1033–86.

Glass transition temperature (T_g) was measured by differential scanning calorimetry (DSC) method. DSC was employed with a Du Pont Model 910 at a heating rate of 10 °C/min in a nitrogen atmosphere.

3. RESULTS AND DISCUSSION

3.1 Reaction Mechanism and Cured Structure of System I ~ IV

Dielectric properties of polymer depend on its chemical structure, and the structure is associated with the reaction mechanism.

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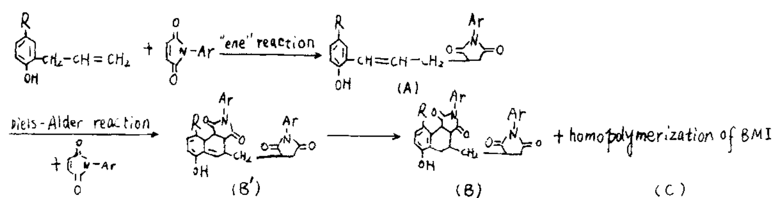
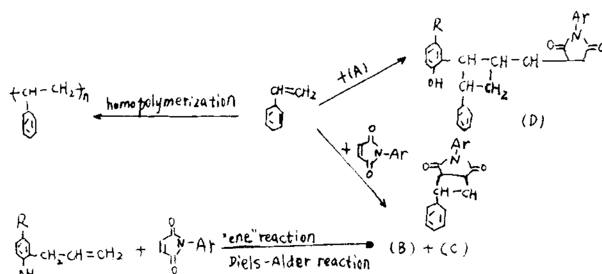
It was well established that the curing reaction of system I can be divided into two steps [5], as shown in Scheme 1. The first step is the addition of the maleimide to the allyl group through a so-called "ene" addition reaction. The second step is a combination of the Diels-Alder process and an anionic imide oligomerization.



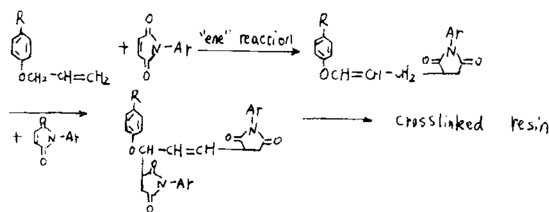
Scheme 1

The curing reaction of system II is the copolymerization of MBMI and DBAE, as shown in Scheme 2.



Scheme 2

System III is made up of MBMI, DBA and styrene, its copolymerization is complex. In addition to the reaction of system I, there are reactions between MBMI and styrene as well as the oligomerization of styrene, as shown in Scheme 3.



Scheme 3

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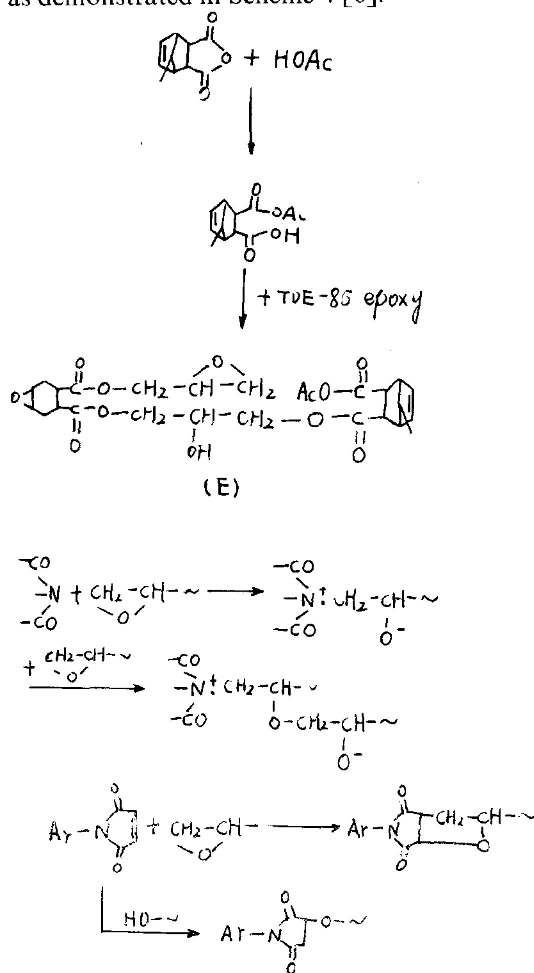
System IV has four components, its product is a combination of B and E obtained by the reaction of TDE—85 epoxy/MNA anhydride and copolymers developed by reaction between E and compounds containing hydroxy, as demonstrated in Scheme 4 [6].



Scheme 4

3.2 Relationships Between Cured Structure and Dielectric Properties of Neat Resins

Table I lists dielectric properties of various resins, it indicates that cured structure is very closely correlated with dielectric properties. Dielectric

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TABLE I Dielectric properties of neat resins

System / *Item*	*I*	*II*	*III*	*IV*
ε	2.94	2.92	2.90	2.93
tgδ	0.0117	0.0116	0.007	0.0142

properties of polymer depend on orientation and relaxation of dipole in electric field, so polarity and activity of dipole of polymer are key features to determine the dielectric properties. System I and II have alike cured structure, so their dielectric properties are alike. Both of them have polar groups such as —CO—, and —OH, but they are restricted in hybrid rings which develop rigid coupled and symmetric structure. In addition, —OH and benzenic ring also develop coupled system and the whole moleculare is in cross-linking state, so polar groups of polymers are difficult to orientation and relaxation in electric field, and their dielectric properties, especially tgδ is low. If styrene was employed to copolymerized with system I (as system III), the cured structure III will have little polarity, and as a result, ε and tgδ of system III are low. In contract, adding TDE—85 epoxy and MNA anhydride in system I (as system IV), the tgδ of system IV will be high because polar groups (such as —COOH, —OH, etc) in the chain increase and they will relax in alternating electric field.

In the term of cross-linked polymer, cross-linking will hind the action of dipole, so the degree of cross-linking density has effect on dielectric properties. This can be manifested by dielectric properties of resins after postcured at different temperature. It can be seen from Table II that when the postcure temperature is high, the tgδ of neat resin is low.

TABLE II tgδ of neat resins after postcured at different temperature

System / *Postcure condition*	*I*	*II*	*III*	*IV*
220°C 12hrs	0.0117	0.0116	0.0007	0.0142
240°C 12hrs	0.0110	0.0108		0.0127

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3.3 Catalyst's Effect on Dielectric Properties of Neat Resins

System I and II have good dielectric properties, but their postcure temperatures are as high as 220 °C. In order to reduce them, imidazole and DIPBP are employed as catalysts. Table III lists the correlation of chosen catalysts with ε and tgδ of neat resins. It can be seen that the postcure temperatures of system I and II can reduce from 220 to 200 °C, but their ε and tgδ have little change. This reflects that catalysts used in system I and II can accelerate their curing reactions, but have little effect on cross-linking structure.

3.4 Mechanical and Thermal Properties of Neat Resin I ~ V

Cure reactions of system I ~ V belong to the addition reaction class. During curing, no by-products of low molecular weight were generated, the cure structure obtained is compact and has fewer defects. Table IV shows the neat resin properties. It can be seen that properties of system I are similar to that of system II, and all of them are good. Thermal properties of system III and IV are not as good as that of system I and II, this is because of the presence of styrene and TDE—85 epoxy/MNA anhydride in system III and IV, respectively.

System V has the best thermal properties of all systems presented in Table IV, which are manifested in the high HDT, T_g and strength retention. In the case of flexural strength, when tested at 150, 180 and 200 °C, 93, 88 and 81% of the original room temperature strength is retained, respectively. These values indicate that imidazole and DIPBP can greatly improve the thermal properties of system I.

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TABLE III Relationship between catalysts and dielectric properties of System I ~ II

Property / *Postcure condition*	*System*	*I*	*II*	*III*	*IV*
220 °C/12hrs	ε	2.94	2.92	/	/
	tgδ	0.0117	0.0116	/	/
200 °C/12hrs	ε	/	/	2.93	2.92
	tgδ	/	/	0.0118	0.0111

TABLE IV Mechanical and thermal properties of neat resins

Property / *System*	*I*	*II*	*III*	*IV*	*V*
Density, g cm^{3}	1.21	1.21	1.21	1.23	1.21
R.T. Tensile					
Strength, MPa	73	72	69	60	74
Modulus, GPa	3.61	3.65	3.45	4.0	3.82
Elongation, %	2.02	2.0	2.7	2.1	1.93
Flexural Strength, MPa					
R.T.	112	110	97	124	110
150 C	70	72		73	103
180 C	61	59		/	96
200 C					88
Impact Stength, kJ m^{2}	14.5	13.8	10.4	11.3	9
G_{IC}, J m^{2}	178			/	/
HDT, C	268	272	198	224	290
T_g (by DSC), C	274	276	250		317
IDT[a], C	425	429	418	382	456
PDT^{b}_{max}, C	447	451	470	419	510
Y^{c}_{c}, %	24.2	24.5		29.2	29.4

[a]Temperature of initial weight loss.
[b]Maximum polymer decomposition temperature.
[c]Char yield at 700 C.

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4. CONCLUSIONS

Dielectric properties of modified bismaleimide resins depend on their cross-linking structure, so modifiers have great effect on dielectric properties of modified bismaleimide resins. In this paper, styrene modified resin has the best dielectric properties, the two resins modified by daillyl bisphenol A and dially bisphenol A ether, respectively, have the alike dielectric properties due to their alike chemical structure. The worst dielectric properties obtained by the system containing TDE—85 epoxy/MNA anhydride.

The bismaleimide system modified by diallyl bisphenol A can be cured and postcured at lower temperature while remaining good dielectric properties and improving thermal properties by adding desirable catalysts.

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