Thermal and Dielectric Properties of Bismaleimide Polymers

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A series of bismaleimide monomers and polyaspartimides with various structures were synthesized and their structures were confirmed by Fourier transform infrared (FTIR) and proton nuclear resonance (^{1}H-NMR) spectroscopy. Chain extension of bismaleimides was accomplished by incorporating various ether or other groups. Polymers based on these bismaleimides were prepared by the Michael addition of diamines with various structures to bismaleimides. Thermal and dielectric properties of these polymers were studied.

Keyword: bismaleimides, polyaspartimides, thermal and dielectric properties

BMI-based resins have been steadily attracted attention because of their remarkable heat resistance, mechanical and dielectric properties. These resins are of great interest also because they have a good retention of the mechanical properties even after long ageing times at 250 °C, excellent chemical and radiation resistance [1-4]. Also bismaleimide resins are of great interest due to their processability by resin transfer molding, without formation of volatile by-products. Polybismaleimide resins possess many desirable properties, which make them very attractive for various applications. The application areas for these resins are as composites for printed circuit boards and structural laminates with glass, aramide and carbon fibers [5-7]. Major applications of these resins are for aero-engines and military aircraft parts. These polymers have potential applications in second order, non-linear optical (NLO) materials, which maintain the critical orientation of the NLO chromophore [8].

The reactivity of bismaleimide monomers is determined by the abilities of their double bond to add monomers bearing an active hydrogen atom, to act as a dienophyle in Diels-Alder reactions, and to enter into reactions of radical and anionic homopolymerization and copolymerization with other monomers containing unsaturated bonds or with cyclic compounds.

Unfortunately, these resins have a number of disadvantages, such as brittleness (due to their high crosslink density), high melting and curing temperatures and poor solubility in ordinary solvents which considerably restrict their applications [9-10].

Bismaleimide monomers and diamines were varied systematically with the target of identifying a system with the lowest possible dielectric constant, yet without compromising their significant properties.

Experimental part

Materials

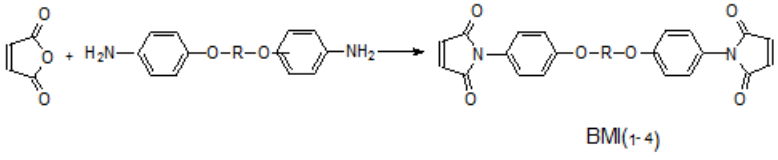
The materials used in this research were: maleic anhydride, triethylamine (TEA) and 4,4'-oxydianiline (DDE) (Fluka), and acetic anhydride (Merck). The diamines used in this study, except DDE, were prepared according to the method of Feld *et al.* with some modifications [11], and are as follows: 1,4-bis(4-aminophenoxy)-2-phenyl-benzene (BAPPB), 4-[4-[1-[4-(4-aminophenoxy)phenyl]-1-phenyl-ethyl]phenoxy]aniline (BAPDP), 2,7-bis(4-aminophenoxy)naphthalene (BAPN), 2,2-bis[(4-aminophenoxy)phenyl]propane (BAPPP) and 1,2-bis-[2-(4-aminophenoxy)ethoxy]ethane (BAPEE).

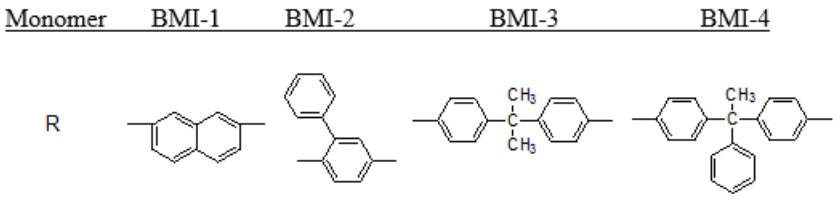
General procedure for the preparation of bismaleimides BMI (1-4)

The bismaleimides BMI(1-4) were prepared from the corresponding diamines and maleic anhydride by a modification of the method of White *et al.* [12] (scheme 1). Diamine (0.03 mol) dissolved in 50 mL acetone was reacted with maleic anhydride (0.06 mol) in 50 mL acetone, to give the corresponding bismaleamic acid. The mixture was stirred for 30 min at 20-25°C, and then the temperature was raised to 40°C. Over a period of 15 min, TEA (0.03 mol), acetic anhydride (0.20 mol) and magnesium acetate (0.05 g) were added. The mixture was refluxed for 1.0 h under nitrogen atmosphere. The hot solution was filtered, cooled and poured into cold water. The product was washed with a solution of sodium carbonate (10%) until free from acetic acid. Finally, it was washed with water and dried in vacuum.

Synthesis of polyaspartimides P(1-7)

Into a 50-mL three-necked flask fitted with a mechanical stirrer, a thermometer, and a nitrogen inlet, bismaleimide (0.02 mol), diamine (0.02 mol) in *N*-methyl-2-pyrrolidone





Scheme 1

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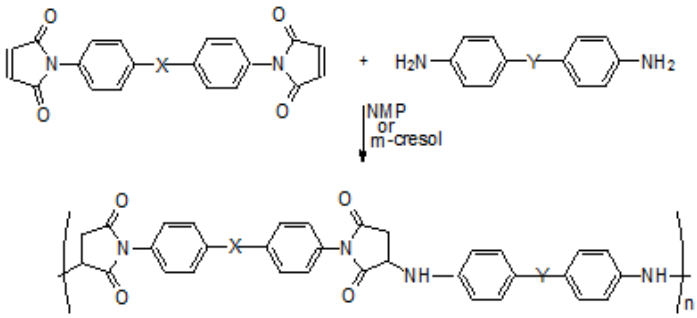

Scheme 2

(NMP) or *m*-cresol as solvent (up to 10 -15% of monomer concentration) and a small amount of acetic acid were charged. The reaction mixture was kept in a water bath at 90-95°C, for different time intervals. The polymer was isolated by pouring the reaction mixture into methanol. All polymers were redissolved in fresh solvent, precipitated in a nonsolvent medium, and dried for 20 h in a vacuum oven at 90°C [13]. The synthesis pathway to prepare these polymers is illustrated in scheme 2.

Results and discussions

Monomer synthesis

The chemical structure of all synthesis compounds was confirmed by means of elemental analysis, FTIR and ^{1}H-NMR spectroscopy. The FTIR spectra of bismaleimide monomers showed two doublet characteristic peaks in the range 1773-1772 and 1715-1713 cm^{-1} attributed to C=O from imide group. All monomers showed an absorption band in the range 1247-1231 cm^{-1} due to the ether unit, whereas BMI(3-4) exhibited bands at 2977-2924 cm^{-1} attributed to the aliphatic group.

All bismaleimides BMI (1-4) were characterized and by ^{1}H-NMR spectroscopy which confirmed their chemical structure. Figure 1 shows the ^{1}H-NMR spectrum of compound BMI-2. The aromatic protons appear as a doublet in the 7.54-7.52 ppm range, attributed to the protons H_g, while a triplet appears in the 7.41-7.30 ppm range corresponding to the protons H_h, H_i, H_d and H_f. The aromatic protons in the 7.27-7.25 ppm range are attributed to the protons H_b (*ortho* to maleimide). A triplet in the 7,23-7.20 ppm range is due to the aromatic protons H_e. The signal in the 7.19-7.17 ppm range is attributed to the protons $H_{b'}$ and H_a. Other singlet appears at 7.17 ppm and is due to olefinic protons $H_{a'}$ and a quartet between 7.14 and 7.12 ppm region is attributed to protons H_c. The doublet in the 7.02-7.00 ppm region is due to the aromatic protons $H_{c'}$.

The thermal properties of monomers were evaluated by DSC and TGA (table 1). The onset temperatures for curing reaction of these bismaleimides were in the 215-230 °C range. The reactivity of the C=C double bond from maleimide ring is influenced by the chemical nature of the residue between maleimide groups. The higher the electron-withdrawing capacity of the maleimide substituents, the higher the cure temperature and the slower the cure rate are. The thermal stability of samples was investigated by TGA in nitrogen.

The initial decomposition temperatures (IDT) of monomers are in the range 427-457°C and the rapid weight loss occurs in the region 448-553°C. It is observed that IDT is higher for BMI(2-4) while BMI-1 shows lower value of IDT. The percentage char yield at 700 °C varied between 49 and 53 %.

Polymer synthesis

A series of linear polyaspartimides was obtained by a Michael addition reaction (scheme 2) and the results are summarized in table 2.

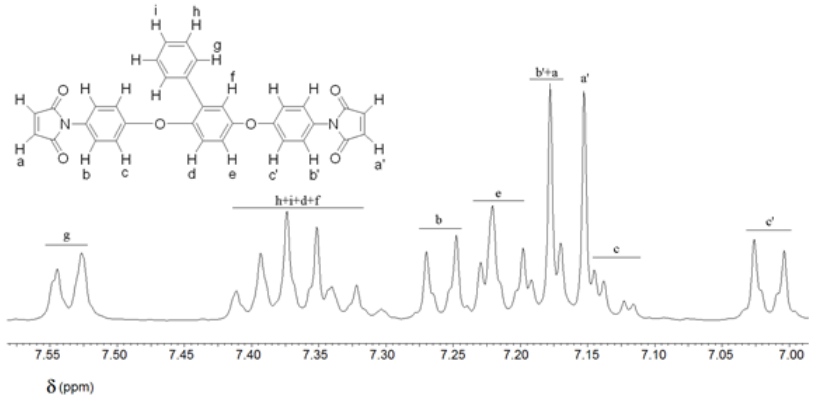

Fig. 1. ^{1}H-NMR spectrum of monomer BMI-2

Monomer	mp (°C)	T_{end}[b] (°C)	T_p[c] (°C)	IDT[d] (°C)	PDT_{max}[e] (°C)	Y_c[f] (%)
BMI-1	92-96	91	225	427	448,553	50
BMI-2	169-173	177	215	455	480	53
BMI-3	140-143	142	230	457	485	49
BMI-4	107-111	110	227	451	487	52

Table 1
THERMAL PROPERTIES OF MONOMERS BMI(1-4)

[a] *thermogravimetric measurements were carried out in air;* [b] *endothermic peak temperatures were evidenced by DSC;*
[c] *onset temperature for curing reaction;* [d] *initial decomposition temperature;* [e] *maximum decomposition temperature;*
[f] *residual weight percent at 700 °C;* [g] *melting point was determined by DSC*

Polymer	BMI	Diamine	Reaction temp (°C)	Reaction time (h)	Solvent	η^a (dLg^{-1})	Film
P-1	BMI-2	BAPPP	90	25	NMP	0.42	flexible
P-2	BMI-4	BAPPE	95	25	NMP	0.37	flexible
P-3	BMI-1	BAPPE	90	20	NMP	0.33	flexible
P-4	BMI-2	BAPPE	95	25	*m*-cresol	0.38	flexible
P-5	BMI-4	BAPDP	95	25	NMP	0.41	flexible
P-6	BMI-1	DDE	95	35	NMP	0.34	flexible
P-7	BMI-4	DDE	95	28	*m*-cresol	0.39	flexible

Table 2
REACTION BETWEEN BISMALEIMIDES AND DIAMINES P(1-7)

[a] Inherent viscosity, measured at a concentration of a 0.5 gdL^{-1} in NMP at 25 °C

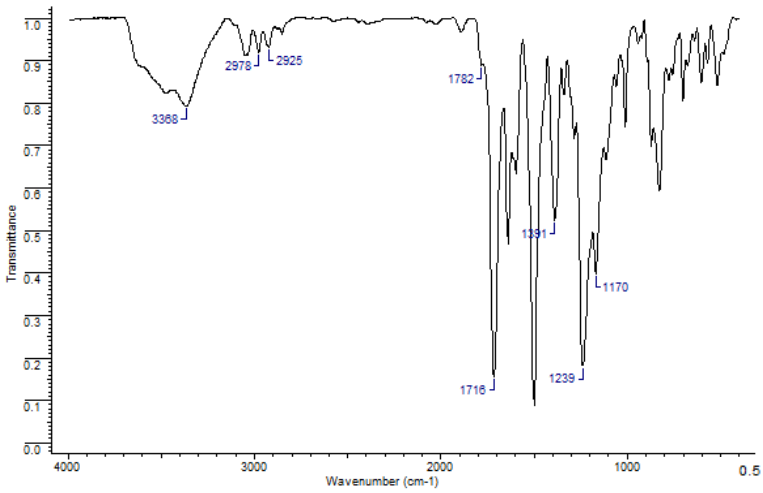

Fig. 2. FTIR spectrum of polymer P-7

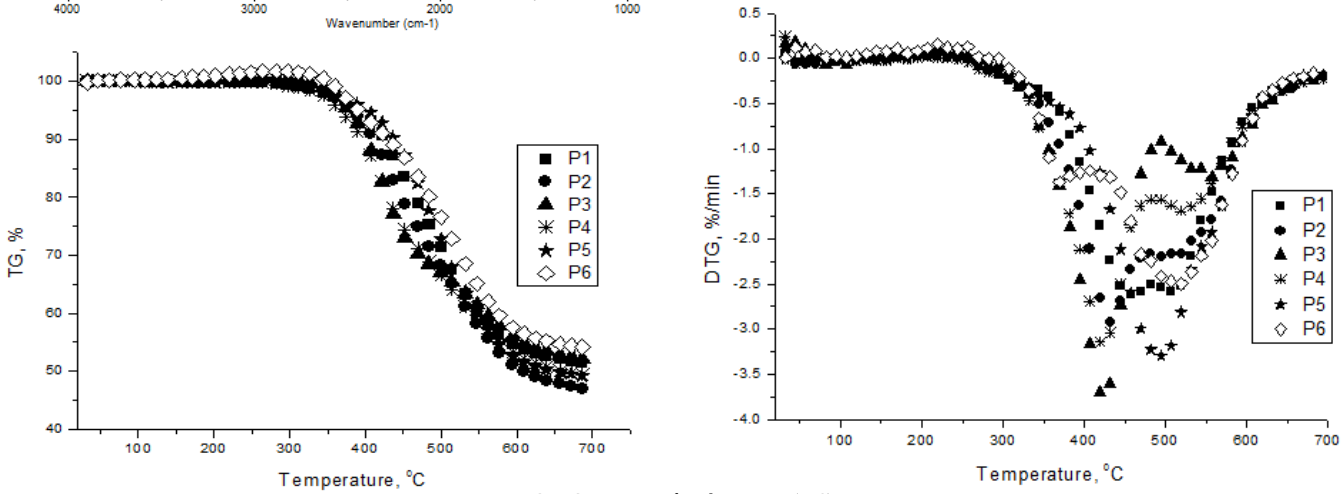

Fig. 3. TG curves of polymers P(1-6)

Polymer	Tg[b] (°C)	IDT[c] (°C)	PDT_{max}[d] (°C)	T_{25}[e] (°C)	Y_c[f] (%)
P-1	-	366	456. 509	478	51
P-2	206	355	428	460	47
P-3	198	358	436. 560	444	52
P-4	-	325	426. 520	445	49
P-5	211	331	377. 508	407	38
P-6	225	324	490	495	49
P-7	208	340	377. 517	508	54

Table 3
THERMAL PROPERTIES OF POLYMERS[a] P(1-7)

[a] thermogravimetric measurements were carried out in nitrogen atmosphere. [b] glass transition temperature. [c] initial decomposition temperature. [d] maximum decomposition temperature. [e] the temperature at which 25% weight loss was recorded. [f] residual weight percent at 700 °C.

	1Hz	10Hz	10^2Hz	10^3Hz	10^4Hz	10^5Hz	10^6Hz
150°C	3.59	3.57	3.56	3.55	3.53	3.52	3.50
P-1							
175°C	4.19	4.06	3.99	3.95	3.90	3.87	3.84
150°C	3.80	3.61	3.65	3.61	3.57	3.54	3.51
P-2							
175°C	10.04	5.80	5.05	4.76	4.60	4.47	4.38
150°C	3.48	3.45	3.44	3.42	3.39	3.36	3.32
P-3							
175°C	3.73	3.67	3.64	3.61	3.58	3.55	3.50
150°C	6.21	4.29	3.88	3.69	3.57	3.48	3.41
P-4							
175°C	37.37	14.26	6.48	4.93	4.38	4.06	3.84
150°C	3.17	3.15	3.13	3.11	3.08	3.06	3.05
P-5							
175°C	3.32	3.25	3.22	3.20	3.16	3.13	3.11

Table 4
DIELECTRIC CONSTANTS *VS* FREQUENCY AT 150 AND 175°C OF POLYMERS P(1-5)

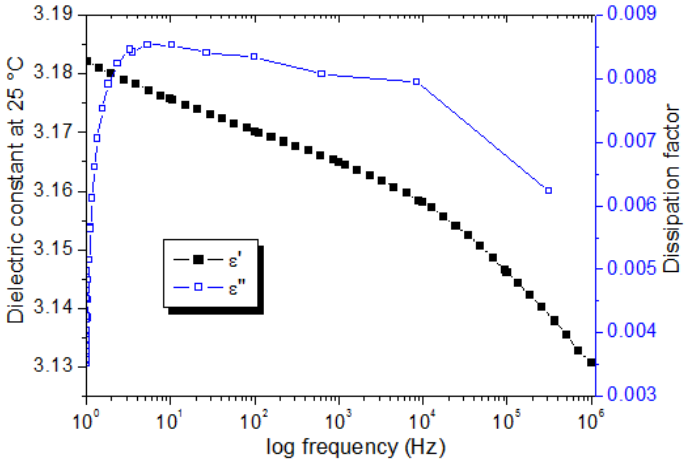

Fig. 4. Dielectric const. and loss *vs* frequency at 25°C of polymer P-1

The structure of the polymers was confirmed by means of FTIR spectroscopy. Figure 2 presents the spectrum of polymer P-7. Two characteristic carbonyl bands around 1782 and 1716 cm^{-1} are due to asymmetric and symmetric stretching vibration, respectively. Other bands were observed in the range 2978-2925 cm^{-1} and are ascribed to aliphatic groups (-CH_2). At the same time, the band at 1147 cm^{-1}, due to maleimide ring, disappeared, and a band at 1170 cm^{-1}, due to succinic ring, appeared, which indicated that maleimide C=C bond reacted.

The thermal properties of polyaspartimides P(1-7) were evaluated by DSC and TGA. The representative TGA curves of these polymers obtained in nitrogen atmosphere are shown in figure 3. The thermal behavior data of these compounds are summarized in table 3.

The T_g values of the compounds P(2-3) and P(5-7) were in the range 198-225 °C, depending on the stiffness of the polymer chain, while polymers P-1 and P-4 do not show any glass transition temperature up to 350°C. T_g's of these polyaspartimides were influenced by the asymmetry and irregularity which disturbed the chain interaction and induced the decrease of T_g. At the same time, the attachment of bulky substituents on the aromatic units resulted in an increased rigidity of polymer backbone and the consequent hindrance brought about the increase of T_g. All polymers were stable up to 325-366 °C and the weight loss (1-3%) observed in this interval was associated with evaporation of humidity and solvent traces. The highest values of IDT were obtained for polymers P(1-3). The polymers P-4 and P-6 showed lower IDT. The char yield of the polyaspartimides was in the range of 38-54 % when heated to 700 °C in nitrogen.

The dielectric properties (dielectric constant and loss) of the polyaspartimide films were evaluated from -100 to 200 °C at a heating rate of 2 °Cmin^{-1}. The frequency range used for measurements was from 1 to 10^6 Hz. For signal propagating, a material with low dielectric constant and loss is good for enhancing the speed and reducing the loss, so low dielectric constant and dielectric loss are necessary and characterized feature of the materials for producing high-performance dielectrics [14].

It is known that structures with low polar linkages and bulky groups show low dielectric constant and low dielectric loss, on one hand due to the low polarity of the groups and on the other hand due to the less efficient chain packing leading to an increase in the free volume of the polymer.

In figure 4 are represented the curves of dielectric constant and dielectric loss at 25 °C versus frequency for polymer P-1. It is observed that the value of dielectric constant decreases from 3.18 at 1 Hz to 3.13 at 10^6Hz, while dielectric loss also decreases within this frequency interval.

The dielectric constants of these polymers show a small and gradual increase with temperature up to 175°C. In table 4 are represented the variation of dielectric constant *versus* frequency of polymers P(1-5) at 150 and 175°C. These are between 3.08 and 3.50 at 100 °C and 1Hz frequency while at the same temperature and 10^6 Hz frequency these values are between 2.93 and 3.38.

Conclusions

Bismaleimides and polyaspartimides with various structures containing flexible linkages were synthesized and characterized. Thermal properties of the monomers

and polymers were influenced by the rigidity, symmetry and conditions of reaction. The dielectric constant values of the polymer films P(1-5) at -100 °C were in the range 2.58–3.05 and at 150 °C were in the range 3.08-3.57 at frequency of 10^4 Hz. It is expected that these polymers, which combined advantages of good dielectric constant, high-temperature resistance and easy processing, would contribute to extend the field of their applications as high performance polymers.

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