Materials Based on Bismaleimide Polymers with Potential Applications

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A series of bismaleimides were used to prepare polymers in an attempt to achieve materials with improved properties. Structurally different bismaleimide compounds were synthesized by the reaction between 3(4)-maleimidobenzoylchloride with various diphenols having or not substituents to the aromatic rings. Polymers based on these compounds were prepared by the Michael addition of diamine to bismaleimides. Fourier transform infrared (FTIR), proton nuclear resonance (^{1}H-NMR), differential scanning calorimetry (DSC), thermogravimetric analysis (TGA) and atomic force microscopy (AFM) were used to characterize these materials.

Keywords: bismaleimide monomers and polymers, thermal characterization

Bismaleimide polymers are an addition polyimides class obtained from bismaleimide monomers which contain unsaturated end groups.

Bismaleimide resins are of great interest because of their unique dimensional, excellent processing characteristics, without the formation of volatile by-products, good retention of thermomechanical properties even after long ageing times at 250°C, excellent chemical, radiation and corrosion resistance, easy processability by resin-transfer molding [1-10].

These resins are widely used as high performance composite matrices, multi-layer printed circuit boards for large-scale computers, advanced composites for aerospace industries, structural adhesive [11-15].

These compounds are the easiest to fabricate and can be processed using similar conditions to epoxy resins.

Unfortunately, these resins have a number of disadvantages, such as brittleness (due to their high crosslink density), a high melting and curing temperature, and poor solubility in ordinary solvents [16-18].

To obtain polymers with improved mechanical properties, thermal resistance and processability, bismaleimide monomers that have various structures have been synthesized.

Experimental part

Materials

Maleic anhydride (Fluka), 3(4)-aminobenzoic acid (Fluka), acetic anhydride (Merck), triethylamine (Fluka), bromine (Fluka), 2,2-bis(4-hydroxyphenyl) propan (Fluka), 4,4-(hexafluoroisopropylidene)diphenol (Fluka), bis(4-hydroxy phenyl)sulfone (Fluka) are commercially available products and were used as received.Thionyl chloride (Fluka) was purified by distillation under reduced pressure.Commercial solvents such as, acetone (Chemical Company S A), 1,2-dichloroethane (Fluka), chloroform (Fluka), glacial acetic acid (Fluka) and N-methyl-pyrrolidone (Riedel-Haen) were dried and purified by standard methods.

1.2-Bis[2-(4-aminophenoxy)ethoxy]ethane (APEE) was prepared according to the method Feld et al.[19]. 1,4-Bis(aminophenoxy)diphenylsulfone (APDPS) (Fluka), 4,4-diaminodiphenylether (DDE) (Fluka) and 1,4-bis(4-aminophenoxy) benzene (APB) (Fluka) have been provided by commercial source and purified by recrystallization

Synthesis monomers

3(4)-Maleimido Benzoic Acid (3(4)-MBA). The products were obtained as described [20], m.p. 3-MBA; 236-240°C, toluene; m. p. 4-MBA; 228-230°C, toluen 239-241°C and 225-228°C, respectively 3(4)-Maleimido Benzoic Acid Chloride (3(4)-MBAC) [21]. The products were prepared as described in literature [22], m.p. 3-MBAC; 125-128°C, dichlorethane; m.p. 4-MBAC; 169-171°C, m.p.4-MBAC; 170°C [23].

Tetrabromobisphenols (tetrachlorobisphenols)

Brominated(chlorurate) bisphenols were preparated as follows [24]:

- in a 100 mL flask, 0.02 mol of bisphenol was dissolved in 100 mL of glacial acetic acid. To this solution, 0.07 mol of bromine was added slowly under stirring. The reaction was carried out at room temperature, over a period of about 15 min, and then the temperature was raised up to 60°C when the reaction medium appeared turbid. Finally, the reaction temperature was maintained at 80-85°C for 1.5 h to ensure complete bromination. After cooling, the product was filtered and then washed with a few drops of sodium bicarbonate solution for removing bromine. The product was recrystallized from acetic acid solution. The yield was 70%.

Preparation of bismaleimides

Monomers BMI (1-9) were synthesized as presented in scheme 1, [21].

3(4)-MBAC (0.2 mol) in 200 mL chloroform ($CHCl_3$), was cooled in an ice bath. Triethylamine (TEA) (0.2 mol) as acid acceptor and a solution of diphenol (0.1mol) in 200 mL $CHCl_3$ were added. After stirring for 1.0 h, the mixture was filtred and precipitated in heptane. The product was filtred and treated with sodium bicarbonate solution and then thoroughly washed with water. The filtred precipitated product was recrystalized.

Some characteristics of the bismaleimide monomers are presented in table 1.

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(0.1 mol) in 200 mL $CHCl_3$ were added. After stirring for 1.0 h, the mixture was filtered and precipitated in heptane. The product was filtered and treated with sodium bicarbonate solution and then thoroughly washed with water. The filtered precipitated product was recrystallized.

Synthesis of Polymers

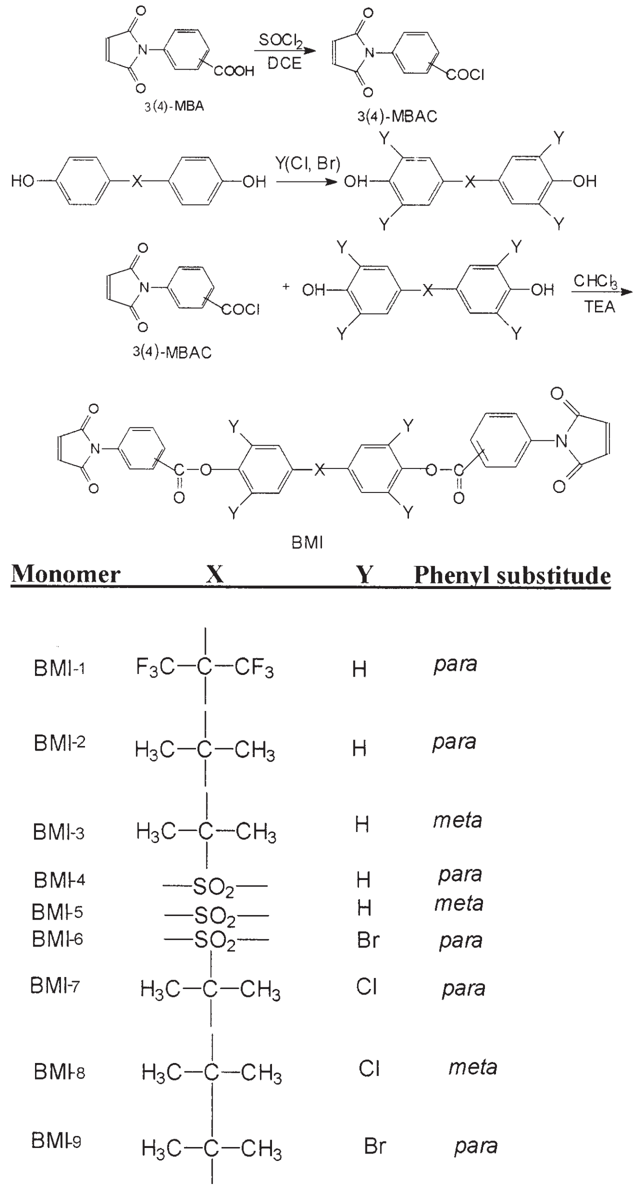
The polymers were prepared as described in literature [25] (scheme 2).

Into 50 mL three-necked flask fitted with mechanical stirrer, thermometer and nitrogen inlet, 0.01 mole of bismaleimide, 0.01 mole diamines, N-methylpyrolidine -2-one (NMP) as solvent (up to 10-15% of monomer concentration), were charged. Small amounts of acetic acid at various reaction time intervals were added. The reaction mixture was kept in a water bath at 95°C. The polymers were isolated by pouring the mixture into methanol to give brown powder polymers.

The products were filtered and washed thoroughly. In order to obtain higher molecular weight polymers, the reaction conditions (time, solvent, concentration) were varied.

Measurements

The IR spectra were recorded on a Specord M90 Carl Zeiss Jena spectrophotometer using KBr pellet technic. ^1H-NMR spectra were recorded on a Bruker NMR spectrometer Avance DRX 400 MHz, using DMSO-d_6 as solvent and tetramethylsilane as internal standard. Differential scanning calorimetry (DSC) measurements were done by using a Mettler instrument DSC 12E, with a heating rate of 10°C/min in air. Melting points were determined with Gallenkamp hot-block melting point apparatus and by DSC. TGA was carried out in air with a F. Paulik Derivatograph, at a heating rate of 12°C/min. Atomic force microscopy (AFM) images were collected in semicontact mode with a Solver PRO-M, NT-MDT, Russia, atomic force microscop.



Monomer	X	Y	Phenyl substitude
BMI-1	$F_3C-C-CF_3$	H	*para*
BMI-2	$H_3C-C-CH_3$	H	*para*
BMI-3	$H_3C-C-CH_3$	H	*meta*
BMI-4	$-SO_2-$	H	*para*
BMI-5	$-SO_2-$	H	*meta*
BMI-6	$-SO_2-$	Br	*para*
BMI-7	$H_3C-C-CH_3$	Cl	*para*
BMI-8	$H_3C-C-CH_3$	Cl	*meta*
BMI-9	$H_3C-C-CH_3$	Br	*para*

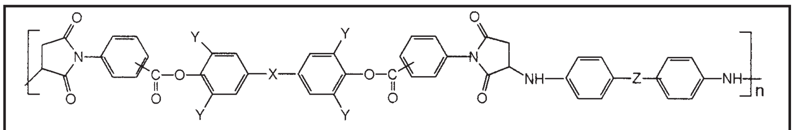
Scheme 1

Table 1

A SERIES OF PHYSICAL AND THERMAL CHARACTERISTICS OF THE MONOMERS

Monomer	Colour	M. P.[a] (°C)	T_p[b] (°C)	IDT[c] (°C)	IR spectra data of monomers			
					C=O Imide	Ester group	HFI[d] group	SO_2 group
BMI-1	Light-yellow	210-214	245	443	1730	1750	1250-1150	-
BMI-2	Yellow	276-279	-	382	1720	1740	-	-
BMI-3	Yellow	167-170	236	397	1720	1740	-	-
BMI-4	Cream	236-240	272	390	1725	1755	-	1330, 1160
BMI-5	Cream	91[e]	191	335	1715	1745	-	1320, 1150
BMI-6	Light-yellow	98-101	153	260	1725	1750	-	1320, 1160
BMI-7	Pale-yellow	225-228	257	375	1730	1760	-	-
BMI-8	White	240-243	-	403	1730	1760	-	-
BMI-9	White	281-283	-	325	1720	1745	-	-

a. Melting point determined visually in a capillary tube melting point apparatus
b. The onset temperature for the curing reaction of these monomers by DSC
c. Onset degradation temperature by TGA
d. Hexafluoroisopropylidene
e. Melting point determined by DSC



Polymer	X	Y	Z	Phenyl substituted
P-1	$C(CF_3)_2$	H	APEE	*para*
P-2	$C(CH_3)_2$	H	APEE	*para*
P-3	$C(CH_3)_2$	H	APEE	*meta*
P-4	$C(CH_3)_2$	H	APDP	*para*
P-5	$C(CH_3)_2$	Cl	APEE	*para*
P-6	SO_2	H	APB	*meta*
P-7	SO_2	Br	DDE	*para*
P-8	$C(CH_3)_2$	Br	DDE	*meta*
P-9	SO_2	Br	APEE	*para*
P-10	$C(CF_3)_2$	H	DDE	*para*
P-11	$C(CH_3)_2$	Cl	APEE	*meta*

Scheme 2

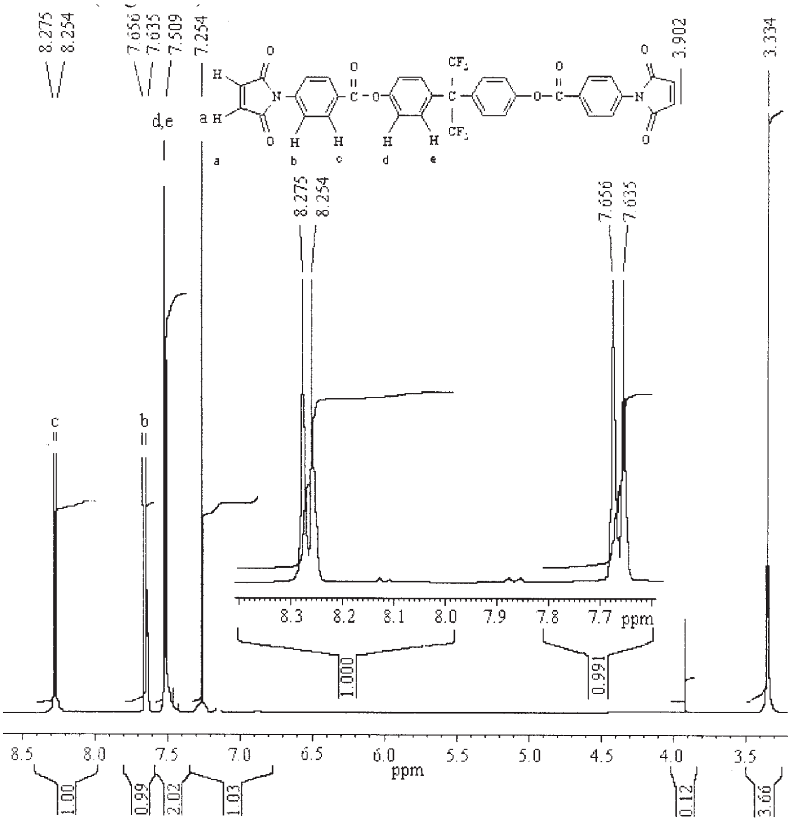


Fig. 1. ^{1}H-NMR spectrum of bismaleimide BMI-1

Results and discussions

The monomers BMI(1-9) showed carbonyl peak in the range 1730-1715 cm^{-1} attributed to C=O imide units and a band at 1760-1740 cm^{-1} due to ester groups. In addition, the characteristic absorption of $-SO_2$ groups (BMI(4-6)) appeared at 1330-1320 and 1160-1150 cm^{-1}. Also an absorption band at 1250-1150 cm^{-1} appeared due to hexafluoroisopropylidene units (BMI-1).

The ^{1}H-NMR spectrum of bismaleimide BMI-1 confirmed its chemical structure (fig.1).

The aromatic protons of monomer BMI-1 appears as a two doublets in the range 8.275-8.254 ppm (Ar-H, *ortho* to –COO) and in the range 7.656-7.635 ppm (Ar-H, *ortho* to –N=). A singlet at 7.509 ppm is due to aromatic protons *ortho* to –O- and *ortho* to $-C(CF_3)_2$. Monomer BMI-1 exhibited a singlet in the region 7.254 ppm associated to olefinic protons.

The monomers were analyzed by differential scanning calorimetry (DSC). DSC curves for all compounds BMI(1-9) were characterized by a sharp melting endotherm in the temperature range 140-290°C. It is noticeable that BMI-5, bearing SO_2 groups and substituents in the *meta* position, has a lower endotherm (91°C), while monomer BMI-2, which contains chlorine atoms, has the endotherm at the highest temperature (290°C). The reactivities of these monomers (T_p) are in the temperature range of 153-272°C (except for BMI-2 and BMI (8-9) for which the onset temperature for curing reaction was overshadowed by the melting endotherm).

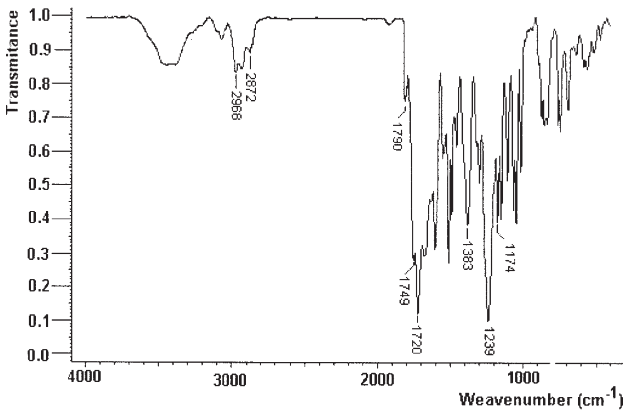


Fig. 2. FTIR spectrum of polymer P-9

The thermal stability of monomers was evaluated by dynamic TGA. The initial decomposition temperatures (IDT) of these compounds are in the range 260-443°C. The highest value of IDT was obtained for BMI-1 (hexafluoroisopropylidene group has a beneficial influence), while BMI-6 showed the lowest IDT.

Polymer Synthesis

The polyaspartimides were synthesized by Michael addition of diamines, such as 1,2-bis [2-(4-aminophenoxy)ethoxy]ethane (APEE), 1,4-bis(aminophenoxy) diphenylsulfone (APDPS), 4,4'-diamino-diphenylether (DDE) and 1,4-bis(4-aminophenoxy)benzene (APB) to bismaleimide monomers in NMP at 90-95°C.

The polymers were isolated by pouring the reaction mixture into methanol, followed by filtration and washing. An optimization study on the reaction parameters (time, temperature, concentration) was carried out to achieve polymers with high molecular weights.

The structure of polymers was confirmed by analysis FTIR spectroscopy. The FTIR spectra showed that polymers are characterized by the same absorption bands as monomers, but they are wider. Figure 2 presents the FTIR spectra of the polymer P-9.

Two characteristic carbonyl band appeared at 1790 and 1720 cm^{-1}. Other characteristic bands were observed in the range 2968-2872 cm^{-1} because of the aliphatic groups, and the band at 1383 cm^{-1} was attributed to $-SO_2$ moiety. A band at 1749 cm^{-1} appeared in the spectrum due to ester groups. The reduction of the band at 3100 cm^{-1} and disappearance of the band at 1150 cm^{-1} (maleimide ring) and the appearance of the band at 1174 cm^{-1} (succinic ring) proved that the reaction took place .

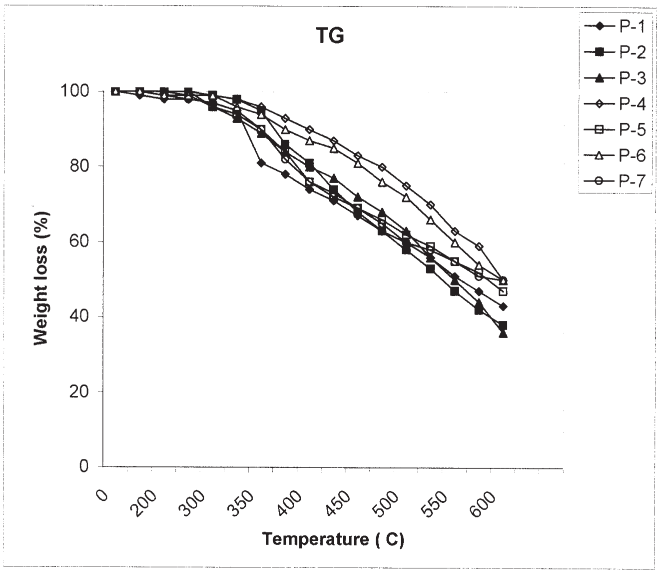


Fig. 3. TGA thermograms of polymers P (1-7)

The thermal behaviour of polymers was evaluated by the means of thermogravimetric analysis. The thermogravimetric curves of polymers P (1-7) are shown in figure 3.

Some thermal data of polymers P (1-7) are shown in table 2. The initial decomposition temperatures of the polymers are in the range 277-332°C. It is observed that IDT is higher for polymer P-4 (based on brominated bismaleimide which have a $-SO_2$ group and APEE amine component). The polymers P-4 and P-6 showed similar decomposition patterns after 340°C, whereas polymers P(1-3) showed similar decomposition patterns after 425°C. It is noticeable that polymers P(1-6) showed a two-stage decomposition, whereas P-7 showed a three-stage

Table 2
SOME THERMAL PROPERTIES OF POLYMERS P(1-7)

Polymer	Color	IDT^a (°C)	PDT$_{max}$^{b} (°C)	T$_5$^{c} (°C)	T$_{20}$^{d} (°C)	Y$_c$^{e} (%)
P-1	Brown	320	330, 555	330	395	42
P-2	Reddish-brown	320	365, 410	345	403	38
P-3	Brown	300	325, 524	310	401	36
P-4	Reddish-brown	332	400, 503	355	463	50
P-5	Brown	277	385, 505	306	385	47
P-6	Reddish-brown	310	350, 565	345	442	50
P-7	Cream	310	367, 470, 565	320	387	49

a Initial decomposition temperature
b.Maximum decomposition temperature
c.and d. Temperature at which 5 and 20% weight loss, respectively was observed
e. Char yield at 600°C.

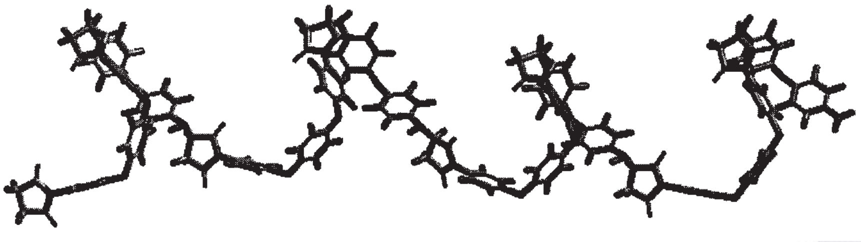


Fig. 4. Model of fragment of polymer P-10

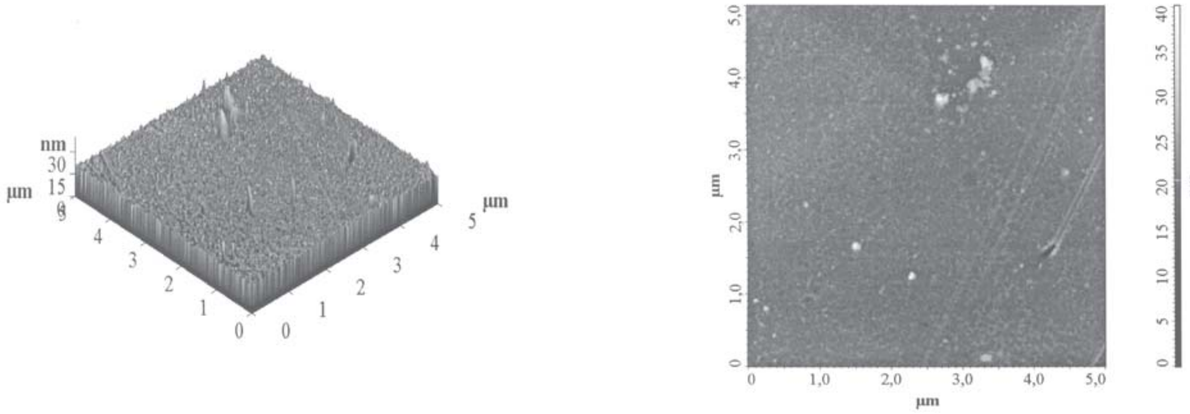
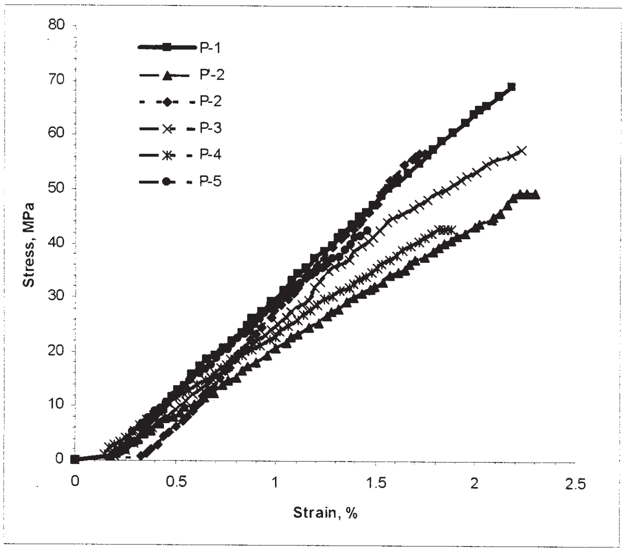


Fig. 5. AFM picture of the film made from polymer P-10(side view and top view)



Polymer P'-2 was obtained from the same monomers and working under the same conditions as for polymer P-2, except for solvent: m-cresol was employed instead NMP

Fig. 6. Stress-strain curves of polymer P(1-5)

decoposition because of the combination of different chemical segments in the polymer chain.

Model molecules of polymer P-10 are shown in figure 4.The disturbance packing of the macromolecular chain facilitated the diffusion of small molecules of solvent between the polymer chain and led to the improve of solubility.

Some polymers possess film-forming ability. Their solution in NMP having a concentration of about 10% were cast onto glass substrates and dried to yield thin reddish-brown films. The quality of such films was studied by AFM. A typical AFM image is shown in figure 5. These films are smoothy and homogeneus and they did not shown any pinholes or cracks.

The stress-strain curves of polymers P (1-5) are shown in figure 6. The polymer composition influences the tensile strength, which is between 40-70 MPa. The films have elongation at break of 2.1-3.4 and tensile modulus of 1795-2430 MPa.

The high level of rigidity of these polymers is reflected by resin modulus. Both tensile strength and modulus of samples were influenced by structural peculiarities of each polymer and component fraction.

Conclusions

Bismaleimide compounds (monomers and polymers) with different structures (ester, ether units, hexafluoroisopropilidene, sulphonyl groups, having bromine or chlorine atoms) were synthesized and characterized by spectroscopy (FTIR and ^{1}H-NMR) .

Thermal behaviour of these compounds was evaluated by DSC and TGA. Mechanical and thermal properties of these compounds are influenced by the structure of bismaleimides and diamines involved, and the reaction conditions as well. As in the past future developments of addition polyimides will focus on the requirement on high thermal and thermal oxidative stability of the crosslinked polymers and on a satisfactory processing behaviour of the uncured precursors.

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