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Bismaleimides derived from polyurethane. Thermal, mechanical, dielectrical and wettability properties

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A series of bismaleimides with urethane groups in the main chain, were synthesized from maleic anhydride and polyurethane prepolymers based on various diisocyanate and polyether, polyester diols with various chain lengths. The products were characterized by FTIR, ^{1}H-NMR and elemental analysis. Thermogravimetric analysis (TGA) was performed in order to evaluate the thermal properties. The mechanical behavior of these polymers was investigated by stress-strain measurements on films at room temperature. Dielectric properties and wettability values were performed using the Novocontrol "Concept 40" broadband dielectric spectrometer and respectively Sigma 700 tensiometer.

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Keywords: Bismaleimide, FTIR analysis, Mechanical properties, Polyurethane, Thermal properties.

1. Introduction

Polyaspartimides is an addition-type polyimide produced from bismaleimide which has unsaturated end groups. Addition polyimides are best defined as low molecular weight, at least difunctional monomers or polymers or mixture thereof, that carry functional reactive terminations. The reactivity of bismaleimide is determined by the ability 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 (vinyl, allyl, propenyl, arinyl, etc.,) bonds or with cyclic compounds (cyclobutane, derivatives or heterocycles). The reactive of the double bond is a consequence of the electron withdrawing nature of the two adjacent carbonyl groups which create a very electron-deficient double bond and therefore is susceptibility to homo and copolymerization reactions.

These resins are subject of great interest because of their attractive properties, such as: high thermal stability (its thermal stability is high than that of the epoxy resins, but lower than that of conventional polyimides), outstanding mechanical properties, excellent radiation and corrosion resistance, good flame resistance, low water susceptibility, excellent chemical behaviour, good retention of thermomechanical properties, even after long ageing times at 250 ºC [1-14].

Bismaleimides (BMI) based polymers are good matrix resins for high-performance composites, multi-layer printed circuit boards for large-scale computers, advanced composites for aerospace and electronic industries, structural adhesive [15-19].

However, unmodified BMI resins suffer from brittleness (due to their crosslinking density after curing) and poor processability. Also, these resins have a high melting and curing temperature [20, 21].

Polyurethane compounds are a class of materials that can be prepared by the reaction of diols and diisocyanates [22]. Unfortunately, polyurethanes have a disadvantage because their poor thermal stability [23, 24]. The introduction of BMI into epoxy, siliconized epoxy, and unsaturated polyester modified epoxy resin enhanced the thermomechanical properties.

A series of urethane-modified bismaleimide (UBMI) was synthesized, through the imidization of NCO-terminated PU prepolymer and maleic anhydride [25]. The advantage of using isocyanate instead of the conventionally used amine is that imidization is achieved is a single-step at a lower temperature [26, 27]. Thus, the flexible chain of polyurethane (PU) was introduced into backbone of the cured BMI and finale products show good mechanical properties and much better thermal stability then that of the traditional PU elastomers.

2. Experimental

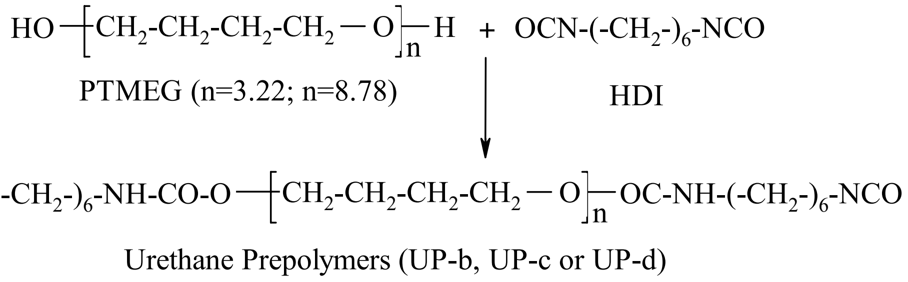
2.1. Materials

The materials used in this research were: Terathane (polytetramethylene-ether-glycol- PTMEG-generous gift from INVISTA BV, Nederland), Mw 250 and 650 g/mol, mp 15-45 ºC, hydroxyl number 448 and respectively 173 mg KOH/g; poly(ethyleneadipate) diol (PEA - local market) oligomers with a molecular weight of about 2800 were dried at 100 ºC under vacuum before use; hexamethylene diisocyanate (HDI-Fluka), Mw 168.20, bp

82-85ºC, d_4^{20} 1.05, n_D^{20} 1.453; isophorone diisocyanate (IPDI-Fluka) was used as received; 4,4-methylenebis (cyclohexyl-isocyanate (Aldrich); maleic anhydride (Fluka); N,N-dimethyl formamide (Fluka) was dried by vacuum distillation on MDI: triethylamine (Fluka).

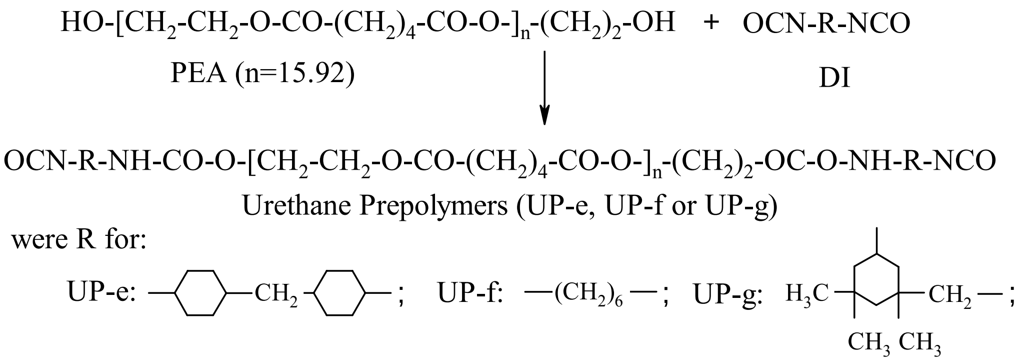
2.2. Preparation of urethane prepolymers (UP)

The prepolymers were synthesized in solution using DMF as solvent [28, 29]. The synthesis was performed in a glass vessel at normal pressure, under nitrogen blanket and vigorous stir. The molar ratio (polyether/diisocyanate) of all formulation was 1:2. In first stage PTMEG was reacted with HDI at 80 ºC for 1 hour to give up a prepolymer that was diluted in the second step with DMF to realize a solution with 50% wt. concentration. Under these conditions the addition of catalyst was necessary, using two drops of dibutyl tin dilaurate (DBTDL) (Scheme 1). When the –NCO content reached the theoretical value, the reaction was stopped.



Scheme 1

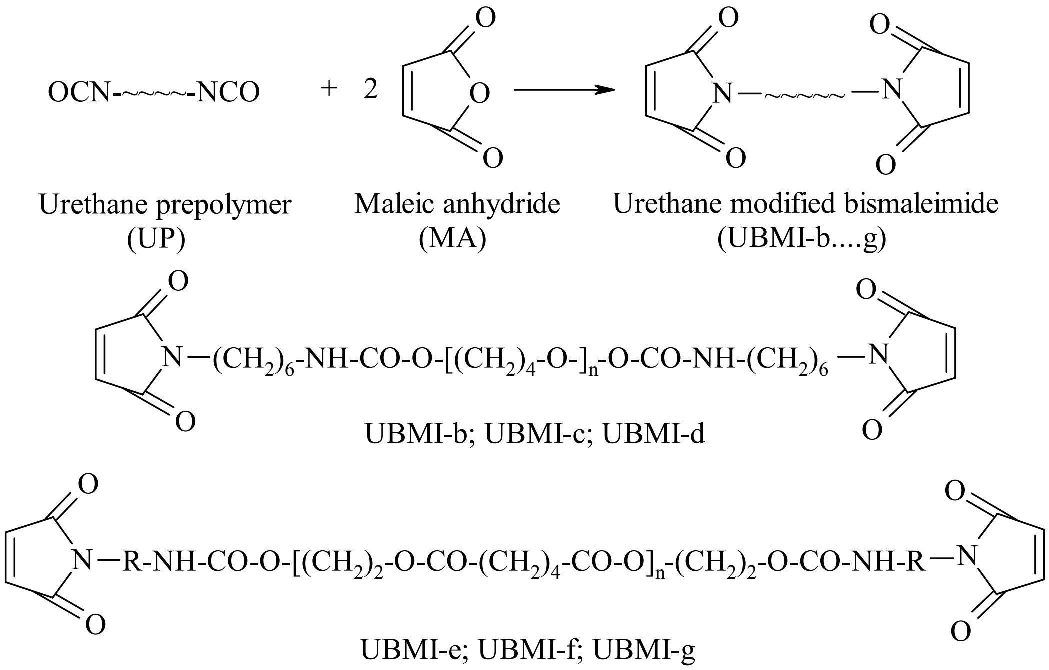
In the same manner were synthesized urethane prepolymers with ester groups (Scheme 2)



Scheme 2

2.3. Synthesis of urethane-modified bismaleimide (UBMI)

The urethane-modified bismaleimide (UBMI) was synthesized by the condensation reaction of maleic anhydride (MA) and urethane prepolymer (UP), according to the following reaction [24, 30] (Scheme 3). The reaction were carried out in a three-necked flask which was equipped with a stirring device, a reflux condenser, heating mantle, thermometer and constant flow of dry nitrogen. Urethane prepolymer, dissolved in DMF, was added to the solution of maleic anhydride and triethylamine (TEA) catalyst at 70 ºC. The amount of solvent used was about 1.5 times of the weight of the reactants. The start of the reaction was observed by the evolution of CO_2 gas. The reaction was stopped when the –NCO absorption peak at 2270 and 1848 cm^{-1} (peak of acid anhydride) disappeared.



Scheme 3

2.4. Measurements

The FTIR spectra were recorded on a Bruker Vertex 70 spectrophotometer. ^{1}H-NMR spectra were recorded on a Bruker NMP spectrometer Avance DRX400 MHz, using DMSO-d_6 as solvent and tetramethylsilane as an internal standard. Thermogravimetric analysis (TGA) was carried out using a Mettler Toledo TGA/SDTA851e - thermogravimetric analyzer under a flow of nitrogen (20mL/min) with a heating rate of 10 °C/min from room temperature to 700 °C and 3-5 mg of sample mass. Stress-strain measurements were performed at room temperature on dumbbell-shaped samples cut from thin films on an Instron Single Column Systems tensile testing machine (model 3345) equipped with a 5kN load cell and activated grips which prevented slippage of the sample before break. The used cross-head speed was 10 mm/min. All samples were measured three times and the averages were obtained. Hardness was measured on Instron Shore Durometer instruments, using scale A. Contact angles were measured by the static drop technique at room temperature, using a KSV CAM 101 goniometer, equipped with a special optical system and a CCD camera connected to a computer to capture and analyze the contact angle (five measurements for each surface). A drop of liquid (~1 μl) was placed, with a Hamilton syringe, on a specially prepared plate of substratum and the image was immediately sent via the CCD camera to the computer for analysis. The angle formed between the liquid/solid interface and the liquid/vapor interface is the contact angle. Temperature and moisture was constant during the experiment (23°C and 68 % respectively). Dielectric spectroscopy was performed using the Novocontrol "Concept 40" broadband dielectric spectrometer (Hundsangen, Germany). Samples were subsequently mounted between gold platens and positioned in the Novocontrol Quatro Cryosystem. The dielectric experiment was carried out keeping the frequency fixed but sweeping the temperature. A heating rate of 5 °C/min over the temperature range of from -120 to 100˚C was utilized, and six decades of frequency, 1 to 1000 000 Hz, were scanned. The ε' and ε" have a direct physical interpretation. The ε' is related to the energy stored reversible in the material whereas ε" is proportional to the energy which is dissipated per cycle.

3. Resuls and discussion

3.1. FTIR analysis

The urethane prepolymers were synthesized by the reaction of diols with varied diisocyanate compounds. The reaction was monitored by the FTIR spectra. The absorption peak of the –NCO group at 2273 cm^{-1}gradually decreased during the reaction, and this indicated that the hydroxyl groups of diol compound had reacted with the isocyanate groups. The structure of the urethane prepolymer was confirmed by FTIR spectroscopy (Figure 1).

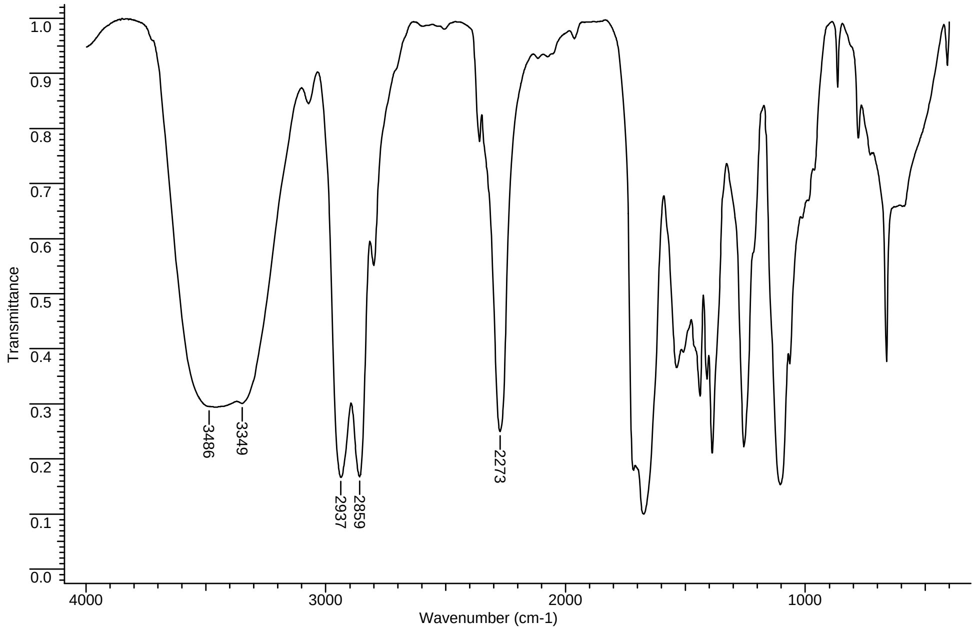


Fig. 1. FTIR spectra of urethane prepolymer UP-g

The reaction between urethane prepolymer and maleic anhydride was monitored by the disappearance of the characteristic peak of isocyanate group (2273 cm^{-1}) and acid anhydride (1848 cm^{-1}) in FTIR spectra as shown in Fig. 2.

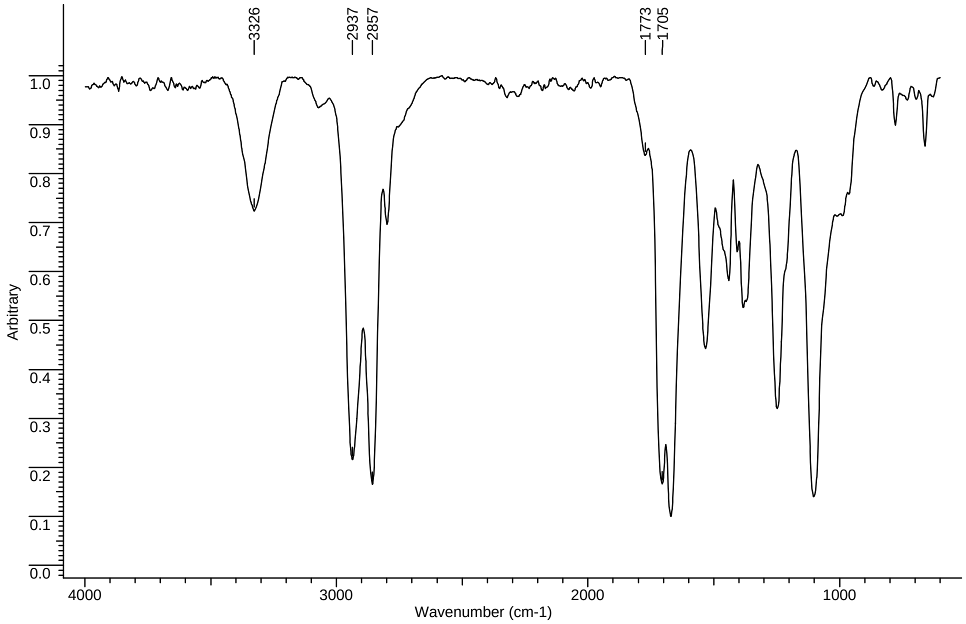


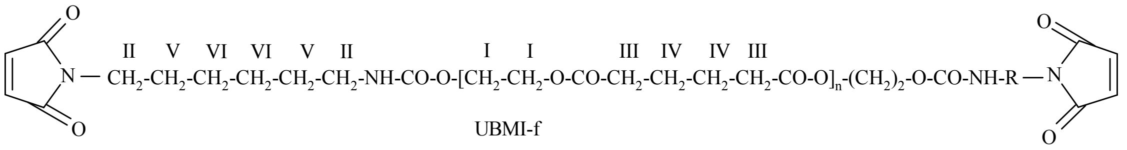
Fig. 2. FTIR spectra of UBMI-g

Also, an absorption peak appeared at 3326 cm^{-1} due to N-H stretching. Other characteristic bands were observed in the range 2937-2857 cm^{-1} due to aliphatic group. The polymer also showed characteristic carbonyl group at 1773 and 1705 cm^{-1}.

3.2. H NMR analysis

The proton NMR spectra of UBMI-, along with the assignments corresponding to each type of proton are given in Table 1.

Table 1. The H NMR spectrum assignments for UBMI-f structure.

Group	δ (ppm), Multiplicity	Proton Type
 UBMI-f		
-NH-	9.185 , s	Urethane NH
-CH=CH-	7.018 ,s	Olefinic proton
$-CH_2-$ (I)	3.933-3.903 , t	CH_2 group adjacent to O
$-CH_2-$ (II)	2.957-2.893 , m	CH_2 group adjacent to N
$-CH_2-$ (III)	2.312 ,s	CH_2 group, adjacent to carbonyl
$-CH_2-$ (IV)	1.551-1.504 , m	$CH_{2,}$ central methylen group
$-CH_2-$ (V)	1.377-1.346 t	CH_2,group adjacent to center methylene of hexamethylene isocyanate
$-CH_2-$ (VI)	1.269-1.219 t	$CH_{2,}$ center methylene group of adipic acid

The singlet at 9.185 ppm is attributed to the urethane protons -NH-. Other signal at 7.018 ppm corresponds to the olefinic protons. The triplet in the range 3.933-3.903 ppm ascribed to the CH_2 (I) groups adjacent to oxygen from carbonyl and urethane groups, whereas the multiplet in the range 2.957-2.893 ppm is attributed to CH_2 (II) groups adjacent to N (imide cycle and urethane unit). The CH_2 (III) groups adjacent to the carbonyl units showed a signal at 2.312 ppm whereas the multiplet in the range 1.551-1.504 ppm is due to the CH_2 (IV) group of adipic acid. Other signals appeared at 1.377-1.346 ppm due to CH_2 (V) group neighbouring to the center methylene group of hexamethylene diisocyanate. The signal in the range of 1.269-1.219 ppm is due to center methylene (VI) groups from the adipic acid.

3.3. Thermogravimetric study

The thermal behaviour of these compounds was evaluated by means of thermogravimetric analysis (TGA). The thermogravimetric curves of the polymers UBMI (b,c,d) and UBMI (e,f,g) are shown in Figure 3 and weight losses, decomposition temperature ranges and residue are listed in Table2. Generally, UBMI analyzed decomposed in two steps and the temperature which the weight losses were maximum is 300-440 ºC.

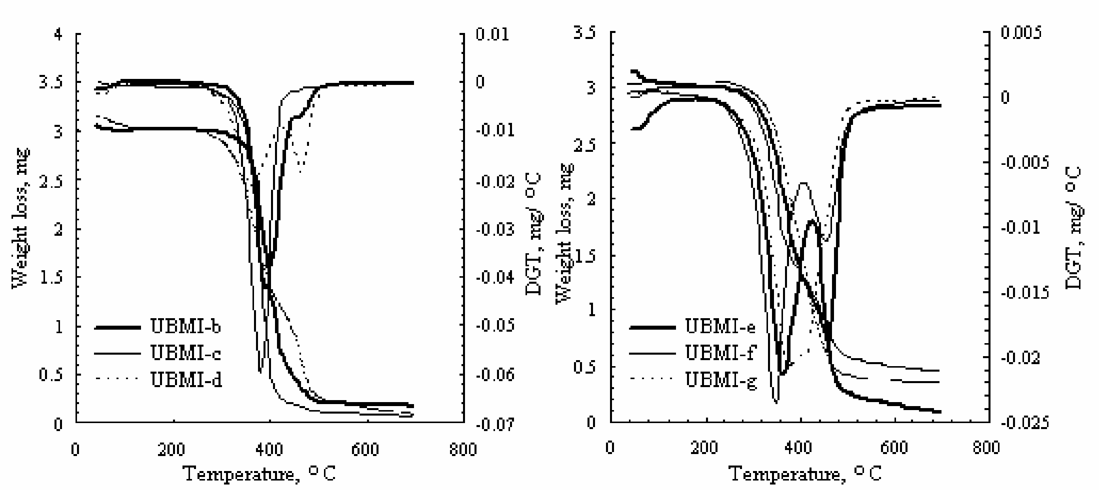


Fig. 3. TG and DTG of UBMI (b,c,d) and respectively UBMI (e,f,g)

Table 2. Thermogravimetric data of urethane-modified bismaleimide

Sample code	Reaction order*		Weight losses (%) and decomposition temperature ranges			Activation energy * kJ/mol	
	Step I	Step II	Residue %	Step I	Step II	Step I	Step II
UBMI-b	1.0	0.3	5.02	79.59(360-425)	15.39(425-480)	180.11	15.97
UBMI-c	0.8	-	1.77	98.23(335-410)	-	156.01	-
UBMI-d	0.5	-	2.09	93.91(350-410)	-	44.46	-
UBMI-e	0.6	0.4	5.33	63.15(310-430)	31.52(430-480)	78.38	50.25
UBMI-f	0.7	0.2	14.67	55.73(295-400)	29.6(400-480)	130.13	18.76
UBMI-g	1.0	0.4	10.03	75.72(325-440)	14.25(440-480)	100.15	26.86

** Calculated through Reich-Levi method.*

The polymers UBMI-b and UBMI (e,f,g) showed two stage decomposition due to the combination of chemical different segments in the polymer chain. Imide rings are considered to be the most stable units among these linking groups, but urethane groups must be the most labile units and will be the first to decompose and start the initial thermal degradation. Maleic anhydride from the samples offers relative stability, because the possibility of order in the molecular chain is high. In the case of polymers UBMI (b,c,d), the major weight loss (79-98%) occurred in the range 335-425 ºC, whereas in the case of polymers UBMI (e,f,g), 55-75 % weight loss occurred in the range 295-440ºC. The study of these thermograms indicated that compounds UBMI (b,c,d) are less stable that polymers UBMI (e,f,g). The compound UBMI-c, showed the highest value of weight loss in first step, but UBMI-f, showed the lowest value of weight loss. On the basis of residue, the following order may be given for the thermal stability of these compounds.

UBMI-f > UBMI-g > UBMI-e > UBMI-b > UBMI-d > UBMI-c

The thermal stability of these polymers depends on the linking groups (ether or ester) on the polymer chain.

The reaction orders, calculated through Reich-Levi method, are close to unity for first step, this suggest that some diffusion processes accompany decomposition in various conditions. Energy activation versus conversion is presented in Figure 4.

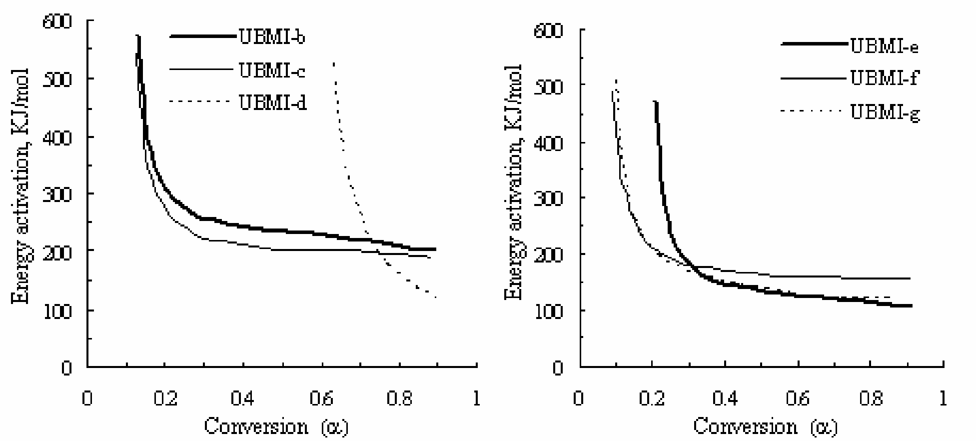


Fig. 4. Energy activation of UBMI (b,c,d) and respectively UBMI (e,f,g) versus conversion.

3.4. Mechanical measurements

The mechanical behavior of polymers UBMI (e,f,g) was studied by stress-strain measurements at room temperature on dumbbell-shaped samples cut from thin films on a Instron Single Column Systems tensile testing machine (model 3345) equipped with a 5 kN load cell and activated grips which prevented slippage of the sample before break. The use crosshead speed was 10mm/min. All samples were measured three times and the averages were obtained. The stress-strain traces and results for the polymer analyzed are presented in Fig. 5 and Table 3.

The polymer composition influences the tensile strength, which are between 1-5 MPa. It is observed that tensile strength value of UBMI-e is the highest, most probably due to influence of polyethylene group, and UBMI-g is the lowest. Also, the same compound (UBMI-e) has the highest hardness value. In opposition with the values of elongation at break from a prevue article [31] the influence of the polyurethane matrix it is evidence, elongation values are between 35-84 % until the maximum values of the poly(aminobismaleimide)s was 2.3%.

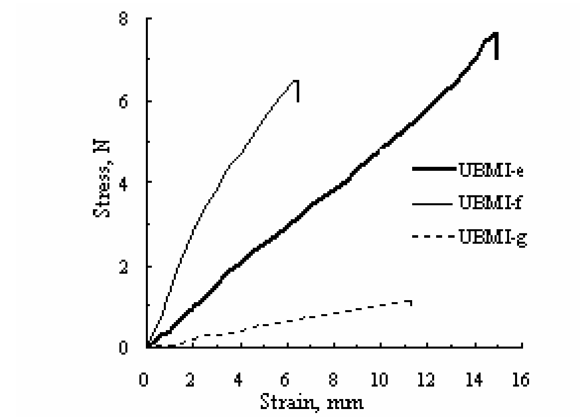
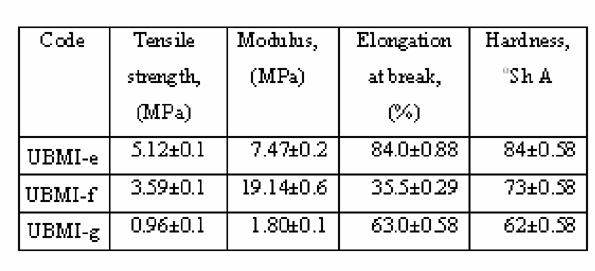


Fig. 5. Stress strain behaviour of polymers UBMI-...f, at room temperature.

Table 3. Stress-Strain measurements of polymers UBMI-e...f



Code	Tensile strength, (MPa)	Modulus, (MPa)	Elongation at break, (%)	Hardness, °Sh A
UBMI-e	5.12±0.1	7.47±0.2	84.0±0.88	84±0.58
UBMI-f	3.59±0.1	19.14±0.6	35.5±0.29	73±0.58
UBMI-g	0.96±0.1	1.80±0.1	63.0±0.58	62±0.58

3.5. Wettability study

The knowledge of the surface free energy of polymers plays a prominent role in many high technology applications like: biomedical, microelectronics, thin film coating, etc. In the contact angle measurement process, which enables the determination of the surface free energy, the selection of appropriate test liquids is sometimes sophisticated. In many medical applications, polymers, in general, play an important role for the production of high-quality devices. In this connection, the UBMI materials have of particular importance. In these processes problems sometimes occur because the polymer surfaces have relatively poor wetting properties. This is due to the relatively low surface free energy of these materials and the absence of polar surface groups. To improve the wetting properties, the plastics are generally submitted to a surface treatment such as for instance plasma or a corona treatment. In this way, polar groups are introduced on the surface, and the surface free energy increases. The knowledge of the surface free energy of a treated plastic with its polar and dispersive portions is therefore of crucial importance when producing biomedical devices.

To determine the surface free energy of a polymer with its polar and dispersive portions, the contact angle is measured with a number of test liquids and evaluated according to the Wu's method [32]. The method requires the use of at least two test liquids with known surface tension and its polar and dispersive contributions. Each additional liquid will increase the accuracy of the estimation.

Three types of UBMI films were examined. In Table 4 the measured contact angles are showed.

Table 4. Contact angle of samples with different liquids in degrees.

Samples	Water	Ethylene Glycol	Diiodomethane
UBMI e	86.20±3.09	67.62±0.86	54.49±0.34
UBMI f	85.90±3.42	64.47±1.01	47.09±4.17
UBMI g	75.47±3.65	56.10±2.18	24.78±0.34

The results show clearly that there are some differences in the contact angles, done in principal by influence of the diisocyanate component. The contact angles of water are less than 90 degree so, inserting of urethane structures in polymers increase the wetting properties. When evaluating according to Wu, the values as shown in Table 5 are obtained for the surface free energies of the films

Table 5. Surface free energies and their dispersive and polar contributions in mN/m

Samples	Surface Free Energy	Dispersive Portion	Polar Portion
UBMI e	22.87	13.89	8.98
UBMI f	24.80	17.28	7.52
UBMI g	29.54	14.33	15.21

From the table it becomes obvious that the diisocyanate structure leads an essential increase of the surface free energy. It is remarkable that this structure influences the polar portions.

Zisman developed a technique for determining of the critical surface tension (γ_{CST}), described completely by A. Adamson [33]. There are measured the contact angle θ for a set of solutions of differing surface tensions γ_{LV}. When the cosine of the contact angles is plotted against the surface tensions, a more-or-less straight line is formed. This line is extrapolated to the point of $\theta = 0$ which is where $\cos\theta = 1$.

Table 6. Data for determining of the critical surface tension (γ_{CST}).

Liquid	Surface tension mN/m	cos θ of sample		
		UBMI-e	UBMI-f	UBMI-g
Water	72.8	0.06616	0.07138	0.25077
Ethylene glycol	48	0.38075	0.43098	0.55775
Diiodomethane	50.8	0.58080	0.68085	0.90792

The calculation of the critical surface tension of samples from the data of Table 6 is shown in Figure 6. The best straight line for the experimental points was determined by linear regression. The intercept of this line with $\cos\theta = 1$ is γ_{CST}.

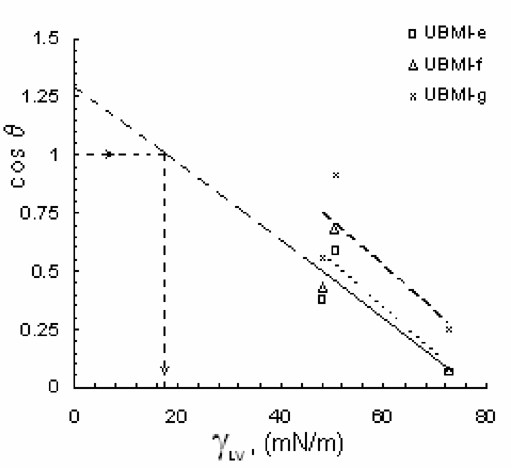


Fig. 6. Critical surface tension by Zisman method (example for sample UBMI-e)

From Figure 6 it's possible to be appreciated the value of critical surface tension of UBMI-e (γ_{CST} =17.97 mN/m). In same manner there are determined critical surface tension for UBMI-f (γ_{CST} =26.25 mN/m) and respectively for UBMI-g (γ_{CST} =34.66 mN/m).

3.6. Dielectrical behaviour

To be good dielectric functional materials, the dielectric constant (e') and dielectric loss (tan d) should be as low as possible. Low dielectric constant materials are of particular importance in microelectronic devices and components because propagation delay of electronic rigid is inversely proportional to the square root of the dielectric constant. The dielectric constant and dielectric loss of urethane modified bismaleimides (UBMI-e) under different frequencies and temperatures are shown in Fig. 7 and Figure 8.

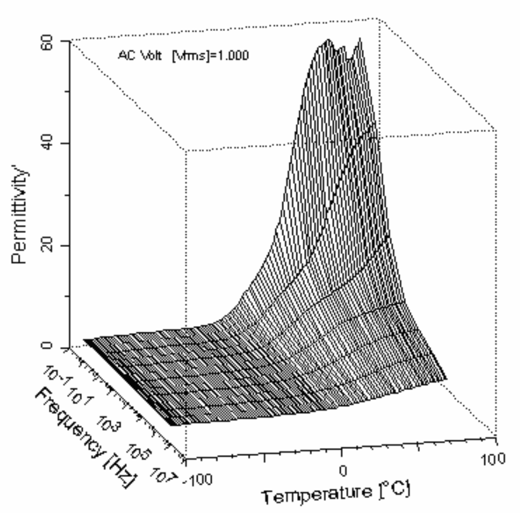


Fig. 7. UBMI-e dielectric permittivity vs. frequency and temperature

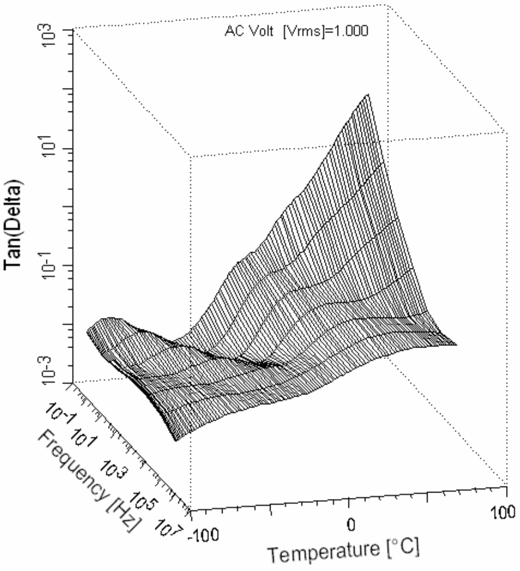


Fig. 8. UBMI-e dielectric loss (tan d) vs. frequency and temperature.

For all polymer samples the dielectric constant and dissipation factor (tan d) were recorded at seven different frequencies (10^0, 10^1, 10^2 … 10^6 Hz). In the range of frequency between 1-10^6 Hz, these polymers have low change in dielectric constant in the range of temperature -100 … 0 °C.

4. Conclusion

The urethane-modified bismaleimides were prepared from reaction of various polyurethane prepolymers and maleic anhydride.

Due to the presence of polar imide rings, these compounds exhibited improved solubility in polar aprotic solvents, and formed flexible films by casting their solution.

The study of thermal stability showed, that polymers UBMI (e,f,g) with ether linkages are more stability, compared to compounds UBMI (b,c,d).

The thermal stability and the mechanical properties of these compounds depend on the structure of the diols and diisocyanate component.

The compounds based on aliphatic diisocyanate are more hydrophilic than aromatic diisocyanate; see UBMI-g and UBMI-f.

All polymers have a great dielectric stability in the range of temperature -100 … 0 °C.

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