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BISMALEIMIDE RESINS CONTAINING URETHANIC MOIETIES

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ABSTRACT

A series of novel bismaleimide (BMIs) resins were prepared from 4-maleimidophenyl isocyanate and oligoether diols and oligoester diols. All the BMIs were characterized by IR, ^{1}H-NMR spectra and elemental analysis. DSC studies indicated that the thermal polymerization of the BMIs carried out in the 80-260°C range, and their curing behavior was significantly affected by the molecular weight of the BMIs. The poly(aminobismaleimide) resins (V1a-e, V2a-e) obtained by Michael addition of 4,4'-diaminodiphenylmethane and 4,4'-oxydianiline in 1-methyl-2-pyrrolidinone, led to elastic films showing good mechanical properties and better thermal stability than the traditional polyurethane elastomers.

INTRODUCTION

Bismaleimide resins are known as a class of high temperature thermosetting addition-type polyimides, and widely used as matrices for composite in electronics and aerospace industries [1-4]. The advantage is their reactive maleimide end groups; thermally polymerizable without the elimination of volatile by-products that cause voids in highly crosslinked polymeric materials. However, the cured resins are brittle as a result of the aromatic nature and the high crosslinking density of the network [5].

Various attempts have been made to improve the impact and fracture toughness of bismaleimide materials. One possible modification involves the introduction of long chains in the backbone of bismaleimides to reduce crosslink density [6-11].

We already reported the synthesis of new bismaleimides with urethane-aliphatic methylene links [12]. Liao and Hsoch [13], synthesized new bismaleimides from maleic anhydride and polyurethane prepolymers based on 4,4'-diphenylmethane diisocyanate and polyether/polyester diols with various chain lengths.

In this work, we have synthesized new bismaleimides from 4-maleimidophenyl isocyanate and polyether/polyester diols with various chain lengths and their poly(aminobismaleimide) resins. The studies reported here are part of a more detailed paper underwork.

EXPERIMENTAL

Measurements

The IR spectra were recorded on a Specord M90 Carl Zeiss Jena Spectrophotometer by using the KBr pellet technique. Proton ^{1}H-NMR spectra were run on a Jeol 60 MHz NMR Spectrometer at 60°C in DMSO-d_6 as the solvent, using TMS as the interval reference. Melting and softening points were determined with a Gallenkamp hot-block melting point apparatus. Thermogravimetric analysis (TGA) was carried out in air with an F. Paulik Derivatograph at a heating rate of 12°C/min. Differential scanning calorimetry (DSC) measurements were done by using a Mettler TA Instrument DSC 12E with a heating rate of 6°C/min in nitrogen. The stress-strain properties of the polymer films were measured at room temperature at a crosshead speed of 100mm/min on an Instron Tensile Tester TIRA TEST-2161 using a “E-MODUL UND DEHNERENZEM” program. For each specimen, 4 measurements were taken and the average value was used to determine the tensile strength and elongation.

Reagents and Materials

The chemicals employed are listed in Table 1, poly(oxytetramethylene)glycols (PTHF-650, PTHF-1000, PTHF-2000) and polyesters-glycols (PBA-2000 and PEA-2000) were dried under vacuum at 70°C over phosphorus pentoxide for 24 hours. 1,2-Dichloroethane (DCE) and 1-methyl-2-pyrrolidinone (NMP) were

TABLE 1. Raw Materials

Designation	Chemical Identification	Supplier
Polytetrahydrofuran-650 (PTHF-650)	Poly(oxytetramethylene)glycol Mw 650	BASF
Polytetrahydrofuran-1000 (PTHF-1000)	Poly(oxytetramethylene)glycol Mw 1000	BASF
Polytetrahydrofuran-2000 (PTHF-2000)	Poly(oxytetramethylene)glycol Mw 2000	BASF
FORMREZ V135-98 (PEA-2000)	Poly(ethyleneadipate)glycol Mw 2000	BAXENDEN
FORMREZ W11-42 (PBA-2000)	Poly(tetramethylene-adipate) glycol Mw 2000	BAXENDEN
Dibuthyltin dilaurate	Dibuthyltin dilaurate	Aldrich
1,4-Diazobicyclo [2,2,2]octane (DABCO)	1,4-Diazobicyclo[2,2,2] octane	Aldrich
N-Methyl-2-pyrrolidinone (NMP)	1-Methyl-2-pyrrolidinone	Merck

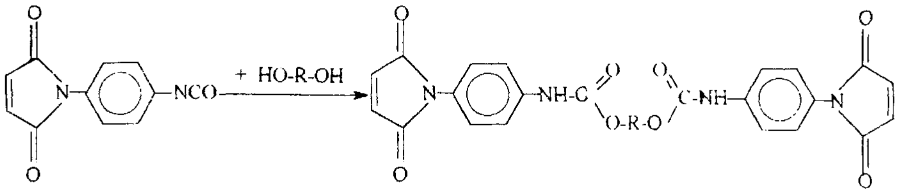
distilled before use. Dibuthyltin dilaurate (catalyst), and 4,4'-oxydianiline (ODA) (Merck, mp 190°C) and 4,4'-diaminodiphenylmethane (DDM) (Aldrich), were used as received.

4-Maleimidophenyl Isocyanate (MPI)

It was prepared as described elsewhere [14], and recrystallized from carbon tetrachloride before use. Mp 115-117°C (Ref. 14, 115-117°C).

Synthesis of BMIs (Mw>2000)(BMT-2000, BPBA-2000, BPEA-2000)

All the bismaleimides (Mw>2000) were synthesized using the following general procedure. A 250 mL four-necked flask equipped with a mechanical stirrer, dry nitrogen inlet, thermometer and condenser was charged with 0.01 mol (20 g) PTHF-2000, 150 mL DCE and 0.0002 mols (0.126 g) dibuthyltin laurate (catalyst), then purged the solution of few minutes with dry nitrogen under vigorous stirring, and 0.021 mol (4.5 g) MPI was added.



I II (a-e) III (a-e)

	II	Cod bismaleimides (III)
a	PTHF-650	BMT-650
b	PTHF-1000	BMT-1000
c	PTHF-2000	BMT-2000
d	PBA-2000	BBA-2000
e	PEA-2000	BEA-2000

SCHEME 1

The reaction mixture was maintained 2 hours at room temperature and refluxed for 2 hours. After cooling, the reaction mixture was filtered. The solid product obtained contains mainly N,N'-diphenylureabismaleimides [14]. 100 mL solvent (DCE) was distilled under low pressure. The reaction mixture was cooled and poured into 50 mL petroleum ether. The yellow precipitate was separated and washed several times with petroleum ether, and dried under vacuum at 60°C overnight. Yield: 89%.

Synthesis of BMIs Mw<2000 (BMT-650; BMT-1000)

The following general procedure was used. A 250 mL four-necked flask equipped with a mechanical stirrer, dry nitrogen inlet, thermometer and condenser was charged with 0.02 mol (13 g) PTHF-650, 150 mL DCE and 0.0004 mols (0.253 g) dibuthyltin laurate. The solution was purged off few minutes with dry nitrogen, then under vigorous stirring, 0.041 mol (9 g) MPI was added.

The reaction mixture was stirred 2 hours at room temperature and then refluxed for 2 hours. After cooling, the solid product obtained was filtered, washed

TABLE 2. Elemental Analysis of Bismaleimides.

Monomer	Softening range[a] (°C)	Elemental Analysis C% Calcd.	C% Found	H% Calcd.	H% Found	N% Calcd.	N% Found
BMT-650	98-105	63.31	63.14	8.21	7.29	5.17	5.84
BMT-1000	95-104	64.12	63.86	8.93	8.25	3.91	4.15
BMT-2000	94-102	65.15	64.75	9.85	9.25	2.30	2.57
BBA-2000	65-70	59.73	59.18	7.28	7.38	2.37	2.02
BEA-2000	55-60	56.34	56.16	6.45	6.83	2.34	2.05

[a]Determined with a Gallenkamp hot-block melting point apparatus.

several times with petroleum ether, and dried in vacuum at 60°C overnight. Yield: 75%.

Synthesis of BMIs Resins

A 50 mL three-necked flask equipped with mechanical stirrer, dry nitrogen inlet was charged with a solution of 0.002 mol (0.5 g) BMT-2000 in 20 mL NMP and 0.001 mol (0.2 g) DDM. The solution imediately acquired a reddish color. The reactive mixture was stirred at 80°C for about 3 hours. To prepare films, polymer solutions were casted on glass plates at 100°C. After 90 minutes, the solvent was evaporated at 150°C for 2 hours in a vacuum oven. Then, the final cure was performed at 200-220°C for 4 hours. The film was removed from the glass plate by soaking it in cold water. The thickness was about 0.3-1.2 mm.

RESULTS AND DISCUSSION

Five bismaleimide monomers III (a-e) were prepared via a classical addition of various polyols II (a-e) to a MPI [16] (Scheme 1). The structure of bismaleimides were identified by IR, ^{1}H-NMR spectra, and elemental analysis. Elemental analysis data for are in good agreement with the calculated values (Table 2). The IR spectra of these monomers (Figure 1) showed characteristic absorption peaks at 3350 cm^{-1} (s, N-H), 3080 cm^{-1} (m, vinyl), 2960-2880 cm^{-1} (s, -CH$_2$-), 1710-1705

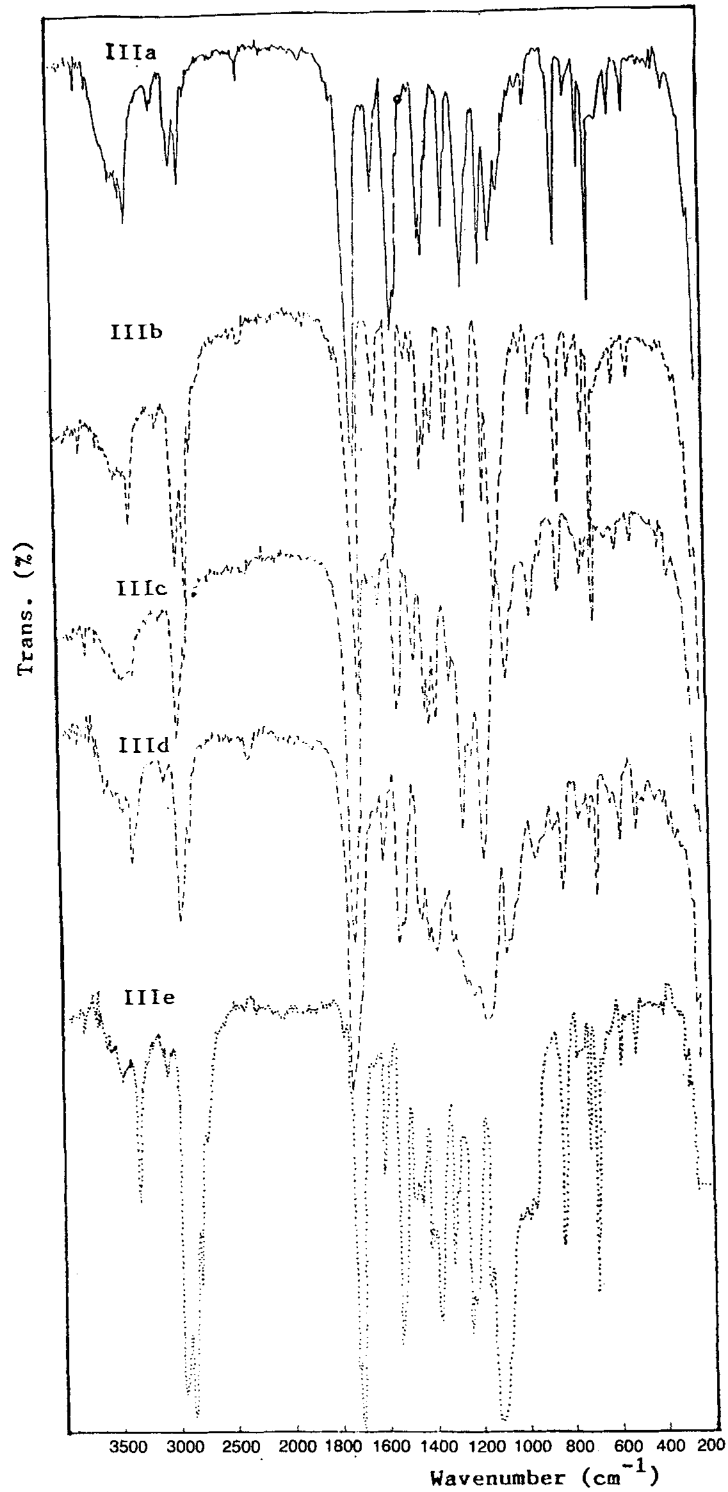


Figure 1. The IR spectra of bismaleimides III (a-e).

TABLE 3. Thermal Properties of Monomers and their Cured Resins.

Monomer	Curing Temperatures[a] (°C)				Temperatures(°C) for % weight loss			PDT^b_{max} (°C)
	T_m	T_1	T_2	T_3	5%	10%	20%	
BMT-650	105	106	126	170	295	318	355	340;428
BMT-1000	100	106	160	230	305	322	364	335;410
BMT-2000	39	250	280	305	295	320	355	320;418
BBA-2000	50	66	140	260	322	340	368	402
BEA-2000	42	65	140	285	328	352	372	403

[a]Determined from the DSC, first heating cycle.

[b]Maximum polymer decomposition temperature.

cm^{-1} (s, -C=O), 1385 cm^{-1} (s, imide II), 1175-1140 cm^{-1} (imide III) and 700 cm^{-1} (imide IV). The monomers III (a-c) have presented a band at 1125 cm^{-1} due to CH_2-O-CH_2 linkage. The infrared spectrum of monomers IIIe and IIId exhibit a strong band at 1745 and 1750 cm^{-1} assigned to ester group.

The ^{1}H-NMR spectra of monomers confirmed their structure. The aromatic protons of bismaleimides III (a-e) appeared as two separated doublets at 7.60-7.65 and 7.5-7.30 ppm, respectively. All monomers exhibited a singlet in the region 7.125-7.175 ppm associated with the olefinic protons. The bismaleimide III (a-c) exhibited three characteristic peaks at 1.525 ppm (-CH_2-), 3.30 ppm (-CH_2-O), and 4.15 ppm (-CH_2-OOC). The ^{1}H-NMR spectra of bismaleimide IIIe, and IIId showed three peaks at 4.15-4.20 ppm (-CH_2-OOC), 2.35 ppm (CH_2COO), and 1.525 ppm (-CH_2-).

All the BMIs monomers were characterized by softening points, thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) measurements (Table 3). Crosslinking behavior of the BMIs monomers III (a-e) were studied by DSC in nitrogen, at a heating rate of 6°C/min, using the first heating cycle. Some of the DSC results are listed in the Table 3 and Figure 2.

The increasing of the molecular weight of the oligomers used to obtain BMIs BMT-650, -1000, and -2000, respectively is accompained by a decrease of the melting temperature of corresponding BMIs from 105, 100 to 39°C, respectively, and by the increasing of T_{exo} from 126, 160 to 280°C, repectively (Table 3). For BMIs BMT-650, the endotherm process overlapped the exotherm,

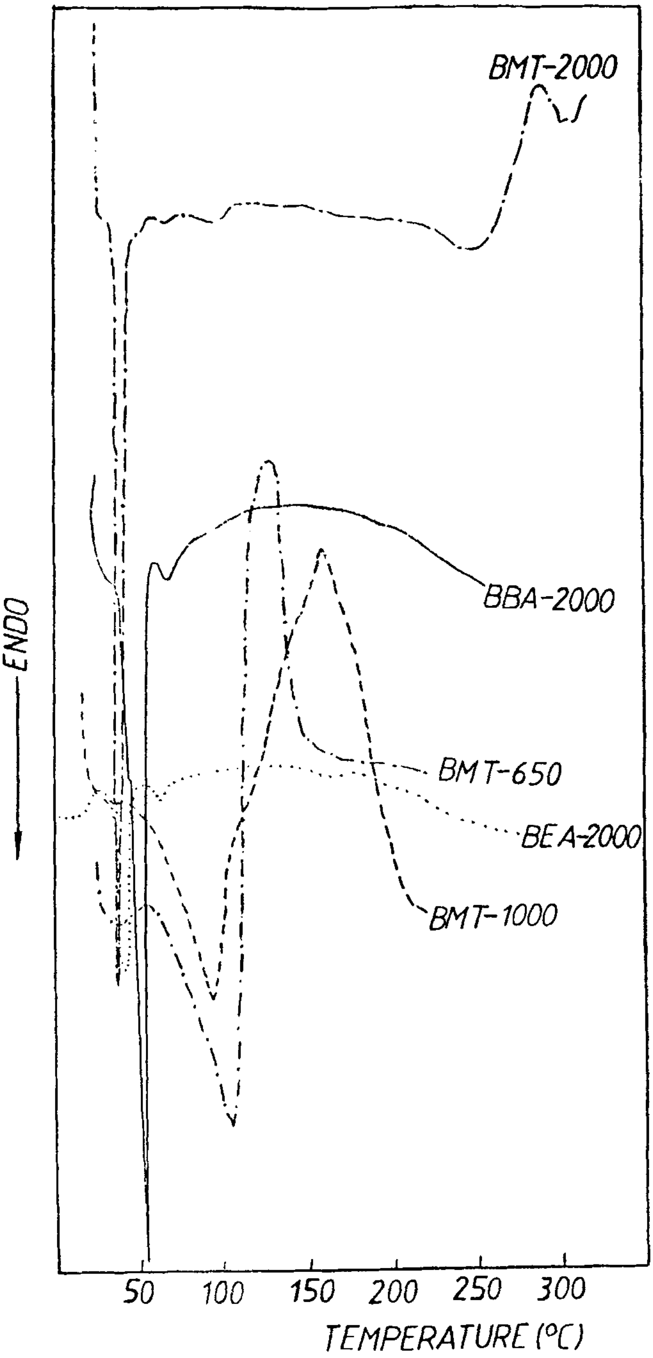
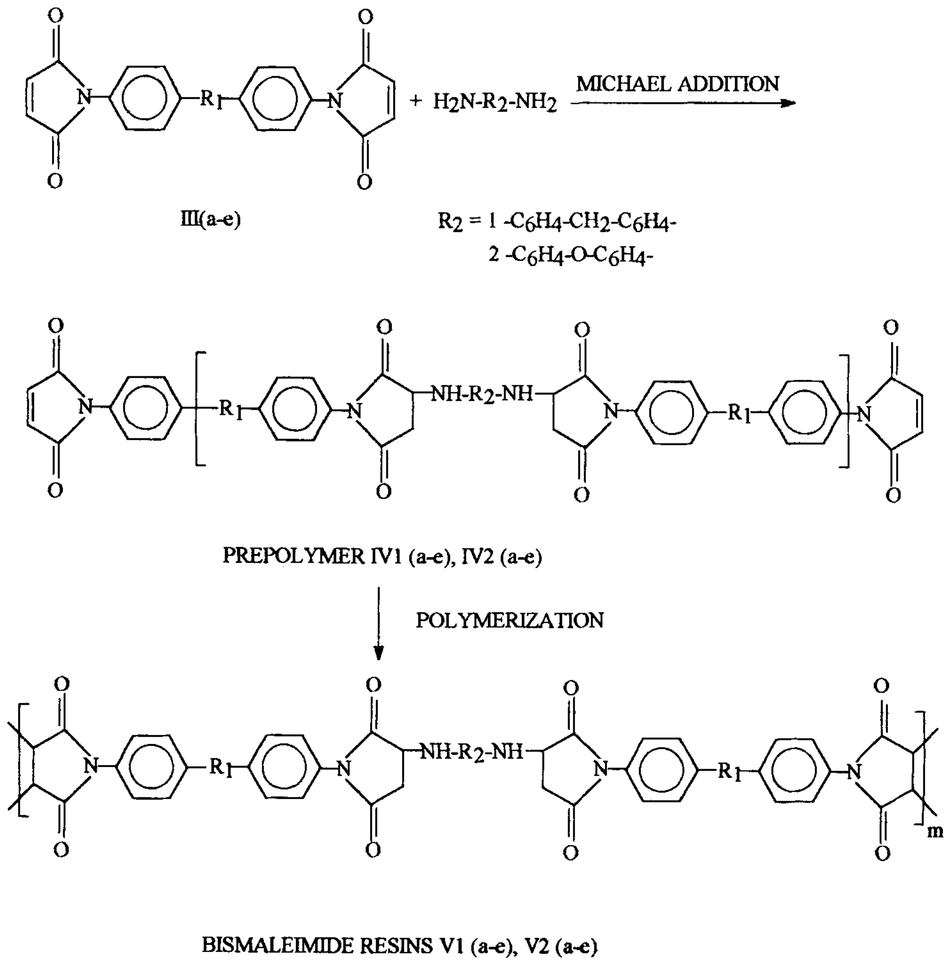


Figure 2. The DSC curves (6°C/min) of bismaleimides III (a-e).



SCHEME 2

while for BMIs BMT-2000, the exotherm maximum of polymerization overlapped the exotherm assigned to the decomposition of the bismaleimide. The low endotherms for BMIs BMT-2000, could be a result of the polydispersities of oligomer used in the synthesis of bismaleimide. The BMIs BBA-2000 and BEA-2000, having more rigid structure, presented an melting endotherm at 42 and 50°C, respectively, and broad exotherms corresponding to the polymerization process.

The thermal stability of the BMIs monomers was evaluated by TGA in air, at a heating rate of 12°C/min (Table 3). The BMIs BMT-650, BMT-1000 and BMT-2000, showed two stage decomposition patterns, while the BMIs BBA-2000

TABLE 4. The Thermal Behavior of Polyaminobismaleimide Resins.

Resins	IDT[a] (°C)	PDT_{max}[b] (°C)	Temperatures (°C) for % weight loss			Yc_1[c] (%)	Yc_2[d] (%)
			5%	10%	20%		
V1 a	240	323;418	290	315	355	22.61	58.93
V1 b	248	323;420	303	323	365	28.21	39.92
V1 c	285	338;428	338	370	398	16.21	40.04
V1 d	282	388	335	348	365	20.67	60.93
V1 e	252	390	330	352	370	18.29	59.63
V2 a	240	375;418	303	328	360	25.63	-
V2 b	242	323;420	303	323	365	27.75	38.80
V2 c	270	325;420	318	352	395	15.22	28.93
V2 d	293	398	342	360	375	30.67	50.89
V2 e	270	328;410	308	318	338	28.78	37.25

[a] Initial decomposition temperature.

[b] Maximum polymer decomposition temperature.

[c] Weight loss at 270°C for 18 hours in static air.

[d] Weight loss at 310°C for 21 hours in static air.

and BEA-2000 showed similar decomposition patterns. The temperature at which 10% weight loss of bismaleimides occurred (T_{10}) ranges from 318 to 352°C.

The poly(aminobismaleimide) resins V1(a-e) and V2(a-e) were prepared in two steps (Scheme 2). In the first step, from a Michael addition of 0.5 mol diamine (DDM or ODA) to 1.0 mol BMI, in NMP, the intermediar maleimide end-capped prepolymer [IV1(a-e) and IV2(a-e)]. In the second step, the maleimide end-capped prepolymer was cured on preheated glass plates, at 100°C for 90 min then at 150°C for 2 hours, and then maintained at 200-220°C for 4 hours. Flexible and brittle films were obtained. The initial mixture composition and the conditions of reaction, the inherent viscosities of prepolymers were presented in Table 4. The films were characterized by IR spectroscopy, TGA, and mechanical measurements and isothermal weight loss in air, at 270°C and 310°C, for 18 and 21 hours, respectively, were determined.

The thermal stability of the aminobismaleimide resin (V1,2) films containing urethane links were presented in Table 5. As can be seen, a good thermo-

TABLE 5. Formulations and Processing Conditions of Bismaleimide Resin Films Prepared in NMP as Solvent.

Resins	Composition of Reaction Mixture	η_{inh}[a] (dL/g)	Temperature, Reaction Time and Comments
V1a	4g BMT-650 + 0.366g DDM + 20mL NMP	0.87	80°C/3h, 100°C/90min then 150°C/2h and 200-220°C/4h.
V1b	2gBMT-2000 + 0.138 g DDM + 15mL NMP	0.12[b]	80°C/4h, 100°C/90min, then 150°C/2h and 200-220°C/4h. Films with defects.
V1c	5g BMT-2000 + 0.2g DDM + 20mL NMP	0.33	80°C/4h, 100°C/90min, then 150°C/2h and 200-220°C/4h.
V1d	4g BBA-2000 + 0.163 g DDM + 20mL NMP	0.40	80°C/3h, 100°C/90min, then 150°C/2h and 200-220°C/4h.
V1e	4g BEA-2000 + 0.163 g DDM + 20mL NMP	0.14[b]	80°C/5h, 100°C/90min, then 150°C/2h and 200-220°C/4h. Defect films.
V2a	4g BMT-650 + 0.369g DDO + 20mL NMP	0.55	80°C/3h, 100°C/90min, then 150°C/2h and 200-220°C/4h.
V2b	4gBMT-1000 + 0.271g DDO + 20mL NMP	0.35	80°C/3h, 100°C/90min, then 150°C/2h and 200-220°C/4h.
V2c	4gBMT-2000 + 0.165g DDO + 20mL NMP	0.26	80°C/3h, 100°C/90min, then 150°C/2h and 200-220°C/4h.
V2d	4g BBA-2000 + 0.165g DDO + 20mL NMP	0.37	80°C/3h, 100°C/90min, then 150°C/2h and 200-220°C/4h.
V2e	4g BEA-2000 + 0.165g DDO + 20mL NMP	0.45	80°C/3h, 100°C/90min, then 150°C/2h and 200-220°C/4h.

[a] Inherent viscosity of the prepolymers precipitated before cured, in NMP, at concentration of 0.5 g/dL, at 25°C.

[b] Prepolymers partially soluble.

oxidative stability of resins was found in comparison with that of the polyurethanes obtained from polyethers with MDI, extended with aromatic diamines and cured [17]. The weight loss after 18 hours at 270°C for V1,2 samples varied in the range of 15.22 to 30.67%. After 21 hours at 310°C, the weight loss varied in the range of

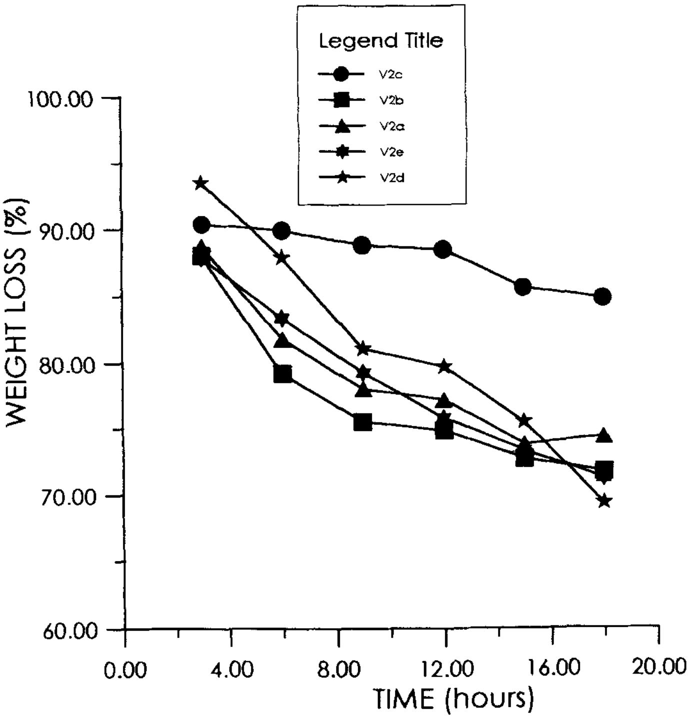


Figure 3. The isothermal weight loss in air, at 270°C for 18 hours and at for 310°C for 21 hours.

28.73 to 50.89%. The higher weight loss is observed for bismaleimide resins containing urethane polyester moieties. The samples of the bismaleimide resins lost their mechanical properties and became dark in color after cured at 270°C and 310°C, respectively, for 18 and 21 hours. Figure 3 showed the weight loss of the bismaleimide resins at constant temperature in air. As can be seen, the PTHF based imide resins are more thermally stable, while their stabilities ranged between those of the poly(aminobismaleimide) resin derived from BMI/DDM (V1), and the polyurethane derived from MDI and polyethers .

The mechanical properties of the bismaleimide resin films were presented in Table 6. The stress-strain curves of the aminobismaleimide resins (Figure 4) showed an elastic-plastic behavior with low elastic domains and a plastic flow until break. From Table 4, 6 can be seen a good concordance between mechanical properties of resins, and the inherent viscosities of the prepolymers. The

TABLE 6. Physical Properties of Bismaleimide Resins Films.

Resins	Tensile strength [MPa]	Elongation at break [%]	Tensile[a] Modulus [MPa]	Elastic Resilience [MPa]	Elongation in elastic domain [%]
V1a	114.56	50.28	223.80	7.83	8.90
V1c	43.45	60.15	28.65	3.50	23.45
V1d	114.79	14.76	399.65	18.74	14.36
V2a	123.84	44.49	156.52	5.07	8.40
V2b	83.41	50.35	142.55	6.70	9.94
V2c	34.92	62.35	26.66	1.81	50.88
V2d	40.04	13.67	328.83	11.10	8.40
V2e	42.83	10.67	350.25	—	—
KINEL[b] 5505	40.67	<1	~5300	—	—
U.M.P.[c]	6.18	223	—	—	—
D.[d]	49.23	590	11.06[e]	—	—

[a] Initial tensile modulus for stress 0.1-1N.

[b] Mechanical properties of KINEL 5505 resins [19].

[c] Mechanical properties of urethane modified polyimide [18].

[d] Mechanical properties of cast urethane elastomers [20].

[e] Modulus at 300% for urethane elastomers [20].

prepolymers with inherent viscosity higher than 0.4 dL/g (V1a, V1d, V2a, V2b) led to aminobismaleimide resin films with tensile strenght higher than 80 MPa. The mechanical properties of the films were affected by the molecular weight of the polyol used in synthesis of the bis-maleimide (Figure 4a). With increasing of the molecular weight, the tensile strength and modulus decreased. For the same molecular weight, the nature of aliphatic chain leads to different values of tensile strength and modulus (Figure 4b). Also, the mechanical properties can be influenced by the nature of the diamine used in the synthesis of the prepolymer. The resins with DDM showed a higher modulus than those with ODA (Figure 4c).

The stress-strain properties of the poly(aminobismaleimide) resins were superior to Kinel 5505 [19], polyurethane modified with aromatic polyimides

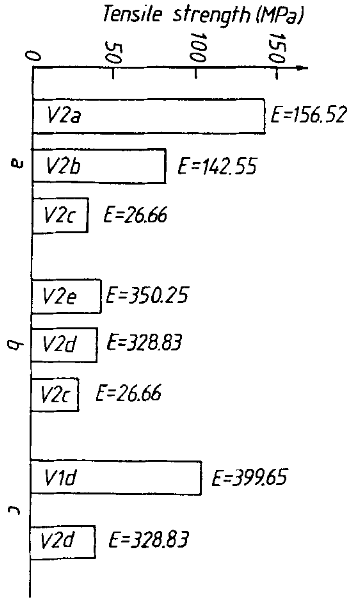


Figure 4. Effect of structure bismaleimide resins on tensile strength and Young modulus: a) same structure, different molecular weights of the polyol; b) same molecular weight, different structures of the polyol; c) same polyol, different diamines.

containing pyromellitic anhydride [18], or urethane elastomers synthesized from PBA-2000 and 4,4'-methylenediphenyl-diisocianate [20].

CONCLUSIONS

New bismaleimides and their poly(aminobismaleimide) resins with urethane linkages were synthesized by addition and polymerization reactions.

The physical and mechanical properties of the poly(aminobismaleimide) resin films, prepared by us ranged between those of the polyurethanes and the classical poly(aminobismaleimide) resins reported in literature.

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