Mono- and Bis- Maleimide Resins in Preimpregnated Fibres

Heinrich Horacek[*]

A-4048 Puchenau, Am Wiesenrain 1, Austria

Abstract: Fibres are preimpregnated by solutions of mono- and bis-maleimides with comonomers. Imides alone polymerize to resins with too low energies of fracture. In the presence of Methylene dianiline or Aniline Diphenylmethylenebismaleimide reacts via Michael addition to equimolar addition products. When fibres are preimpregnated with these addition compounds alone or in combination with flame retardants, B-prepregs are obtained, which after curing show high glass temperatures and sufficient energies of fracture. 2.5 moles of Diphenylmethylene bismaleimide and 1mol Methylene dianiline or 1mole Aniline react to resins with glass temperatures of 350 and 380°C and energies of fracture of 75 and 100J/m^2. The resins contain no carcinogen or blood harming free amines. A one pot reaction starting from Methylene dianiline and Maleic anhydride is possible and more economic. As polymerized bismaleimides possess their imide bonds in the side chain, they are strictly spoken no polyimides with imide bonds in the main chain. Diphenylmethylenebismaleimide and styrene as copolymer react to an insoluble crosslinked polymer. Fibres are preimpregnated with equimolar mixtures of 2- Bromophenylmaleimide and styrene. After curing laminates with 285°C glass temperature and sufficient energies of fracture are obtained. The heat resistant resins are charring polymers and display higher Limiting Oxygen Indices, when the heats of combustion are increased. Differential Scanning Calorimetry determines the temperatures and the heats of glass transition, which indicate that the glass temperature is raised, when the enthalpy is increased and the entropy reduced, which is achievable by Diphenylbismaleimide and 2-Bromophenylmaleimide with their large side groups appropriate for intermolecular forces and steric hindrance.

Keywords: Thermodynamic, heat resistant, burning behaviour, brittleness, toxicity.

INTRODUCTION

Polyimides PIs are thermo resistant polymers with imide groups in the main chain. The most popular route to PI is based on the reaction of aromatic diamines with dianhydrides. PI is offered as thermoplastic granules, as thermoset powders or as semi finished products like preimpregnated fibres so-called prepregs, circuit boards, coil coatings, composites, varnishes or fibres for fire protective clothes. Since 1955 they are commercially available and since then many investigations documented in numerous publication have been performed [1-22]. On the one hand PIs compete with engineering and commodity plastics and on the other hand with iron and aluminium. PIs show residues between 25 to 50% and belong to the group of charring plastics. They are highly related to graphite, electric conductive polymers and organic colour pigments, which all have in common a conjugated double bond structure. They resist against heat up to 250-350°C and are expensive with prices of 15 to 100€/kg. The commodity plastics polyethylene PE, polystyrene PS and the engineering plastic polyamide PA are products with prices from 1 to 4€/kg and with heat stabilities from 100 to 240°C. They belong to the non charring polymers and decompose completely without residues. Table **1** allows a view on the market. In comparison with the engineering plastic Polyamide 6 and 66 with 10^7 to in 2015 PIs are niche products of still small volume. The reason for this is to be seen in their high prices, which allow only selected applications.

BMI are available under the brand names Matrimid from Ciba Geigy/BASF, Kerimid or Kinel from Rhone Poulenc, Compimide from Technochemie now Evonik Industries, IM-AD/BTL from Speciality Resin, Desbimide from DSM, M-S-series from Mitsui Toatsu and Homide from HOS Technik.

Other suppliers and data from the market are provided by the studies:

Kline & Company INC: Advanced Materials Technologies high temperature Polymers 1989 Report 13

Global Bismaleimide Market by Manufactures, Regions, Type and Application, Forecast to 2021 Business Development Development Executive damandeep.k@absolutereports.com [17].

Since long PAI, PEI and PI are well established and no further developments are observed. Only the small group of BMI have experienced larger changes.

---

[*]Address correspondence to this author at the A-4048 Puchenau, Am Wiesenrain 1, Austria; E-mail: aon.913086025@aon.at

E-ISSN: 1929-5995/20

Table 1: World Wide Consumption of Polyimides and Polybismaleimides from 1988 to 2015

Products	1988		1995		1998		2015	
	10^3 to	10^6\$	$10^3$to	10^6\$	$10^3$to	10^6\$	$10^3$to	10^6\$
Polyamidimides PAI	1.5	103	2.3	115	3.6	187.5	6	300
Poletherimides PEI	4.5	49	8.0	112	15.8	170.5	39	390
Polyimides PI	1.8	213	4.5	517.5	7.2	1158	20	2200
Polybismaleimides BMI	0.5	21.5	0.7	35	0.9	49	2	100

Bismaleimides are the reaction product of diamines with maleic anhydride. They possess two double bonds. In the presence of amines or other H donating compounds they perform the Michael reaction and react to the precursor resin.

1957 the patent US 2,818,405 [23] was granted to DuPont, in which liquid diamines and bismaleimides reacted to elastomers. 1968 in the patent US 3,380,964 from Rhone Poulenc [24] homo and copolymerization of BMI are claimed. In the same year the synthesis of polyaminobismaleimides from bismaleimides and aromatic diamines is described in Brit 1,190,718 [25]. The early market leader Rhone Poulenc withdraws Kerimid based on the carcinogenic Methylene dianiline MDA. Ciba Geigy, now BASF, develops Matrimid 5292 a 1:1 mixture of diphenylbismaleimid DPBM and diallyl bisphenol A claimed in the patent US 4,100,140 [26].

In 1990 HOS Technik enters into the market with the precursor resin Homide 250, Pyrrole 2,5dione 1,1‘(methylene di 4,1 phenylene) and methylene bis(benzene amine) CAS 26140-67-0 with reduced amount of free MDA. The procedure is described and claimed in WO 97/33933 [27].

Toxicity and price largely depend on the aromatic diamine applied in the synthesis of BMI as well as on the amine, which serves as comonomer in the Michael reaction.

Table **2** shows possible candidates as alternatives for MDA: 5 (6) Amino 4`aminophenyl -1,3 trimethylindane, 2, 5 Bis(4-aminophenylthio) thiadiazole BDT [28-30], 2(4-5 Aminophenylthio) 4(4-aminophenyloxo) thiazol BT, Tris (3 -aminophenyl) phosphine oxid TAP, 4, 4 Bis (4 -aminophenoxyphenyl)sulfone p-BAPS and 4, 4 Bis (3-aminophenyloxyphenyl)sulfone m.BAPS and 2, 5 Bis(4-aminophenylthiophenyl)sulfone BDS.

Aniline, which reacts with formaldehyde to Methylenedianiline MDA, is the cheapest amine in the list of diamines in Table **2**, but as mono amine aniline can be only applied in the Michael reaction. MDA and Naphthene diamine NDA are key products for polyurethanes and are available in large quantities. Also 5(6) Amino 1- (4‘aminophenyl) 1, 3 trimethylindane DAPI, a reaction product of two molecules alpha Methylstyrene, is moderate in price. m- Aminophenol and m-Aminobenzoic hydrazide are building parts in commercial products.

Diamines can be used as reactants for the synthesis of bismaleimides and or as ingredients for the Michael reaction. Mono amines can only react in the synthesis of mono maleimides or in the Michael reaction. Mono maleimides and styrene polymerize to heat resistant styrene maleimide polymers. When the same diamine is used in the synthesis of bismaleimide and in the Michael reaction, the two stage reaction can be performed in a one pot reaction starting from one mole diamine and two moles maleic anhydride for the bismaleimide reaction followed by the Michael reaction between bismaleimide and diamine to the BMI resin.

Many bismaleimides BMI, which are based on MDA and other diamines such as those given in Table **2** are described in the literature [3,33]. Their data as far as available are represented in Table **3** and **3a**: Their formulas, molecular weights MW, heats of formation Hf, heats of melting and polymerization hm/hpol as well as combustion and decomposition hcomb and hdec, the temperatures of melting, of polymerization, of glass transition and decomposition Tm, Tpol, Tg and Tdec and the amount of residue Rdec are summarized.

The data for the heats of formation Hf and of combustion hcomb are calculated according to van Krevelen [42,43].

The heats of decomposition hdec as well as the residuals after degradation Rdec result from balances of weights and heats.

The most important measure for the achieved thermo resistance is to be seen in the glass transition

Table 2: Aromatic Amines their Abbreviation, their CAS and Formula

Product	Abbreviation	CAS	Formula	Tf (°C)
Aniline	A	62-53-3	C_6H_7N	-6
Methylene dianiline	MDA	101-77-9	$C_{13}H_{14}N_2$	80
5 (6) Amino 4‘aminophenyl- 1,3 trimethylindane	DAPI	62929-12.6	$C_{18}H_{22}N_2$	-
2, 5 Bis(4-aminophenylthio)thiadiazol	BDT		$C_{14}H_{12}N_4S_3$	253
2 (4-aminophenylthio) 4(4-aminophenyloxo)thiazol	BT		$C_{15}H_{14}N_3S_2O$	175
4,4 Bis(4-aminophenylthiophenyl)sulfone	BDS		$C_{24}H_{20}N_2S_3O$	250
4,4 Bis(3- aminophenoxyphenyl)sulfone	m-BAPS		$C_{24}H_{20}N_2O_4S$	-
4,4 Bis(4-aminophenoxyphenyl)sulfone	p-BAPS	13080-89-2	$C_{24}H_{20}N_2O_4S$	188
Tris(3-aminophenyl)phosphine oxide	TAP	36 357-49-0	$C_{18}H_{18}N_3O_4P$	260
m- Aminophenol	m-AP	591-27-5	C_6H_7NO	122
m- Aminobenzoic hydrazide	m-AH	5351-17-7	$C_7H_9N_3O$	105
1,5 Diaminonaphthalene	NDA	2243-62-1	$C_{10}H_{10}N_2$	186

Table 3: Bismaleimides Based on Different Diamines

Diamine	MDA	DAPI	BDS	TAP
Formula	$C_{21}H_{14}N_2O4$	$C_{26}H_{22}N_2O_4$	$C_{32}H_{22}N_2S_3O_6$	$C_{26}H_{18}N_3O_5P$
MW g/mole	358	426	626	483
Hf kJ/mole	-477,5	-545	-316	-831
hm/hpol kJ/g	0.09/-0.27	/-0.09	/-0.13	/-0.22
Tm/Tpol/Tg°C	155/240/435	95/203/-	140/-/-	95/195/320
hcomb kJ/g	-27.3	-30.1	-26.1	-20.4
Tdec °C	490	450	439	460
hdec kJ/g	0.41	0.90	0.19	0.86
Rdec %	45	11	15	25
CAS/ Lit.	13676-54-5	3)34)	35)36) 37)	31)32)33)

Table 3a:

Diamines	BDT	p-BAPS	m-BAPS	BT
Formula	$C_{22}H_{12}N_4S_3O_4$	$C_{32}H_{20}N_2O_8S$	$C_{32}H_{20}N_2O_8S$	$C_{23}H_{13}N_3S_2O_5$
MW g/mole	492	592	592	475
Hf kJ/mole	46	-959	-959	-337
hpol kJ/g	-0.19	-0.16	-0.19	-0.17
Tm/Tpol/Tp°C	263/-/-	250/-/-	90/295/-	205/-/-
hcomb kJ/g	-23.0	-25.0	-25,0	-23.8
Tdec °C	430	460	430	450
hdec kJ/g	0.27	1.56	1.56	0.88
Rdec %	16	30	18	8
Lit.	28)		3)	28)

temperature Tg and the temperature of decomposition Tdec. As the temperatures of degradation for heat resistant polymers do not differ very much and lie at about 450°C, the most important property remains Tg. Bismaleimide BMI based on MDA has a high glass temperature of 435°C. BMI synthesized from Tris (3-aminophenyl) phosphine oxide TAP described by Varma [29-33] exerts a glass temperature of 320°C. From the mentioned BMIs the glass temperatures are not available. Under the assumption that a high Tm will lead to a high Tg bismaleimides based on2,5 Bis(aminophenylthio)thiadiazol bismaleimide BDT with the highest Tm of 265°C followed by p-BAPS 4,4`bis (4-aminophenoxyphenyl)sulfone with Tm= 250°C and 2 (4-Aminophenylthio) 4(4-aminophenyloxo) thiazol bismaleimide BT with Tm= 205°C are those, which promise high Tg. Interesting is the fact that 1-(4-aminophenyl)-1, 3 trimethylindane bismaleimide DAPI evolves about half the heat of polymerization. With Tm =90°C m-BAPS, though nearly related to p-BAPS, has the lowest temperature of fusion. The observed or expected advantages in properties seem not enough to justify a switch over from MDA to a substitute. Therefore a critical look is thrown on BMI based on MDA with the aim of reduction of toxicity and costs of manufacture: The precursor DPBM/MDA 2.5/1 molar ratio with very low MDA free content is produced in a one pot reaction starting from MDA and MSA or the cheap aniline is integrated into the prepolymer DPBM/A 2.5/1 instead of MDA. Equimolar mixtures of Styrene and 2- Bromophenylmaleimide applied on fibres are prepregs, which cure to polymers with high glass temperature and sufficient fracture energy.

EXPERIMENTAL

In Table **4** the ingredients used and their providers were summarized.

For the production of DPBM from MDA and maleic anhydride three different procedures were described:

1. Acetic anhydride dehydration in DMF or acetone US 3,127,414 [38]
2. Closed loop thermal dehydration in toluene and dichloromethane Daman Global Bismaleimide Market by Manufacturers (2017) [17]
3. Azeotropic distillation in toluene WO 97/47597 [39,40]

Table 4: Chemicals used for the Production of BMI Precursor Resins

Chemical	Provider	CAS No
4,4´ Bismaleinimidodiphenylmethylene DPBM	HOS Technik	13676-54-5
Dimethylformamide DMF	DuPont	68-12-2
Maleic acid anhydride MSA	DSM	108-31-6
Diaminodiphenylmethane MDA	BASF	9063-71-2
Acetic acid anhydride	Augusta Laborbedarf	108-24-7
Methane sulfonic acid	elf atochem	75-75-2
N-Xylylmaleimide Xylyl	Chemie Linz	1206-49-1
N-Phenylmaleimide Phenyl	Chemie Linz	941.69-5
2-Bromophenylmaleimide BrPhenyl	Chemie Linz	
Tribromphenylmaleimide TBrP	Chemie Linz	59789-51-4
Ethylene bis tetrabromophthalimide ETBr	Saytex BT93	32588-76-4
Bicyclopentaerythritol phosphate BCPP	Great Lakes Chemical NH 1197	
Dicyandiamide and Melamine DCDA/M	BASF	461-58-5/108-78-1
Melamine polyphosphate MPP	cfb Budenheim Budit 3141	56386-64-2
Glass tissue US 2116 100g/m^2	Tissa Comp.	
Aniline A	BASF	62-53-3
Di-tert butylperoxid	Peroxidchemie	110-05-4
Azoisobutyronitril AiBN	Mainchem Co.	78-67-1
Toluene	INEOS Köln GmbH	108-88-3

The One Pot Process in 40 % Solution WO97/3393 A1 [27]

98g MSA were dissolved in 200g DMF. A solution of 99g MDA in 125g DMF was added. The mixture was stirred for 2 hours at RT. In this time MSA and MDA reacted to the amidoacid. Then 0.5g methane sulfonic acid was added and the temperature was raised to 100°C and a vacuum of 270mbar was applied. A distillate comprising 17% water and 83% DMF evaporated. When 18g water was removed, imidization was finished and the temperature was reduced to 60°C. A solution of 39g MDA in 95g DMF was added. When the viscosity had risen from 5 to 16cSt at 25°C, the solution was cooled to RT. The content was stirred for 1h and then precipitated in 1000g water. The yellow precipitate was filtered, carefully washed with MSA acidic water followed by washing with distilled water. After filtration a yellow cake was obtained, which was dried at 70°C under vacuum. The yield was 213g or 98% of theory. The free MDA content was less 0.1%. Discoloration by formation of aniline black was not observed.

Preparation of BMI Resin 2.5m DPBM and 1m MDA with a Free MDA Content of Less than 0.1% [27]

In a first step DPBM was synthesized [31].

In a second step the Michael reaction took place: 2.5m DPBM and 1m MDA to the precursor in 40%/ 55% solution at 60°C.

A 4l vessel was charged with 1256/942g DMF and 687/945g DPBM. The vessel was stirred and heated to 40°C. When all DPBM was solved 151/207g MDA was added. The whole vessel was floated with N_2. The content was heated to 60°C and kept at that temperature for 3h, until the viscosity had increased 5to 16cSt (40%) or 15 to 60cSt (55%) and the IR band for primary amine band at 3338 cm^{-1} had disappeared. Then the vessel was cooled to 30°C, and the content was precipitated into MSA acidic cold water (pH= 2-3). After filtration the retained cake was washed with MSA acid water (pH=2-3) followed by washing with distilled water. The yield amounted 98% and the content of MDA free was less 0.1%

Preparation of BMI Resin 2.5m DPBM and 1m Aniline A with a Free A Content of Less than 0.1%

The reaction was performed in analogy to the reaction of N-phenylmaleimide with aniline [38].

A 4l vessel was charged with 852.5g DMF and 945g DPBM. The vessel was stirred and heated to 40°C. When all DPBM was solved, 98g A were charged. The whole vessel was floated with N_2. The content was heated to 60°C and kept at that temperature for about 3h, until the viscosity reached 14cSt and the primary amine band had disappeared. Then the vessel was cooled to 30°C. The content was precipitated into MSA acidic water cold water. After filtration the cake was washed with MSA acid water (pH=2-3) followed by distilled water. The yield amounted 1022g or 98% of theory and the content of free A was less 0.1%.

Preparation of Copolymers from Styrene with Phenylmaleimide, Xylylmaleimide, 2-Brom Phenylmaleimide and DPBM

A stirred vessel was loaded with 0.1mole styrene, 0.1 mole maleimide and 400 ml toluene and heated to reflux. Then 0.2% Di tert- butylperoxide and 0.2% AiBN were added. After 2h reflux at 110°C the solvent was eliminated in a Rotavapor. The residue was washed with acetone and dried at 100°C under vacuum for 6h.

Preparation of B Prepregs Comprising BMI Resins with 2.5m DPBM and 1m MDA or 1m A or Styrene-2-Bromophenylmaleimide Resin as well as FRs in Addition in a Tube Reactor Combined with an Impregnation Device for Glass Tissues

The reactor consisted of a stirred 10l vessel with an outlet on the bottom equipped with a pump leading into a copper tube with static mixing elements. A KDM small dosage balance Engelhardt dowitec fed the vessel continuously with a powder mixture comprising 82% DPBM and 18% MDA or 90.6% DPBM and 9.4%A and 0-20% FR and an inlet provided DMF for a 55% solution. The tube with 1.3cm diameter and a length of 50m had a volume of 6.6 l. For the sake of space saving the tube was wounded and placed in a water bath. On one end of the tube was the pump for dosage and on the other end a nozzle with a slit with 1m breadth and a variable width of about 1.3mm. Through the nozzle the solution entered a dipping bath tub. The glass tissue was continuously transported into the bath filled with solution. There it was converted over a diverting roller. The loaded tissue left the bath and entered an IR drying funnel of 1m length. In the funnel it was diverted and passed once more the bath. After twice dipping it entered again the drying funnel and was once more diverted. The temperature in the drying funnel was 130°C and the drying distance after the last dip was 2*1m. The impregnated tissue left the dryer in the B state.

Prepregs with 50% resin and 50% glass content were produced from the glass tissue US 2116 (Tissa Comp.) with a basic weight of 100g/m^2.

The monomers for the resins 1, 2 and 3 were applied as 55% solutions with a densities at 60°C of 1.05g/cm^3.

Resin 1	Resin 2	Resin 3
450g DPBM	498g DPBM	389.3g 2-Bromophenylmaleimide
100g MDA	52g A	160.7g Styrene + 0.6g Benzoylperoxide
450g DMF+5, 10, 15, 20 % FR	450g DMF	450g DMF

In addition flame retardants FR were applied: the halogen flame retardants Trisbromophenyl maleimide TBP, Ethylene bis tetrabromophthalimide EBTBP as well as the halogene free flame retardants Bicyclopentaerythritol phosphate BCPP, equimolar mixture of dicyandiamide and melamine DCDA/M and melamine polyphosphate MPP.

Manufacture of Laminates from B-Prepregs

Laminates with 1.6mm thickness, which are appropriate samples for the UL 94 test, were produced on a Langzauner 220T vacuum press. 14 layers of B stage prepregs were piled and put into the press. Then the press was closed under a pressure of 15bar. Within 30 minutes the press was heated to 180°C and kept at that temperature for 1 hour. In every case about 5% flux of resin was detected. Then the laminate with 1.6mm thickness and about 45% resin content was taken out and cured at 200°C for 48 hours for optimizing the properties.

Characterization of Products

Thermogravimetric Analysis TGA, Thermomechanic Analysis TMA as well as Differential Scanning Calorimetric DSC measurements were performed on a Mettler Toledo TMA/SDTA 840 with TGA/SDTA 851 Modul. Chemicals or extruded samples were placed in aluminium oxide crucibles of 900 µl volume (ME 511119, 960) with 12 mm diameter covered by punctured lids. The TGA measurements took place under nitrogen or air with 80 ml/min at a heating rate of 5-50 K/min. The TMA measurements were performed in aluminium oxide crucibles with 7 mm diameter and 4.6 mm height covered by 6 mm diameter lids in air at a heating rate of 5-50 K/min under nitrogen. The heats of combustion hcomb were measured in a calorimeter according to DIN 51900 Teil 2 (1977) Heizwertbestimmung and calculated. In DSC measurements the chemicals were heated at different heating rates under nitrogen. In this manner the heats and temperatures of fusion hf and Tf as well as those of decomposition Tdec and hdec were determined. TGA measurements under air or nitrogen allowed the determination of residues R.MDA free was determined by gas chromatography Werkvoorschrift Nr. 3002WV-0192 BASF Antwerpen N.V. (1992). The kinematic viscosity was measured in an Ubbelohde viscosimeter according DIN 51562. Fourier- transform absorption spectroscopy was performed on a Bruker IFS 45 spectrometer with the following conditions 4000- 400 cm^{-1} spectral band, liquid state in couvettes.

RESULTS

The Reaction of 2.5moles DPBM with 1mole MDA to BMI Resin

DPBM and MDA were dissolved in DMF in 40 and 55% concentration. The reaction was followed at

Table 5: Production of B-Prepreg without and with FR at 60°C Temperature in a Tube Reactor: Output l/h, Reaction Time h, Speed of the Tissue m/h and Drying Time h at 130°C

Output l/h	Resin 1/2/3 g/h	FR g/h	DMF/DMF+A/ DMF +S g/h	reaction time h	tissue speed m/h	drying time h
1	550/498/389		450/502/611	6.6	5	0.4
1.5.	825/747/583		675/753/916.5	4.4	7.5	0.27
2	1100/		900/	3.3	10	0.2
1.5	804.4/	20.6	675/ TBrP 2.5%			
1.5	783.75/	41.25	675/ TBrP, ETBr, BCPP, DCDA/M, MPP 5%			
1.5	742.5/	82.5	675/ TBrP, ETBr, BCPP. DCDA/M. MPP 10%			
1.5	701.3/	123.7	675/ TBrP 15%			

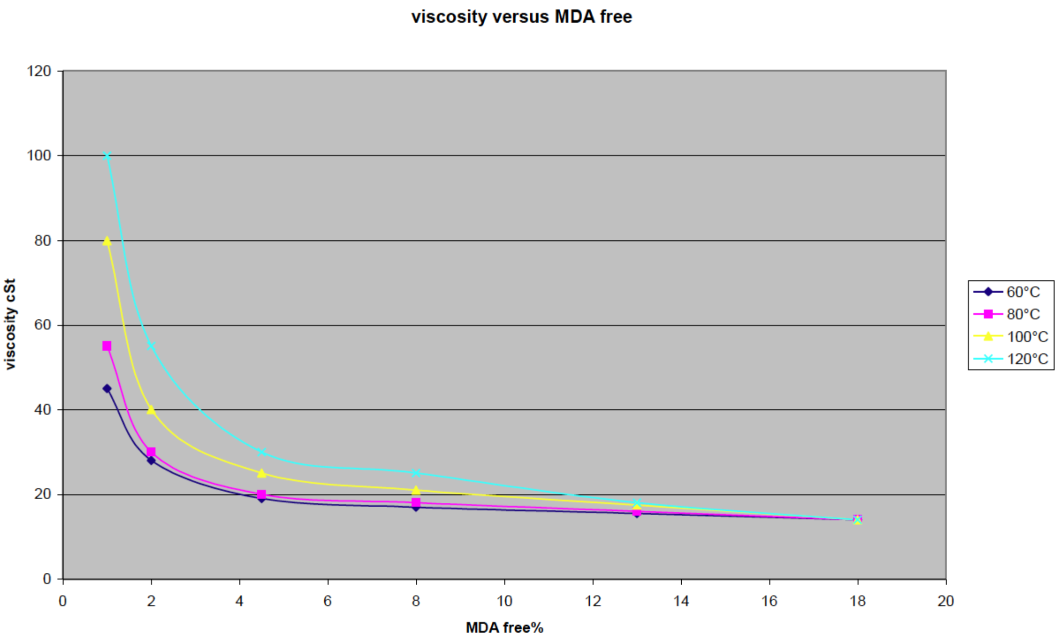


Figure 1: Viscosity cSt versus w% MDA free (solid product) in a 55% solution in DMF.

temperatures between 40 and 120 °C by the content of free MDA and increase in viscosity as given in Figure **1** showing the hyperbolic curves for the free MDA calculated for solid in order to eliminate the influence of concentration and the corresponding viscosity for a 55% solution.

In Figure **1** the curves were of hyperbolic shape, indicating that the product MDA free*v was constant. In Table **6** the viscosities for 40% and 55% solution were listed in dependence of the conversion c.

Equilibrium was observed for the Michael addition. At each temperature the reaction stopped at a definite amount of MDA free. Therefore the equilibrium with the constant Ke was set up in equation 1: 1-c moles MDA and 2.5-c moles DPBM were in equilibrium with c moles MDADPBM at the conversion c.

$$Ke = MDADPBM/(MDA\ free*DPBM) = c/\ [(1-c)(2.5-c)] \qquad equ.1$$

In the Arrhenius plot of MDA free or Ke in dependence of temperature activation energy EA=18kJ/mole was obtained.

When the equilibrium state was reached, the mixture was precipitated in maleic acidic water. After precipitation the equilibrium in solution was no longer valid, MDA free and maleic acid reacted to a soluble salt remaining in the filtrate.

The reaction between 2.5m DPBM and 1m MDA was followed in solution by determining the free MDA content and the viscosity at 25°C as measure for the molecular weight. FTIR, DSC and C^{13} NMR data in the literature [47-50] indicated that DPBM reacted with MDA to MDADPBM in a quick reaction. At temperatures higher than 150°C DPBM in excess reacted to the polymer. In IR a quick loss of 50% primary amine and maleimide were observed and instead of maleimide the succinic group occurred. From

Table 6: Conversion c to prepolymers in 40%/55% solution at 120°C, viscosity v at 25°C

MDAfree	c*	viscosity v (40/55%)	MDA free *v (40/55%)
%	mole	cSt	%*cSt
18	0	5/15	90/270
9	0.5	7/21	63/189
6	0.83	9.5/30	57/ 180
1.8	0.9	20/70	36/126
0	(precipitate)	1	20/40

* c = (18- MDA free)/18; 18 was the initial concentration of MDA in the mixture 2.5DPBM/1MDA.

Table 7: MDA Free and the Constant of Equilibrium Ke as a Function of Temperature. Data of Figure 3

T	t	10^3/T	MDA free	c	Ke
°C	h	K^{-1}	%	mole	$mole^{-1}$
120	4	2.545	4	0.78	2.06
100	3.75	2.681	3	0.83	2.92
80	3.5	2.833	2	0.89	5.03
60	3.25	3.003	1	0.94	10.04
40	3	3.195	0.7	0.96	15.58
20	2.75	3.413	0.4	0.98	32.23

these results it was concluded that one double bond of DPBM reacted with one MDA in a quick reaction.

In Figure **2** the Michael reaction was described as formula. The double bond content of 100% for DPBM was reduced to 82% in the mixture and reached 32% after reaction to the addition product DPBMMDA.

The balances of weight and heat were set up. The heats of formation were calculated from the heats of combustion according to van Krevelen [42,43]:

For the endothermic reaction a heat consumption of 18kJ/mole was introduced, which had been derived from MDAfree or Ke in dependence of temperature.

Reaction to the addition product MDADPBM

hreac ex/cal = +16/+16J/g; Double bond 81.9 => (358/4)+(4/1093) = 32% (DPBM 100% double bond content)

F1: 2.5DPBM +1MDA = MDADPBM +1.5DPBM

|MW 895 +198 = 556 + 537

H -1193.75 + 60 +18 = -399.5 -716.25

The reactions of MDADPBM and 1.5 DPBM to 2.5MDADPBpol were followed by DSC measurements in Figure **3**.

In Figure **3** the heat flux was measured for DPBM and for the adduct comprising 2.5m DPBM and 1m MDA at constant heating rate. DPBM fused at 150°C under 90J/g heat uptake and polymerized at 250°C under heat evolution of-265J/g, which was higher than those of -197J/g [3] and -181J/g [44] given in the literature. For BMI a very small heat of fusion was detected at 80°C and at 230°C the heat of polymerization amounted -190J/g. The heat of polymerization of one double bond 85 kJ/mole [46] was introduced into the balance of weight and heat. Under the assumption that in a first step the molten adduct MDADPBM polymerizes and in a second step the molten DPBM polymerized with only one double bond, the following balances were set up:

hpol ex/cal = /-0.12kJ/g; Double bond 32=> (358/4)*(2.5/1093) = 21%

F2: MDADPBM + 1.5DPBM= MDADPBM+ 1.5DPBMpol

MW 556 +537 = 556 + 537 =1093

H -399.5 - 716.25 + 1.5*85= -399.5 -843.75

hpol ex/cal= /-0.08kJ/g; Double bond 21% => (358/4)*1.5/1093) = 12%

F3; MDADPBM +1.5DPBMpol = MDA2.5DPBMpol

MW 556 +537 = 1093

H -399.5 - 843.75- 85 = -1328.25

hpol ex/cal =-0.19 /-0.19kJ/g; Double bond 81.9=> 12%

F2 +F3: MDA DPBM +1.5DPBM= MDA2.5DPBMpol

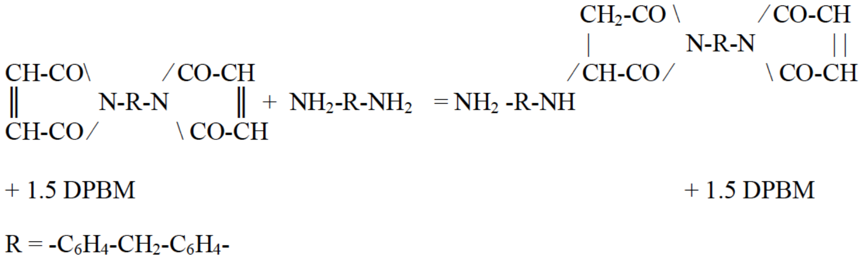


Figure 2: Michael reaction of 2.5m DPBM and 1m MDA to the adduct MDADPBM.

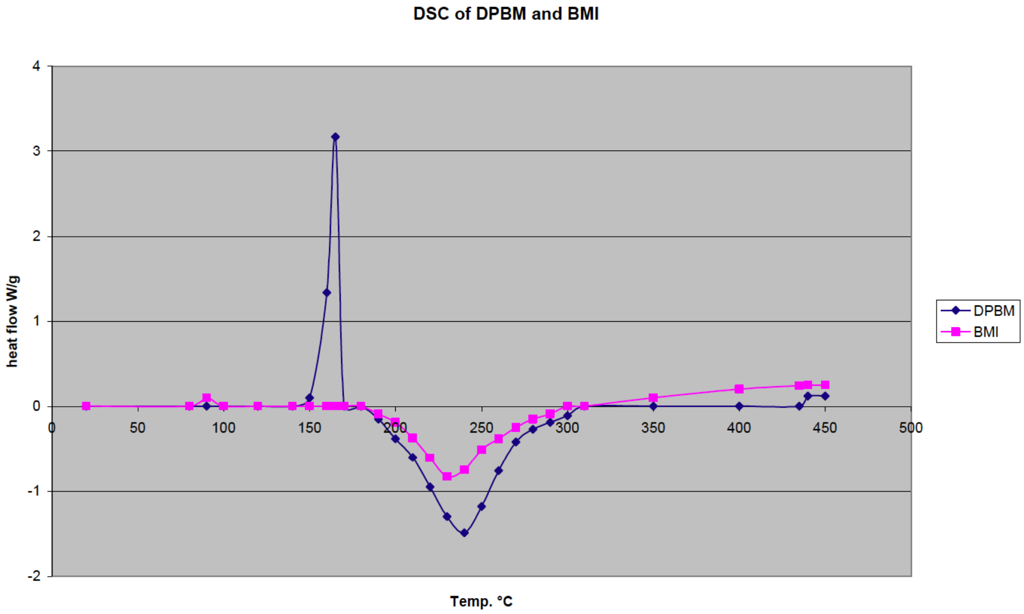


Figure 3: DSC 20K/min heating rate under N_2 : DPBM heat of fusion 0.09kJ/g at 155°C, heat of polymerization - 0.265kJ/g at 240°C and Tg at 435°C. BMI heat of polymerization -0.190kJ/g at 230°C.

MW 556 +537 = 1093

H -399.5 - 716.25 -2.5*85= -1328.25

Giulio [47] investigated the same composition 2.5DPBM/1MDA and observed at 164°C after 5h a double bond reduction from 70 to 40% comparable with F1: 82 to 32% and at 233°C after 5h a residual double bond content of 30% comparable with F2: 32 to 21%.

When Hpol =85kJ/mole was introduced into the balance, measured and calculated heats of polymerization were hpol ex/cal= -0.19/-0.19kJ/g.

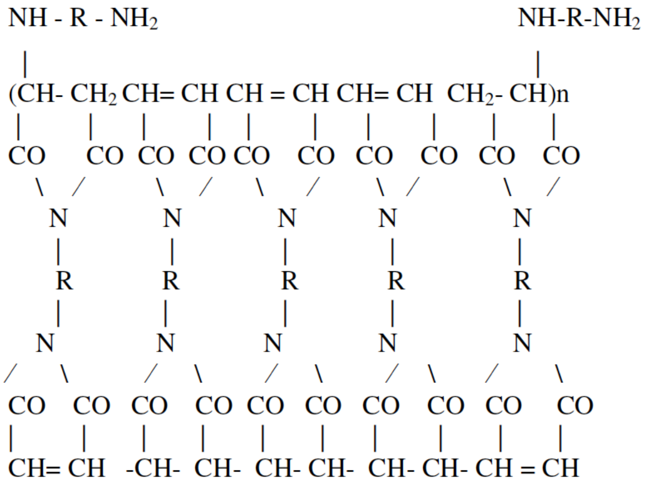


Figure 4: Polymerization of MDA and 2.5DPBM to MDA2.5DPBMpol with a double bond content of 12%.

Under the assumption that DPBM polymerized with only one double bond to a linear chain with a double bond content of 50%, the Succinimide to Maleimide ratio 1/1 was expected

In Figure **5** Poly DPBM with the Succinimide/ Maleimide ratio =1/1 was depicted.

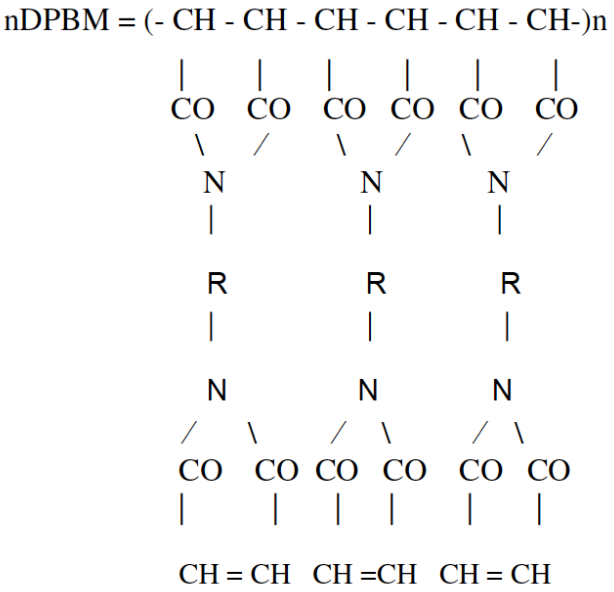


Figure 5: Reaction of DPBM to PolyDPBM with a double bond content of 50%.

The balance of heat and mass was performed for Figure **5** in F5

hpol ex/cal= -0.26/- 0.23kJ/g; Succinimide/Maleimide =1/1; double bond content 50%

F5: 3DPBM = 3DPBMpol

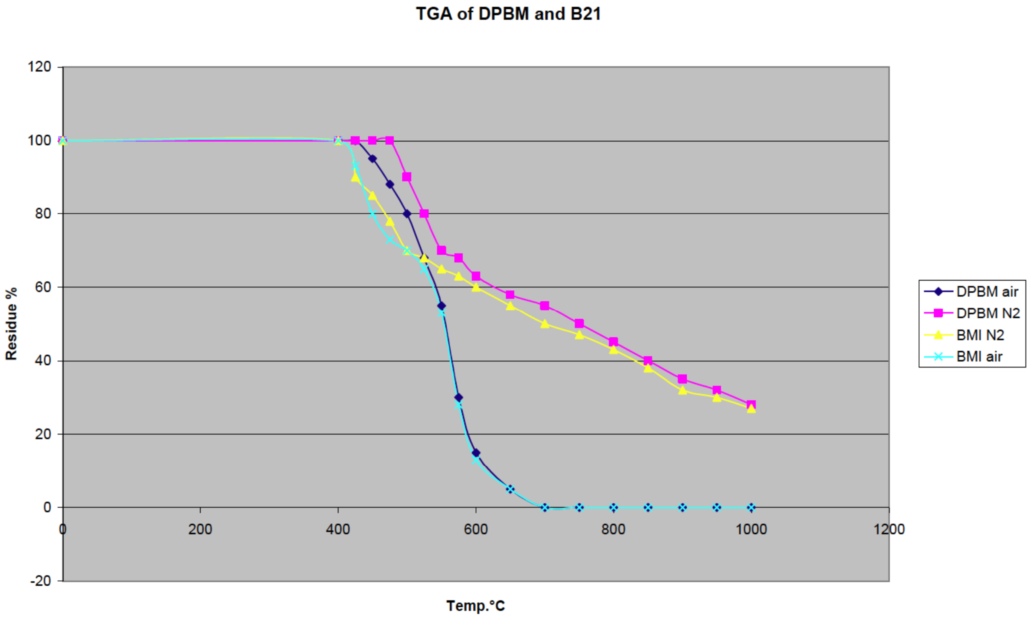


Figure 6: TGA 20K/min N_2 and air of DPBM (DPBMpol) and BMI (MDA2.5.DPBMpol).

MW 3*358 =3*358

H -3*477.5 -3*85= -1687.5

According to Loustalot [48] after 24h at 200°C the ratio of Succinimide to Maleimide was 2/1. In this case a much higher heat of polymerization was obtained by calculation according F5a.

hpol= ex/pol -0,26/-0.32kJ/g; Succinimide/Maleimide =2/1; double bond content 33%

F5a 3DPBM = 3DPBMpol

H -3*477.5 -4*85 = -1772.5

DPBM and MDA2.5DPBM were cured to DPBMpol and MDA25DPBMpol during 24h at 220°C. TGA measurements were taken in air and nitrogen at 20K/min heating rate. In Figure **6** DPBM (DPBMpol) showed the highest heat resistance up to 550°C under nitrogen followed by that under air. BMI (MDA2.5DPBMpol) started to degrade at 450°C and showed two steps of decomposition one at 475 and another at 550°C.

In nitrogen DPBM exerted the first degradation at 490°C and the second at 600°C and 70% residue, in air DPBM degraded at 450°C. Under nitrogen BMI started to decompose at 400°C followed by a second step of degradation at 500°C and 75% residue, in air BMI initiated degradation at 400°C and 450°C at 70% residue.

The events under nitrogen could be expressed by balances of weight and mass.

Degradation of DPBMpol under N_2

hdec ex/cal=/-0.02kJ/g; Rdec ex/cal = 70/69% at 490°C

F6: $C_{21}H_{14}N_2O4$= 4CO + $C_{17}H_{14}N_2$

MW 358 = 112 +246

H- 562.5 - 7= -444- 125.5

hdec ex/cal =/0.40kJ/g; Rdec ex/cal= 30/34% at 600°C

F7: $C_{17}H_{14}N_2$ = $2NH_3$+ C_6H_6+ $0.5C_2H_4$ +10C

MW 246 = 34+ 78+ 14 +120

H -125.5 +142.5 = -92+ 83 +26

hdec ex/cal= 0.40/0.38kJ/g; Rdec ex/cal= 30/34%

F8=F6+F7: $C_{21}H_{14}N_2O4$= 4CO +$2NH_3$+ C_6H_6+ $0.5C_2H_4$ +10C

MW 359= 112+34+78+14 +120

H -591 +164= -444- 92+ 83 +26

Degradation of MDA2.5DPBMpol under N_2

hdec ex/cal = /-0.03kJ/g; Rdec ex/cal = 70/74 at 400°C

F9: $C_{65.5}H_{49}N_7O_{10}$= 10CO + $C_{55.5}H_{49}N_7$

MW 1093 = 280 + 813

H -1328.25- 28= -1110 -240.25

hdec ex/cal= /0.45kJ/g; Rdec ex/cal=40/37.9% at 450°C

F10: $C_{55.5}H_{49}N_7$ = $2C_6H_6$ +$7NH_3$+ C_2H_2 +$3.5C_2H_4$+ 34.5C

MW 813= 156 +119 +26+ 98 +414

H -240.25 + 493.25= 166 - 322 +227 +182

hdec ex/cal= 0.42/0.43kJ/g; Rde ex/cal= 40/37.9%

F11=F9+F10: $C_{65.5}H_{49}N_7O_{10}$= 10CO+ $2C_6H_6$ +$7NH_3$+ C_2H_2 +$3.5C_2H_4$+ 34.5C

MW 1093 = 280 +156 +119 + 26 +98+ 414

H-1328.25 +471.25 = -1110 +166 -322 +227 +182

The experimental hdec ex were obtained from TGA measurement, which were run with different heating rates. The experimental DSC data of Figure **6** were compared with those calculated: DPBM decomposed in N_2 under heat uptake 0.40/0.38kJ/g and BMI degraded in N_2 under heat uptake 0.42/0.43kJ/g.

In Table **8** commercial and experimental products with various ratios MDA/DPBM were collected and compared in respect to their energies of fracture GIC and their heat stabilities quantified in Tg and Tdec.

In Figure **7** the temperature of degradation Tdec, the glass transition Tg, the heat of polymerization hpol and the energy of fracture G_{IC} were correlated with the amount of MDA.

According to Figure **7** BMI comprising 2.5m DPBM and 1m MDA with 18% MDA was a fair compromise between 90J/m^2 energy of fracture and 340°C glass transition temperature. The critical energy of fracture GIC in dependence of the MDA content showed sigmoide shape. At low MDA concentration the relation between G_{IC} and the weight fraction of MDA followed the parabolic equation 2

Table 8: The Influence of the Molar Ratio X/DPBM on the Heat of Polymerization hpol, the Glass Transition Temperature Tg and the Temperature of Degradation Tdec as well as on the Content of MDA Free and the Energy of Fracture G_{IC}

BMI	X/DPBM X= MDA	DPBM - w%	hpol kJ/g kJ/g	Tg /Tdec °C	MDA free w%	G_{IC} J/m^2	CAS
	0/1	100	0.27	435/490	0	0	13676-54-5
	1/3	91	0.25	370/480	1,5	50	
	1/2.5	82	0.23	330/ 475	3	100*	
	1/2	78	0.21	320/470	6	130*	
	1/1	64	0.16	290/450	8	180*	
Kerimid 601	1/ 2.5				8	34	89963-68-8
Kerimid 601	1/1		0.14		8		130777-92-3
Kerimid 601	1/2				6		9063-71-2
Kerimid 607	1/1						35064-37-0
	X= DABPA						1745-89-7
Matrimid 5292	1/3.4	80				30 **	
	1/2	70				60**	
	1/1.6	65				98**	
	1/1.3	60				123**	
	1/0.9	50		273/430		217	
	X= Dipropenylphenoxybenzophenone						
Compimide TM123	1/2			261/459		439	109423-33-8
	X= m-Aminobenzoic hydrazide						5351-17-76
Compimide 796	1/2					63	106856-59-1
	X =Aminmophenol						591-27-5
Compimide 353			0.22				51569-11-0
Compimide 183							98725-11-2

*curing 72h 130°C, 6h 220°C Mittal [8], ** 3h 160°C, 4h 210°C, 5h 240°C [3].
Matrimid 5292 (Ciba Geigy BASF). Kerimid (Rhone Poulenc), Compimide (Evonic Industries).

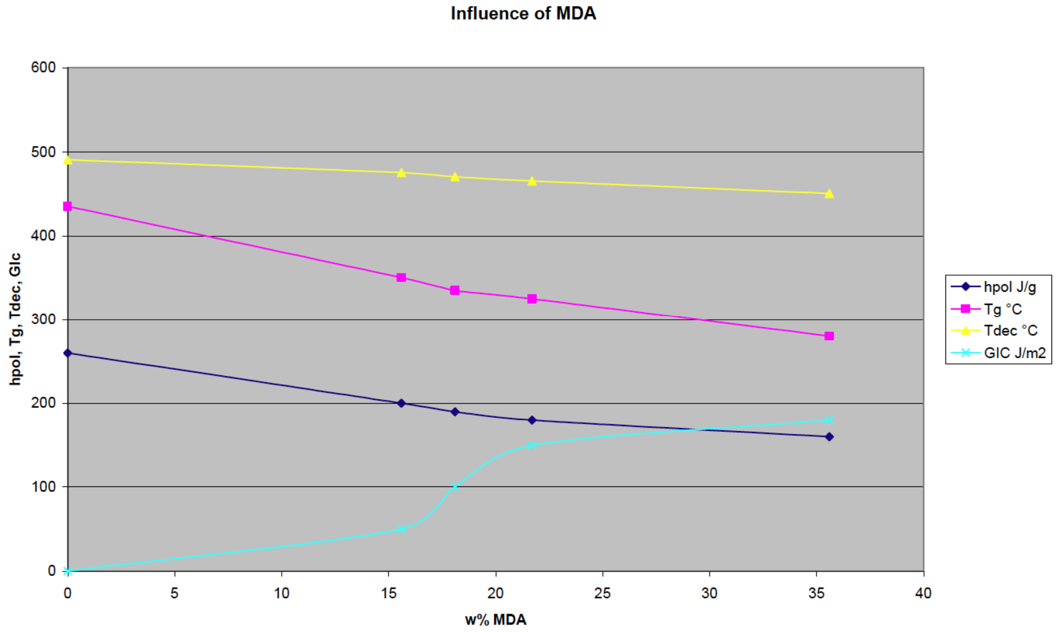


Figure 7: For BMI the energy of fracture G_{IC}, increased with increasing amount of MDA, the temperatures of degradation Tdec, the glass temperatures Tg and the heats of polymerization hpol decreased with increasing amount of MDA.

G_{IC}= 3600*(w%MDA/100)^3 equ.2

The Reaction Product of 2.5moles DPBM and 1mole A

The Michael reaction was also performed with the less expensive aniline A in order to obtain a 2.5DPBM/1A adduct, which was further polymerized to the resin A2.5DPBMpol.

The reaction was transformed in balances of heat and weight using the same heats of reaction for addition and polymerization already used with MDA.

h reac ex/cal = /0.018kJ/g

F12 2.5DPBM + A = ADPBM +1.5DPBM

MW 895 +93 = 451 + 537

H 2.5*477.5 +9 +18 = -450.5 -716.25

hpol ex/cal= /0.24kJ/g

F13: ADPBM +1.5DPBM = A2.5DPBMpol

MW 451 +537 = 988

H- 450.5 - 716.25- 2.5*85 = -1379.25

In the past Technochemie offered BMI resins based on m Aminobenzoic hydrazide ABH and m-Aminophenol AP.

In Table **9** the properties of BMI based on MDA, A (Aniline), ABH (m-Aminobenzoic hydrazide) and AP (m- Aminophenol) were compared.

According to Table **9** the highest glass temperature Tg was achieved by BMI based on A.

Reaction of DPBM with Diallybisphenol A via Diels Alders Reaction

DPBM reacted with the aromatic allyl compounds [44,45,51] like diallylbisphenol A DABPA, dipropargylether of bisphenol A DPBPA and Bis (propenyl phenoxybenzophenon) BPPB via Diels Alder reaction. A recent publication [15] described the reactions of DPBM with dipropargylether of bisphenol A ether DPBPA and hexafluorpropyl bisaniline. The commercial resins such as Matrimide 5292 based on Diallylbisphenol A exerted a fraction energy G_{IC} =210J/m^2 and Compimide TM123 based on Dipropenylphenoxybenzophenone G_{IC}= 439J/m^2. For Diallylbisphenol A and DPBM the fracture energy G_{IC} showed no linear but parabolic relation between G_{IC} and the amount of DABPA gibven as weight fraction.

G_{IC} = 2500*(w%DABPA/100)^3 equ.3

The reaction between DPBM and Diallylbisphenol A DABPA was described in balances of weight and heat using 85kJ/mole as heat of polymerization:

hpol ex/cal = /-0.13kJ/g

F14: DPBM + DABPA = DABPADPBM

MW 358 + 308 = 666

H-477.5 -385.5 - 85 = -946

Table 9: BMI resin of 1m DPBM with X Moles Amine via Michael Addition

Comonomer	MDA	MDA	A	AP	ABH
Product	Kerimide 601	Homide 259		Evonik	Evonik
Company	Rhone Poulence	HOS Technik	Chemie Linz	Technochemie	Technochemie
Formula	$C_{34}H_{28}N_4O_4$	$C_{65,5}H_{49}N_7O_{10}$	$C_{58.5}H_{42}N_6O_{10}$	$C_{27}H_{21}N_3O_5$	$C_{49}H_{37}N_7O_9$
MW g/Mole	556	1093	988	467	867
Hf(kJ/mole	-418	-1325.75	-1586	-704	-1303.5
hpol kJ/g	-0.18	-0.19	-0.24	-0.20	-0.11
Tg °C	280	350	380	300	287
hcomb kJ/g	-30,5	-29.0	-28.1	-27.7	-27.0
Tdec °C	450	470	430	450	450
hdec kJ/g	0.17	0.45	0.35	0.53	0.73
Rdec %	40	49	28	13	12.5
CAS/Lit	35064-37-0	26140-67-0		591-27-5	98725-11-2
X	1	0.4	0.4	1	0.5
Reaction	Michael	Michael	Michael	Michael	Michael
GIC J/m^2	34	100	75		65

Table 10: BMI Resin of 1m DPBM and x Moles of DABPA (Diallylbisphenol A), DPBPA Dipropargylether of Bis Phenol A and BPPB Bispropenylphenoxybenzophenone) via Diels Alder Reaction

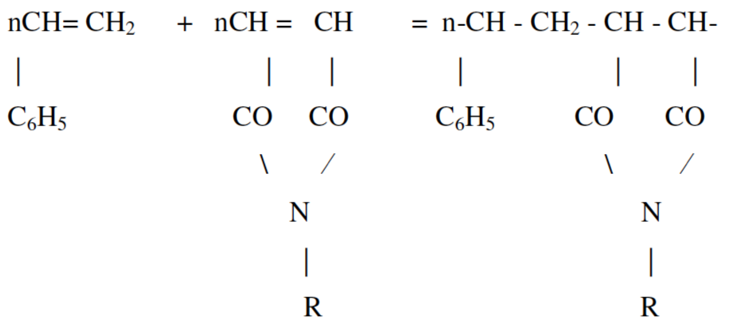
Comonomer	DABPA	DPBPA	BPPB
Product	Matrimid 5292	15)	Evonik
Company	Ciba Geigy		Technochemie
Formula	$C_{42}H_{38}N_2O_6$	$C_{67}H_{51}N_{4.5}O_{11}$	$C_{52}H_{40}N_2O_7$
MW g/Mole	666	1094	804
Hf(kJ/mole	-940	-945	*-2702
Tg °C	280	330	261
hcomb kJ/g	-31.6	-29.5	-31.7
Tdec °C	450	450	450
hdec kJ/g	1.19	1.13	2.5
Rdec %	18	32	25
CAS/Lit	1745-89-7	15)	109423-33-8
X	1	0.4	1
Reaction	Diels Alder	Diels Alder	Diels Alder
GIC J/m2	210		440

Styrene- Maleimide Copolymers MMI

BMI resins were more related with styrene monomaleimide copolymers than with polyimides, because both carry their imide bond in the side chain. From Phenylmaleimide, Xylylmaleimide and 2-Bromophenyl maleimide styrene copolymers were synthesized with the aim of later prepreg production.

Equimolar mixtures of styrene and monomaleimides reacted to linear polymers with alternating styrene and maleimide molecules in the chain, as described in Figure **8**.

Also 1m DPBM was reacted with 1m styrene and a cross linked, insoluble product was obtained. The polymers with monomaleimides were soluble and



R= Phenylmaleimide, Xylylmaleimide, 2-Bromophenylmaleimide

Figure 8: Reaction of styrene and maleimide.

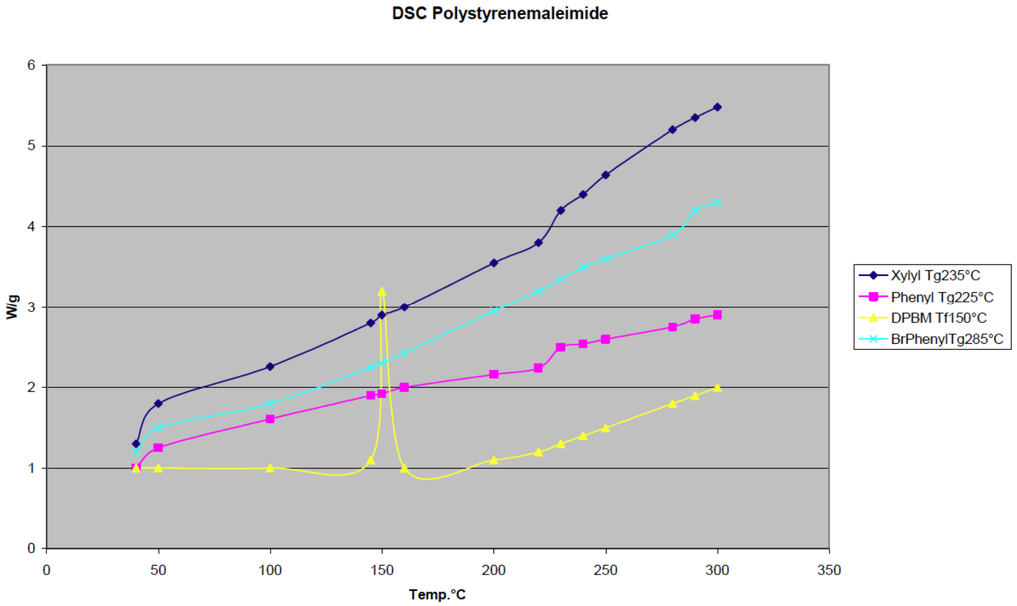


Figure 9: DSC 20K/min N_2 of equimolar styrene Phenyl-, Xylyl- , 2- BrPhenyl- and DPBM- maleimide.

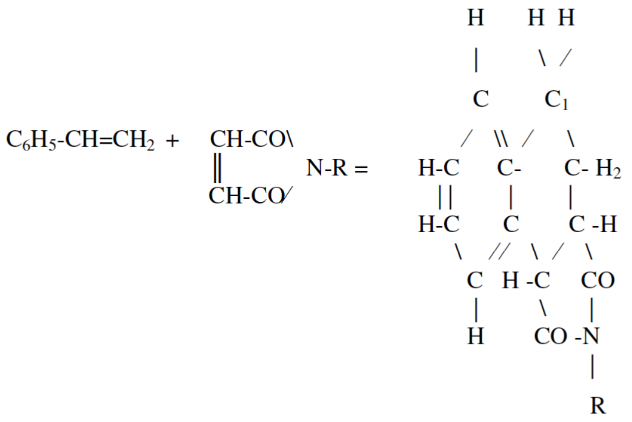
showed all well defined glass transition temperatures. The insoluble polymer with DPBM exerted a melting point at the melting point of DPBM, but evolved only half of the heat of melting. Therefore with high probability one could assume that one half of DPBM had reacted with both double bonds under cross linking and the other half remained not dissolved and melted as DPBM. All products were characterized by DSC measurements in Figure **9**.

The literature postulated for the addition product of styrene or alpha methyl styrene with DPBM a cyclic structure [3]. In Figure **10** this structure was depicted.

A second DPBM should be attached in position C_1 under proliferation of the chain.

The obtained thermoplastic polymers MMI were characterized with their properties, which were given in Table **11**.

BrPhenyl the 2-Bromophenylmaleimide Styrene copolymer showed the highest Tg and was chosen for



R= -CH_2- C_6H_4-N-$(COCH)_2$

Figure 10: Reaction of Styrene DPBM according to literature.

Table 11: Data of Styrene N-maleimide Copolymers MMI

MMI	Xylyl	BrPhenyl	Phenyl
Formula	$C_{20}H_{19}NO_2$	$C_{18}H_{14}NO_2Br$	$C_{18}H_{15}NO_2$
MW g/mole	305	356	227
Hf kJ/mole	-256	-167	-201
hg J/g	1,8	0.20	0.8
Tg °C	/230	/285	/225
hcomb kJ/g	-33.9	-25.1	-32.6
Tdec °C	440	450	460
hdec kJ/g	0.54	1.43	0.70
Rdec %	20	7	17

the manufacture of prepregs. In the case of BMI the B-prepreg consisted of 50% tissue and 50% (51%MDADPBM +49%DPBM). In the case of MMI the B-prepreg comprised 50% tissue and 50% (29%Styrene 71% Bromophenylmaleimide). After curing the B-pregregs to laminates the resins had to be completely polymerized, in order to obtain optimized properties.

As in all balances of weight and heat 85kJ/mole was introduced as heat of polymerization:

Polymerization hpol ex/cal = /-0.48kJ/g

F15: $C_8H_8 + C_{10}H_6BrNO_2 = C_{18}H_{14}BrNO_2$pol

MW 104+ 252 =356

H 58 - 225.5 - 2*85 = -337.5

Decomposition hdec ex/cal =/1.43kJ/g; Rex/cal =10/7%

F16: $C_{18}H_{14}BrNO_2 = 2CO + 2C_6H_6 + Br + 0.5N_2 + C_2H_4 + 2C$

MW 356 = 56 +156 +80 +14 +26 +24

H -337.5 +508.5 = -222 +166+ 227

In Figure **9** the glass temperatures were observed as steps in the heat flow curves. The sigma shaped steps with turning points were characterized by their height W/g and width T= 20*t at heating rate of 20K/min. The width did not differ very much and was about 10°C in any case or t= 60/20=30sec.

By differentiation a maximum was obtained with the coordinates height/2 = (W/g)/2 and width= 30sec.

The area under the maximum was the heat flow integral and could be determined by integration ʃ d(W/g)*30 or approximately by the area of the triangle with the height (W/g)/2 and the width 30sec.

1/2W/g

Heat flow integral hg(J/g) =ʃ d(W/g)*60*T/20 ~ area of triangle = 0.5[1/2(W/g)*30sec] =7.5*W*sec/g equ.4

0W/g

In Table **12** the so determined heats of glass transition Hg, the glass temperatures Tg and the calculated entropies Sg were collected. As dT did not differ very much the value 10°C was taken in every case,

Stoliarov [49,50] investigated charring polymers by DSC measurements and found for PEI a “melting heat or glass transition heat” of 1.0J/g, which fits to the obtained value of 1.7J/g. The observed heats and entropies of glass transition were much smaller than those for melting points. The sterically hindered Xylyl and BrPhenyl copolymers exerted higher Sg values than the non hindered Phenyl. The styrene- Phenyl polymer showed a yellow colour, whereas the styrene Xylyl and BrPhenyl polymers were of white colour. The lack of colour was caused by a breakdown of the conjugated system. For polymers, which change from liquid to solid state without heat development, the glass temperature was equal to the Kauzmann temperature [51,52]. In this case the enthalpy Hg as well as the entropy of glass transition Sg were zero. For polystyrene, PEI, PAI and for equimolar styrene maleimide the glass temperature was not equal to the Kauzmann temperature.

The mentioned PEI and PAI are well known under the brand names Ultem 1000 and Torlon 42030 L and styrene maleimide polymers are sold under the brand names Malecca by Denka Chemicals and styrene maleic acid anhydride copolymers under the brand

Table 12: Non Crystalline Polymers their Glass Transition Temperature Tg, their Heat Flux W/g at Tg and Width of Temperature dT, Heat of Glass Transition Hg and Entropy of Glass Transition Sg

Material	MW g/mole	Tg ° C/K	Hg/ hg J/mole/J/g	Sg = Hg/Tg J/(mole*K)	heat flux W/g	dT °C
PS	104	100/373	200/2.0	0.5	0.27	10
PEI	592	272/ 545	592/1.7	1.8	0.23	10
PAI	354	217/490	531/I.5	1.1	0.20	10
DPBM	358	435/708	358/1.0	0.5	0.13	10
BMI	1093	320/593	(TMA, no signal in DSC)			
Equimolar Styrene maleimide copolymers						
Phenyl	173+104	225/498	305/1.1	1.1	0.15	10
Xylyl	201+104	230/503	458/1.5	0.92	0.2	10
BrPhenyl	252+104	285/558	534/1.5	0.96	0.2	10
DPBM	358+104	no Tg but Tf signal in DSC				
Equimolar Styrene maleic acid anhydride copolymer						
	MW g/mole	**Tg °C/K**	**hcomb kJ/g**	**hdec kJ/g**	**Rdec %**	
MSA	116+104	130/403	- 25.7	2,6	0	

name Dylarc by Nova Chemicals and Xirane by Polyscope Polymers. The styrene DPBM styrene polymer was cross linked and non soluble. No step for the glass temperature could be detected in the DSC. The observed melting point at 150°C and 0.035kJ/g heat of melting could be explained under the assumption that both double bonds of DPBM reacted with styrene S and half of DPBM remained non reacted and non dissolved so that the expected heat of melting was 0.090kJ/g*(358/462)/2 = 0.035kJ/g.

Heat resistant polymers compete with engineering plastics like polyamides as well as with metals like iron and aluminium. In Table **16** enthalpies and entropies were listed for iron, aluminium and crystalline polymers in comparison.

The thermoplastic polyamides achieved their high melting temperature by their high enthalpies caused by hydrogen bonds.

FR- BMI Laminates and their Burning Behaviour

Halogen free and bromine FR from Table **17** were applied by dry powder mixing to the 2.5m DPBM/1m MDA BMI adduct, which thereafter was dissolved in DMF to obtain a 55% solution, which was used in the tube reactor combined with an impregnation device. The solution passed the tube in 4.4 h. The temperature of reaction was 60°C and the output into a bath was 1.4l/h. The reacted solution filled a bath, in which the glass fabric US 2116 was led with a speed of 7.5m/h. After twice dipping and drying a B-prepreg with about 50% resin content was obtained. The brominated flame

Table 13: Metals and Crystalline Polymers their Temperature of Melting Tm, their Heats and Entropies of Melting Hm and Sm

Material	MW g/mole	Tm °C/K	Hm kJ/mole	hm kJ/g	Sm =Hm/Tm J/(mole*K)
Fe	56	1528/1801	15.0	0.268	8.3
Al	27	660/938	10.7	0.396	11.5
PE	26	132/408	7.5	0.288	18.8
PS cryst	104	240/513	9.2	0.089	17.0
PA6	113	220/493	11.1	0.070	23.5
PA66	226	260/ 533	20.1	0.075	37.7

Table 14: Flame Retardants with their Formula, their Molecular Weight MW, their Temperature of Fusion Tf, Heat of Fusion hf, Temperature of Decomposition Tdec, Heat of Decomposition hdec, Residue R and their Char

FR	formula	MW g/mole	Brom %	Tf °C	Hf J/g	Tdec °C	hdec kJ/g	R %	Char
TBrP	$C_{10}H_4NO_2Br_3$	410	58,5	149	50	300/310	-0.006/0.006	20	C
ETBr	$C_{28}H_4N_2O_4Br_8$	952	67,2	445	90	460/480	-0.06/-0.06	12	C
BCPP	$C_5H_9O_5P$	180	0	215	120	310/350	-0.1/-0.1	66	$C_8{*}P_2O_5$
DCDA/M	$C_3H_6N_6/C_2H_4N_4$	210	0	210	140	300-400	-0.36/0.55	40	C_3N_4
MPP	$C_3H_6N_6.HPO_3$	206	0	-	-	410	1.00	80	$C_3N_4{*}0.5P_2O_5$

retardants: Tribromphenylmaleimide TBrP, ethylene bis tetrabromophthalimide ETBr and the halogene free flame retardants Bicyclopenterythritol phosphate BCPP, equimolar mixture of dicyandiamide and melamine DCDA/M as well as melamine polyphosphate MPP were applied in addition.

In Figure **11** TBrP melted at 142°C under heat consumption of 0.05kJ/g and decomposed at 300°C with -0.004 and 0.01kJ/g heat of decomposition, ETBr melted under heat uptake of 0.065 kJ/g at 460°C followed by exothermic decomposition with -0.05 and -0.04 kJ/g heat evolution.

The applied FRs were different in their mechanism of activity. Tribromophenylmaleimide TBrP was integrated into the chain during curing. Ethylene bistetrabromrophthalimide was non reactive. In the case of fire both halogene FRs split off bromine, which interfered with the radical chain of combustion. Bicyclopentaerythritole phosphate BCPP was intumescent and built a cellular char under heat. The mixture of dicyandiamide and melamine DCDA/M evolved non burning gases and reacted to melamine $C_3H_6N_6$ and further to C_3N_4. Under fire Melamine polyphosphate MPP changed to ammonia, water and $C_3N_4{*}(P_2O_5)0.5$.

In Figure **12** DCDA/M melted at 210°C with 0.14kJ/g heat uptake. At 270°C a reaction took place with -0.36kJ/g heat evolution. Decomposition occurred at 320- 430°C with 0.55kJ/g heat of decomposition. The intumescent FR BCPP showed two exotherm peaks at 310 and 350°C with each -0.1kJ/g evolution of heat. MPP degraded at 410°C with of 1.1kJ/g heat of decomposition. The flame retardants bicyclopentaerythritol phosphate $C_5H_9O_5P$, melamine polyphosphate $C_3H_6N_6.HPO_3$ and the equimolar

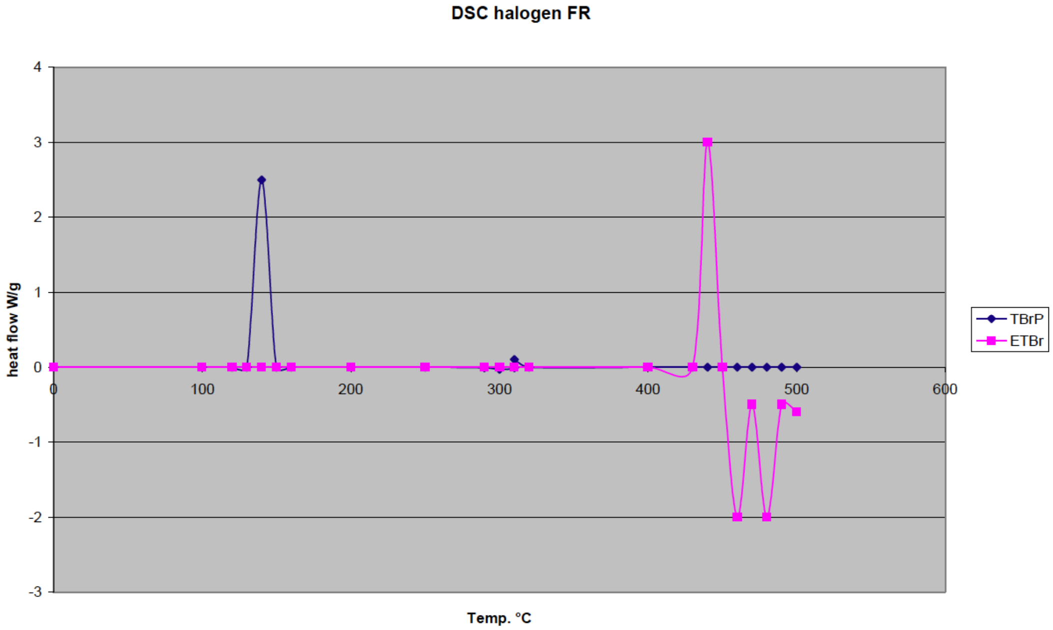


Figure 11: DSC 20K/min N_2 of bromine FRs: tribromophenylmaleimide TBrP Tf=140°C, hf=0.05kJ/g, Tdec=300°C, hdec=-0.006kJ/g, Tdec=310°C, hdec=0,006kJ/g and ethylene bis tetrabromophthalimide ETBr Tf=445°C, hf=0.09kJ/g, Tdec=460°C, hdec=-0.06kJ/g, Tdec=480°C, hdec=-0.06kJ/g.

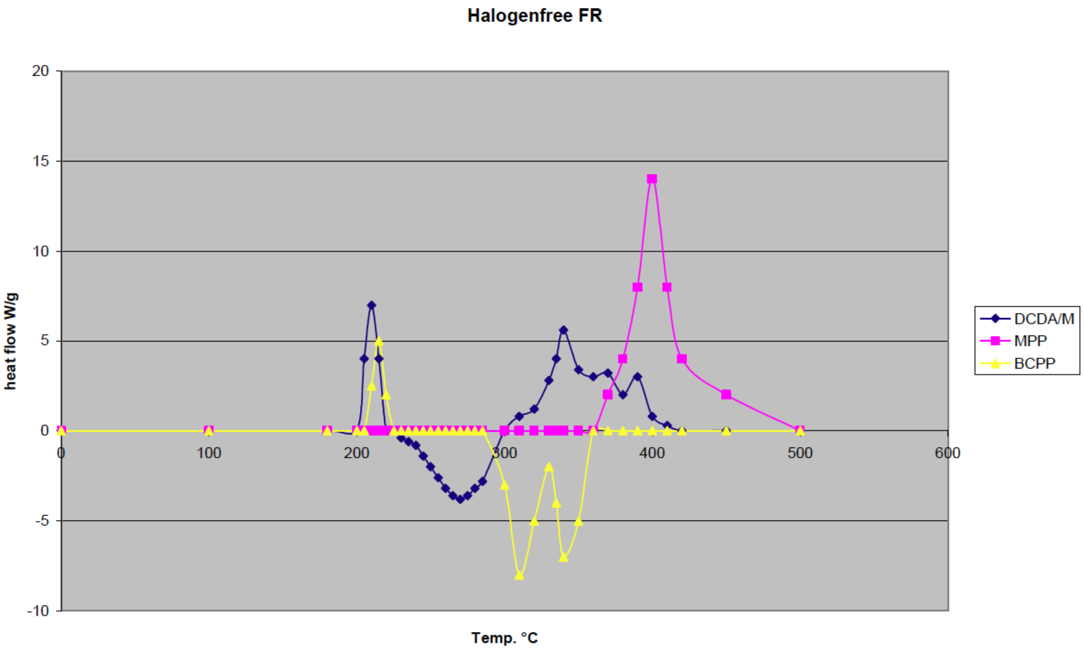


Figure 12: DSC 20K/min, N_2 of halogen free FRs: dicyandiamide/melamine DCDA/M Tf=210°C, hf=0.14kJ/g,Treac=270°C, hreac=0.36kJ/g,Tdec=300-400°C, hdec=0.55kJ/g, melamine polyphosphate MPP Tdec=410°C, hdec=1kJ/g and bicylcopentaerythritol phosphate BCPP Tf=215°C, hf=0.12kJ/g,Tdec=310°C, hdec=-0.1kJ/g,Tdec=350°C, hdec=-0.1kJ/g.

mixture of dicyandiamide and melamine $C_3H_6N_6/C_2H_4N_4$ degraded to chemically different chars.

16 layers of prepregs were staggered one upon the other in a vacuum press in order to achieve samples with 1.6mm thickness for the UL 94 test. The conditions of manufacture were 15bar pressure, within 30 minutes heating to 180°C for 1 hour. The laminates with 1.6mm thickness and 45% resin content were cured at 200°C for 48 hours. In the UL94 the after flaming time took 22 seconds for the virgin samples. When 5% flame retardants were added, the after flaming time was reduced under the necessary limit of 10 seconds.

In Table **15** once more metals, charring and non charring polymers were summarized with their

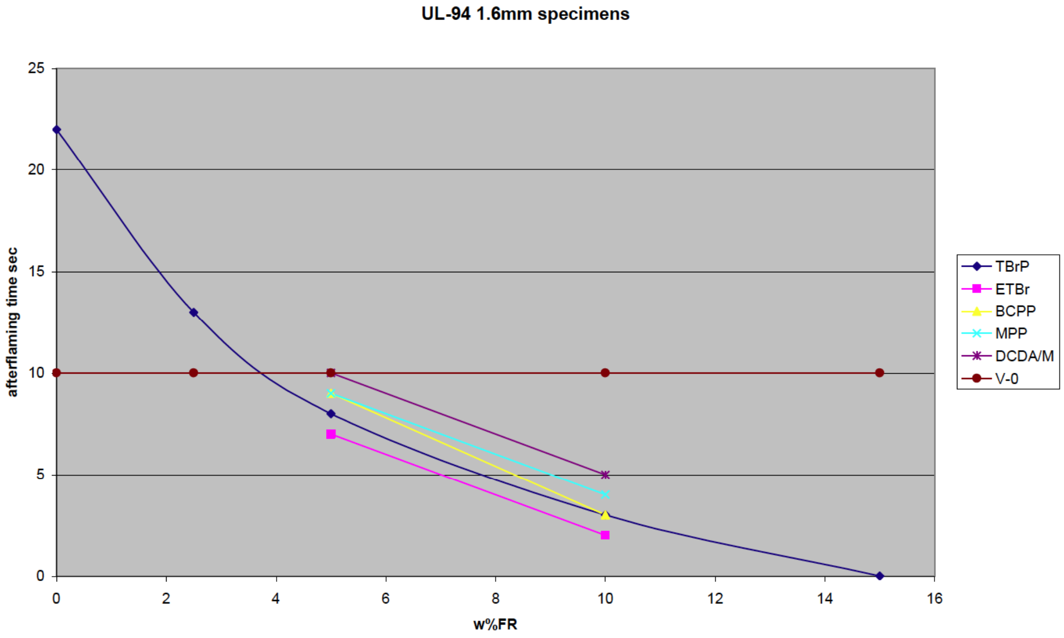


Figure 13: UL94 after flaming time (sec) of BMI (2.5DPBM/1MDA) glass laminates with 45% resin content and 55% glass fabric US 2116 (curing 48h at 200°C) versus amount of FRs.

Table 15: Comparison of BMI with Polyimides, Metals, Engineering Plastics and Cellulose and PAN

Material	MW g/mole	Density g/cm3	Tf/Tg °C	Tdec °C	R %	LOI % O2	h comb kJ/g
BrPhenyl	356	1.15	/285	450	7	60	-25.1
Phenyl	227	1.10	/230	460	17	50	-32.6
Xylyl	305	1.10	/280	450	20	55	33.9
2.5DPBM/1A	988	1.20	/380	450	30	35	-28.1
2.5DPBM/1MDA	1093	1.25	/350	470	47	40	-29.3
PI Kapton	382	1.27		500	50	36.5	-25.0
Matrimid 5218	552	1.20	/280	450	26		-30.8
PSI Techimer	534	1.15		450	22	33	-24.4
PAI Torlon	354	1.38	/280	400	50	45	-29.5
PEI Ultem	593	1.27	/227	450	43	35	-29.5
PEstI	648	1.26		450	35	40	-27.5
Cellulose	324	1.50		300	16	19	-16.1
PAN	53	1.18	/100	300	68	18	-30,8
PBI Celazole	306	1.30	/425	500	75	41.5	-32.5
C graphite	12	2,26		800	100	67	-32,8
Fe	56	7.86	1528	500	100		-14.7
Al	27	2.70	660				-62.1
PVC	62.5	1.40	/80	300	0	42	-17.5
PE	26	0.98	135	420	0	18	-46.3
PS cryst	104	1.08	240	450	0	18.5	-42.0
PA6	113	1.12	220	460	0	25	-38.7
PA66	226	1.12	260	460	0	23	-31.8

* Iron loses 50% of its toughness at 500°C.

densities, temperatures of fusion Tf, glass transition Tg, temperatures of decomposition Tdec, residues R, LOI values and heats of combustion hcomb.

Under the condition of pyrolysis charring polymers like polyimides PI, coPI as well as Polyacrylnitrile PAN and cellulose degraded to carbonaceous residues. In Table **15** PAN with 68% residue was the polymer with the highest residue followed by PI and Copolyimides.

Iron possessed the highest density followed by aluminium and graphite whereas plastics were the lightest materials. Polymers with residues, the so called charring polymers, solidified in the glassy state. The ladder polymer PAN and cellulose could be charred to carbon fibres. The burning behaviour was characterized by the LOI value. Graphite showed the highest LOI value. The highest heat of combustion hcomb exerted aluminium.

When only charring polymers without halogen from Table **15** were taken into consideration and their heats of combustion hcomb were put in relation with the inverse LOI value. The data were situated more less on a straight line, which could be described by equation 5.

$$hcomb= 37- 4.1(1/LOI) \qquad \text{equ.5}$$

The non charring polymers obeyed equation 6 known as Johnson equation.

$$hcomb = 8*(1/LOI) \qquad \text{equ.6}$$

Equation 5 described the situation that charring polymers accumulated more and more carbon approaching graphite with high heat of combustion and low burning.

CONCLUSIONS

In Table **16** and **16a** commercial thermoplastic polyimides, polybenzimidazoles as representatives of heat resistant polymers and polyamide 66 as a representative of engineering plastics are summarized. The thermodynamic approach allows the determination

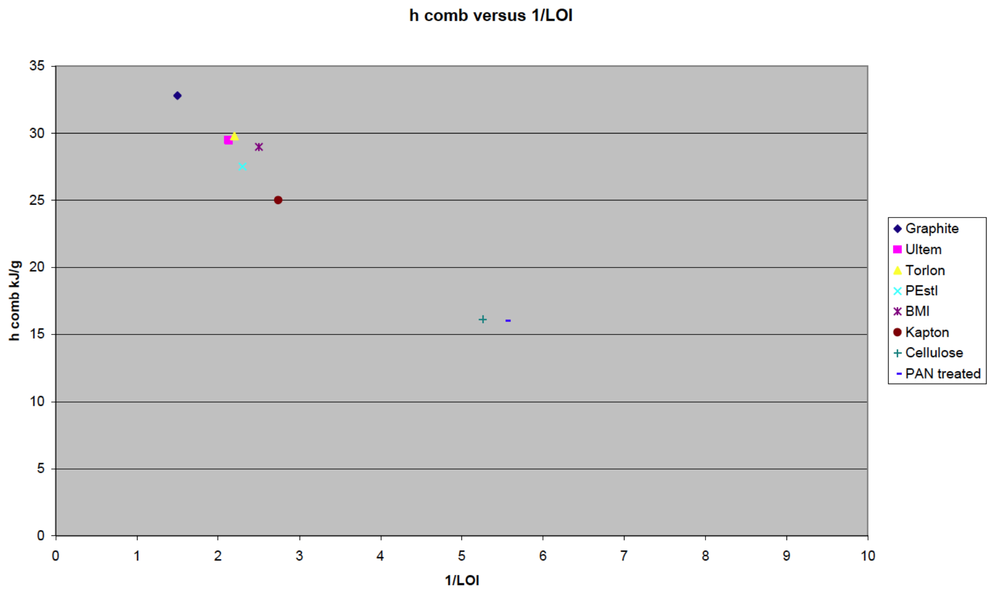


Figure 14: Charring polymers with their heats of combustion hcomb kJ/g and LOI values.

Table 16: Thermoplastic PI, Polybenzimidazol and Copolyimides

Product	**PI**	**PBI**	**PAI**	**PEI**	**PSI**
Brand	Matrimid 5218	Celazole	Torlon	Ultem	Techimer
Company	Ciba Geigy	Hoechst Cel.	Amoco	G.E.	Techimer
Formula	$C_{35}H_{24}N_2O_5$	$C_{20}H_{12}N_4$	$C_{22}H_{14}N_2O_3$	$C_{37}H_{25}N_2O_6$	$C_{29}H_{14}N_2O_7S$
MW g/mole	552	308	354	593	534
Hf kJ/mole	-457	419	-217	-625,5	-660.5
hg J/g			1.5	1.7	
Tg °C	280	425	217	227	
hcomb kJ/g	-30.3	-32.5	-29.5	-29.5	-24.4
Tdec °C	400	450	400	400	400
Hdec kJ/g	0.51	-1.95	-0.20	-0.13	0.19
Rdec %	30	75	41	45	22
CAS	104983-64-4				

Table 16a:

Product	**PEstl**	**PSI S269**	**PA66**	**Br.Phenyl**
Brand	experimental	experimental	DurethaneA31	experimental
Company	Chemie Linz	Chemie Linz	Bayer	Chemie Linz
Formula	$C_{39}H_{24}N_2O_8$	$C_{45}H_{22}N_2O_7S_3$	$C_{12}H_{22}N_2O_2$	$C_{18}H_{14}NO_2NBr$
MW (g/Mole)	648	798	226	356
Hf (kJ/mole	-943,5	-599,5	-650	-167
hg/hm kJ/g			/0.070	0.0015
Tm /Tg °C	/250	/270	269/	/285
hcomb kJ/g	-27.5	-27,3	-32,8	-25.1
Tdec °C	400	400	460	450
hdec kJ/g	-0.49	-0.07	-0,65	1.43
Rdec %	35	8	0	7
Lit.	[43,52-54]	[40,41]		

Table 17: Thermoset BMIs, Kapton and PI

Product	Kapton	PI	MDA	A
Company	Dupont	Chemie Linz	Chemie Linz	Chemie Linz
Brand	Vespel	experimental	experimental	experimental
Formula	$C_{22}H_{10}N_2O_5$	$C_{29}H_{14}N_2O_6$	$C_{65.5}H_{49}N_7O_{10}$	$C_{51.5}H_{42}N_6O_{10}$
MWg/nole	382	486	1093	988
Hf kJ/mole	-517	-581	-1326	-1404
hpol kJ/g			-0.19	-0.24
Tg °C	700	600	/360	390
hcomb kJ/g	-24.6	-26.4	-29.0	-28.1
Tdec °C	550	450	470	450
hdec kJ/g	-0.07	-0.10	0.45	0.35
Rdec %	40	30	49	30
CAS/Lit.			26140-67-0	
X			0.4	0.4
GIC J/m2			100	75

of volatile products and of the amount of heat produced during degradation. PA 66 is a non charring polymer Rdec=0%, polyimides and polybenzimidazoles are charring polymers, which degrade to residues Rdec>0%. The polyimides as well as polybenzimidazole PBI exert exotherm heats of decomposition hdec. High heat resistance and easy workability are contradicting and have to be balanced in each case. PBI shows improved heat resistance but is difficult to handle. The thermoplastic copolyimides PAI, PEI, PEstI and PSI as well 2-Bromphenylmaleimide styrene copolymer reach glass temperatures about 10°C higher than 269°C the melting temperature of polyamide 66. The quantitative treatment of the glass transition temperature determines the enthalpy of glass transition hg about 0.5-1.1J/g, which is small in comparison with the enthalpy of melting hm about 70- 300J/g. Nevertheless the small differences in the calculated enthalpies and entropies indicate that high values of enthalpy due to intermolecular interactions and low values of entropy caused by steric hindrance lead to high Tg. According to Table **16** and **16a** thermoplasts with glass temperatures in the range of 210 to 280°C degrade at temperatures of 400 to 460°C. Their properties have to be compared with those of thermosets in Table **17**.

Thermosets exert higher glass temperatures of 300 to 700°C and degrade between 550 and 450°C. Resins based on 2.5mDPBM/1mMDA and 2.5m DPBM/1mA belong to thermosets like Kapton or Vespel and PI, which comprises benzophenone dianhydride and bis aniline ether. In comparison with thermoplastics all thermosets have the advantage of low processing temperatures but the disadvantage of time consuming curing and processing risks like bubble formation and varying physical properties. PolyDPBM has a high Tg of 435°C and a high Tdec of 475°C but the energy of fracture is too low for practical application. DPBM and BMIs polymerize to linear polymers with imide bonds situated in the side chains. Therefore strictly spoken they are no polyimides, which carry their imide linkages in the main chains. In order to liberate BMIs from their niche existence, cost reduction is needed. A switch from 2.5mDPBM/1mMDA to 2.5mDPBM/1mA has cost reduction as consequence. As both substances are similar in toxicity their monomer content has to be very low. MDA is under the suspicion of causing cancer and A is a poison for blood, their amounts have to be as small as possible. The absence of free amine is achieved by precipitating the reaction mixture in MSA acidic water. In the unsolved state the equilibrium between bounded and free amine is no longer valid. The water soluble amine-maleic acid salt can be washed out completely. The process of manufacture is optimized, when the addition product (DPBM)MDA is synthesized from the reactants MDA and maleic anhydride MSA in an one pot reaction without isolating DPBM. The precursor resin 2.5DPBM)1MDA has a glass temperature of 335°C, a temperature of degradation of 470°C and a energy of fracture of 100J/m^2. The precursor resin 2.5DPBM)/1A has a glass transition temperature of 380°C, a temperature of degradation of 430°C and an energy of fracture of 75J/m^2. As the reaction of DPBM with styrene to a soluble resin fails, 2- Bromophenylmaleimide and styrene are applied on tissues for the production of prepregs. After curing a glass transition temperature of 285°C is obtained. Flame retardants reduce the after flaming time and shift the weight loss curve from that under air to that under nitrogen. The flame retardants though very different in mechanism exert similar efficiency, an amount of 5% is sufficient to reach after flaming times below 10 seconds for a V-0 classification. BMIs belong to the group of charring polymers, for which a correlation between the heat of combustion and the inverse limiting oxygen index is obtained, quite opposite to that valid for non charring polymers. The correlation predicts that polymers with high heats of combustion are low burning. The quantitative treatment of the glass transition temperature showed that the enthalpy of glass transition is much smaller than the enthalpy of melting. Nevertheless the data indicate that high glass temperatures are combined with high enthalpies due to intermolecular bonding and low entropies caused by steric hindrance.

NOMENCLATURE

EA = energy of activation kJ/mole

hcomb = heat of combustion kJ/g

hdec = heat of decomposition kJ/g

Hf = Heat of formation kJ/mole

Hg = heat of glass transition kJ/mole

hm = heat of melting kJ/g

hpol = heat of polymerization kJ/g

LOI = limiting oxygen index

MW = molecular weight g/mole

Sg = entropy of glass transition J/(mole*K)

Tg = glass transition temperature °C

Tm = melting temperature °C

REFERENCES

[1] Othmer K. Polyimides. Encyclopedia of Chemical Technology 3rd ed. John Wiley and Sons/ New York 1982; Vol.18: pp. 704-719.

[2] Othmer K. Polyimides. Encyclopedia of Chemical Technology 4th ed. A. Wiley International Publ. New York 1996; Vol. 19: pp. 829- 834

[3] Othmer K. Composite Materials. Encyclopedia of Chemical Technology 4th ed. A. Wiley Interscience. New York 1993; Vol. 7: 40-60.

[4] Othmer K. Phosphorus-containing Polymers. Encyclopedia of Chemical Technology 3rd ed. John Wiley and Sons/New York 1987; Vol. 11: 101-102.

[5] Polyimides. Ullmann's Encyclopedia of Industrial Chemistry. VCH Publishing Inc. 1992; Vol. A21: 253-268.

[6] Mark, Bikales, Overberg, Menges. Encyclopedia of Polymer Science and Engineering 2nd ed. John Wiley and Sons, New York 1988; p. 364

[7] The Encyclopedia of Advanced Materials, Bloor D, Brook RJ, Flemings MC, Mahajan S, ed. Performance Polymers. Pergamon Press Monomers for High 1993; pp. 1692-1700.

[8] Mittal KL. Polyimide and Other High Temperature Polymers, Synthesis, Characterization and Application. Kindle Edition 2009; Vol. 5. https://doi.org/10.1163/ej.9789004170803.i-424

[9] Stenzenberger H. Constituent Materials. Bisimide Resins 2001; pp. 97-104. https://doi.org/10.31399/asm.hb.v21.a0003364

[10] Der-Jang L, Kung-Li W, Ying-Chi H, Kueir-Ram L, Juin-Yih L, Chang-Sik H. Advanced polyimide materials: Synthesis, physical properties and applications. Progress in Polymer Science 2012; 37(7): 907- 974. https://doi.org/10.1016/j.progpolymsci.2012.02.005

[11] Wilson D, Stenzenberger HD. Polyimide. Taschenbuch Prime 2013.

[12] Behr E. Hochtemperaturbeständige Kunststoffe. Carl Hanser Verlag Munich 1969.

[13] Conley RT. ed. Thermal Stability of Polymers. M. Dekker, New York 1970.

[14] Madorsky SL, Straus S. High Temperature Resistance and Thermal Degradation of Polymers S.C.I Monograph 1961; 13: 60-7414.

[15] Huang F, Huang F, Zhou Y, Du L. Preparation and properties of bismaleimide resins modified with hydrogen silsesquioxane and dipropargylether and their composites. Polymer Journal 2010; 42: 261-267. https://doi.org/10.1038/pj.2009.335

[16] Rattam V. Polyimides Chemistry & Structure. Property relationship. Literature review Modern Plastics mid. Oct. Encyclopedia Issue Polyimide. Thermoset 1999; 146.

[17] Daman, Global Bismaleimide Market by manufacturers, Regions, Type and Application, Forcast to 2021 (2017), damandeep.k.@absolutereports.com.

[18] Fink JK. High Performance Polymers 2nd ed. Elsevier Inc., Amsterdam 2014. https://doi.org/10.1016/B978-0-323-31222-6.00009-1

[19] Elias HG. Neue polymere Werkstoffe. Carl Hanser Verlag/München 1975.

[20] Elias HG. Kunststoffe mit besonderen Eigenschaften, Ullmann 4.Aufl. Bd.15 1979.

[21] Iredale RJ, Ward C, Hamerton I. Modern advances in bismaleimide resin technology: A 21st century perspective on the chemistry of addition polyimides. Progress in Polymer Sci 2017; 69: 1-21. https://doi.org/10.1016/j.progpolymsci.2016.12.002

[22] Miracle DB, Donaldson StL. ed. ASM Handbook Composites Bismaleimide Resin 2001; Vol. 21: pp. 97-104. https://doi.org/10.31399/asm.hb.v21.a0003364

[23] US 2,818,405. DuPont Kovacic P. Elastomeric reaction products of bismaleimides with organic diamines 1957.

[24] US 3,380,964. Rhone Poulenc Rhodiaceto, Grundschober F., Sameth J., Reticulated polyimides and method of producing some from N.N' bismimides 1968.

[25] Brit 1,190,718. Rhone Poulenc Bargain M., Combert A., New cross-linked Resin 1968

[26] US 4,100,140. Ciba Geigy Zalur Abdul-Cader, Renner A. Process for the manufacture of crosslinked polymers, which contain imide groups 1978

[27] WO 97/33933. A1 HOS Technik Horacek H. Sulzer P., Bismaleinimidharze mit einem Gehalt an freiem aromatischem Diamin von weniger als 0,1% 1997.

[28] EP 0330020 A-1. Chemie Linz,Horacek H. Diamines and Bismaleimides as well as Polyimides prepared therefrom 1989.

[29] Metzger JV. Chemistry of Heterocyclic Compounds John Wiley /New York 815 Thiazole and its derivates 1979; 34(1). https://doi.org/10.1002/9780470187067

[30] Müller Houben- Weyl Methoden der organischen Chemie Band IX (1955) G. Thieme/Stuttgart 93 and Band XI/1 1957; 341.

[31] Varma IK, Sanita S, Varma DS. Addition Polyimides: III. Thermal Behavior of Bismaleimides. J Polym Sci Pol Chem Ed. 1984; 22: 1419-1433. https://doi.org/10.1002/pol.1984.170220622

[32] US 4,433,115. NASA, I.K. Varma, G.M.Fohlen, Phosphorus Containing imide resins 1984. https://doi.org/10.1007/978-1-4615-6743-1_8

[33] Varma IK, Fohler GM, Parker JA. Addition polyimides III: Thermal behaviour of bismaleimides, Synthesis of N,N 3,3` maleimidophenylsulfone and its Michael addition product with 44 `aminodiphenylmethane. J Macromolecular Sci Chem Part A 1983; 209-223.

[34] Farr IV, Grass TE, Ji Q, Granth JE. Synthesis and characterization of diaminophenyl indane based polyimides via ester acid solution imidization. High Performance Pol Vol 1997; 9: 345-352. https://doi.org/10.1088/0954-0083/9/3/012

[35] AT 388914. Chemie Holding AG. Greber G, Gruber H, Sychra M, Preparation of bis[(aroylamino)phenyl] diphenylsulfones as monomers for thermostable polymers 1989.

[36] EP 316775 A-1. Chemie Linz, Horacek H, Greber G, Bismaleimide sowie daraus hergestellte Polyimide 1987.

[37] WO 89/04298. Chemie Linz Holding, Greber G. Gruber H. Sychra M., Sulfur containing aromatic Tetracarboxylic acids and their derivatives 1980.

[38] US 3,127,414. DuPont Cole Halbert, Gruber Wilhelm, Preparation of m –phenylenedimaleimide 1964.

[39] WO 97/47597. HOS Technik Horacek H. Steinbauer G., Process for Preparation of twice unsaturated Bisimides with a high level of colour stability and a low level of polymers 1997.

[40] Haas HC, MacDonald RL. Maleimide polymers: A colour reaction. J Pol Sci Polym Chem 2003; 11(2): 327-334. https://doi.org/10.1002/pol.1973.170110202

[41] Beilstein, Addition of aniline to N-Phenylmaleimide via Michael addition. Handbook of Organic Chemistry Vol. XXII p.529; E V 21/10 p.11 Roy. Swan J Chem Soc 1969; 1886-1889.

[42] van Krevelen DW. Properties of Polymers Correlation with Chemical Structure, Elsevier Publ. Corp. Amsterdam 1972.

[43] van Krevelen DW. Properties of Polymers, Elsevier Publ. Corp. Amsterdam. Thermal decomposition 1990; Chapter 21, 463.

[44] Xiong Y, Boey FYC, Rath SK. Kinetic study of the curing behaviour of Bismaleimide Modified with Diallylbisphenol A. J Appl Pol Sci 2003; 90(8): 2229-2240. https://doi.org/10.1002/app.12885

[45] Radue MS, Varshney V, Baur JW, Roy AK, Odegard GM. Molecular Modelling of Cross linked Polymers with Complex Cure Pathways: A Case study of Bismaleimide Resin. Macromolecules 2018; 51(5): 1830-1840. https://doi.org/10.1021/acs.macromol.7b01979

[46] Vollmert B. Grundriß der makromolekularen Chemie. Springer Verlag 1962; 32. https://doi.org/10.1007/978-3-662-25680-0

[47] Giulio CD, Gautier M, Jasse B. Fourier Transform Infrared Spectroscopic Characterization of Aromatic Bismaleimide Resin in Cure States. J Appl Polym Sci 1964; 29: 1771-1779. https://doi.org/10.1002/app.1984.070290530

[48] Grenier-Loustalot MF, Gouarderes F, Joubert F, Grenier Ph. Synthesis, mechanism and kinetic of radical polymerization of bismaleimidetype telechelic oligomers in solvent and in solid state. Polymer 1993; 34(18): 3848-3859. https://doi.org/10.1016/0032-3861(93)90510-H

[49] Barton JM, Hamerton I, Rose JB, Warner D. The synthesis, characterization and polymerization kinetic study of a series of related addition polyimides. High Perform Polym 1994; 6: 21-34. https://doi.org/10.1088/0954-0083/6/1/003

[50] Grenier-Loustalot MF, da Cunha L. Thermostabile polymers: Spectroscopic and thermal studies of bismaleimides systems in solid state. High Perform Polym 1998; 10: 285-308. https://doi.org/10.1088/0954-0083/10/3/006

[51] Phelan JC, Sung CSP. Cure Characterization in Bismaleimide Diallylbisphenol A Resin by Fluorescence FT IR nd UV Reflection Spectroscopy. Macromolecules 1997; 30(22): 6845-6851. https://doi.org/10.1021/ma961887f

[52] Li J, Stoliarov StI. Measurement of kinetics and thermodynamics of thermal degradation for charring polymers. Polym Degrad Stab 2013; 1-14. https://doi.org/10.1016/j.polymdegradstab.2015.03.003

[53] Li J, Gong J, Stoliarov StI. Development of Pyrolysis Models for charring Polymers. Polym Degrad and Stab 2015; 115: 138-152.

[54] Austen AC, Sivarajan S. Encyclopdia of Materials Science and Technology (2004); Reference Moule in Material Science and Material Engineering. Glass Transition 2017.

[55] Ojovan MI, Travis KP, Hand RJ. Condensed Thermodynamic parameters of bonds in glassy materials from viscosity temperature relationship. J Physics 2007. https://doi.org/10.1088/0953-8984/19/41/415107

[56] Loncrini DF. Aromatic Polyesterimides. J Pol Sci Part A-1 1988; 1: 1331-1541.

[57] EP 0597301 A-1. Chemie Linz, Horacek H., Polyesterimide aus Trimellitsäure, Propandiphenol und einem aromatischen Diaminen mit verbesserten Eigenschaften, ihre Herstellung und Verwendung 1994.

[58] Dolui SK, Pal D, Maiti S. Synthesis of a Novel Polyesterimide. J Appl Pol Sci 1985; 30: 3867-3878. https://doi.org/10.1002/app.1985.070300925

Received on 04-02-2020 Accepted on 15-02-2020 Published on 25-02-2020

DOI: https://doi.org/10.6000/1929-5995.2020.09.01