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Synthesis and characterization of thermosetting resins based on 4-(*N*-maleimidophenylester) hydroxypropylmethacrylate

Summary — A hybrid monomer on 4-(*N*-maleimidophenylester) hydroxypropylmethacrylate (MPEHPM) possessing both maleimide and methacrylate groups has been synthesized from 4-*N*-carboxyphenylmaleimide (CPMI) and glycidylmethacrylate (GMA) in the presence of triethylbenzylammonium chloride (TEBAC) as a catalyst. The monomer was modified with diamino-diphenylmethane bismaleimide (MDABMI) and diglycidyl bisphenol A (DGEBA) and cured in the presence of 4,4'-methylenedianiline (MDA). The presence of an epoxy ring, amino groups and the both types of double bonds, makes these systems potential materials for obtaining thermosetting products. The curing and thermal stability of the crosslinked products were studied by differential scanning calorimetry (DSC) and TGA techniques.

Key words: (*N*-maleimidophenylester) hydroxypropylmethacrylate, thermal properties, activation energy.

SYNTEZA I CHARAKTERYSTYKA TERMOUTWARDZALNYCH ŻYWIC NA PODSTAWIE ESTRU 4-(*N*-MALEIMIDOFENYLOWEGO) METAKRYLANU HYDROKSYPROPYLOWEGO

Streszczenie — Zsyntetyzowano ester 4-(*N*-maleimidofenyłowy) metakrylanu hydroksypropylowego (MPEHPM) w reakcji 4-*N*-karboksyfenylomaleimidu (CPMI) z metakrylanem glicydyłu (GMA) w obecności chlorku trietylobenzylamoniowego (TEBAC) jako katalizatora. Otrzymany hybrydowy monomer zawierający zarówno grupy maleimidowe, jak i metakrylanowe modyfikowano za pomocą bismaleimidu diaminodifenyłometanu (MDABMI) bądź diglicydyłowego eteru bisfenolu A (DGEBA) a następnie sieciowano wobec 4,4'-metylenodianiliny (MDA). Obecność w zastosowanym systemie pierścienia epoksydowego, grup aminowych oraz obydwu typów wiązań podwójnych pozwala na uzyskanie termoutwardzalnego polimeru. Budowę syntezowanych produktów badano metodami FT-IR (rys. 1, 5, 6), ¹H NMR (rys. 2) i ¹³C NMR (rys. 3). Proces utwardzania oraz stabilność termiczną usieciowanych związków charakteryzowano przy użyciu różnicowej kalorymetrii skaningowej (rys. 4, tabela 1) i techniką TGA (rys. 7, tabela 2).

Słowa kluczowe: ester 4-(*N*-maleimidofenyłowy) metakrylanu hydroksypropylowego, właściwości termiczne, energia aktywacji.

High performance thermosets such as epoxy and maleimide resins are of great interest as matrix resins for use in numerous industrial applications, including electrical and electronic industry, car industries, aero and hydrospace engineering, transporting, etc. because of their unique properties such as: good pre-lucrability and adherence to different substrates prior to crosslinking, good thermal resistance, superior mechanical and electrical properties and excellent chemical and solvent resistance after crosslinking [1–16]. Bismaleimides are attractive materials for the structural adhesives or as resins for matrices, because they can be polymerized under thermal treatment without the elimination of the by-products.

The objective of the present work is to report the results of the synthesis and crosslinking polymerization of 4-(*N*-maleimidophenylester) hydroxypropylmetha-

crylate (MPEHPM), a monomer that possesses two polymerizable carbon-carbon double bonds with different reactivities (one of which is the vinylene group of maleate type and the other of the methacrylic type), and its characterization by FT-IR, NMR and elemental analysis. The curing and thermal stability of the crosslinked products were also investigated by differential scanning calorimetry and thermal analysis technique.

EXPERIMENTAL

Materials

— Maleic anhydride (MA, Fluka), 4,4'-methylenedianiline (MDA, Aldrich), 4-aminobenzoic acid (*p*-ABA,

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Fluka), glycidylmethacrylate (GMA, Fluka), triethylbenzylammonium chloride (TEBAC, Fluka), acetic anhydride (AcA, Aldrich), hydroquinone (HQ, Aldrich), were purchased as analytical grade products and used as received.

– Carboxy phenylmaleimide (CPMI) was obtained according to a procedure in the literature and has a melting point of 225–227 °C [16, 17]; 1,1'-(methylene-di-4,1-phenylene) bismaleimide (MDABMI) was prepared from 4,4'-methylenedianiline (MDA) according to the method reported by Dix *et al.* [18].

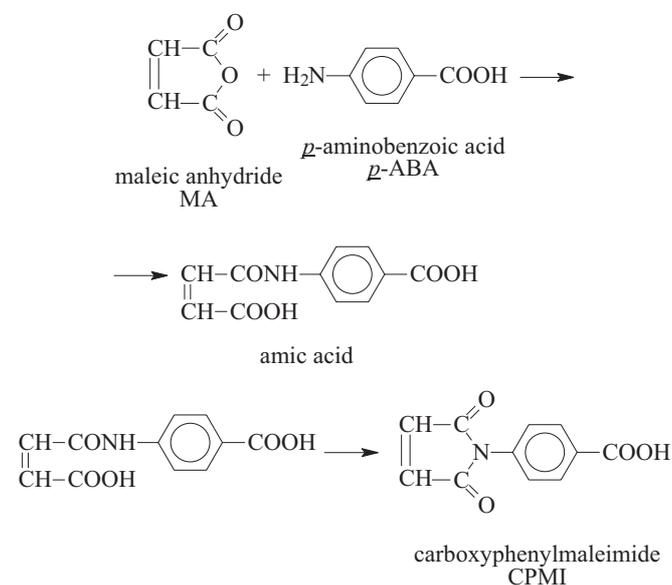
– The epoxy resin (diglycidylether of bisphenol A) (DGEBA, SC Sintofarm SA, Romania) with average epoxy equivalent weight of 200 g · eq⁻¹ was a commercial product and was used without further purification.

All organic solvents were analytical grade products and were used as received or purified by distillation before use.

Syntheses

Synthesis of *N*-(4-carboxyphenyl)maleamic acid

MA and *p*-ABA were dissolved separately in acetone under reflux and cooled at room temperature. *p*-ABA (68.57 g, 0.5 mol) dissolved in 0.5 L acetone was placed in a 1 L four-necked round-bottomed flask, equipped with a mechanical stirrer, a thermometer, a reflux water condenser and an ice bath. The solution was stirred at 0–5 °C for 30 min, then maleic anhydride (49 g, 0.5 mol) in 0.3 L acetone solution was added in portions over 2 h. The temperature of the contents was maintained at 0–10 °C for 30 min and then increased to 25 °C with the stirring was maintained for another 3 h until a yellowish green slurry (4-carboxyphenyl maleamic acid) was obtained. The precipitate were filtered, washed with fresh acetone and dried under vacuum overnight at 50 °C (Scheme A).



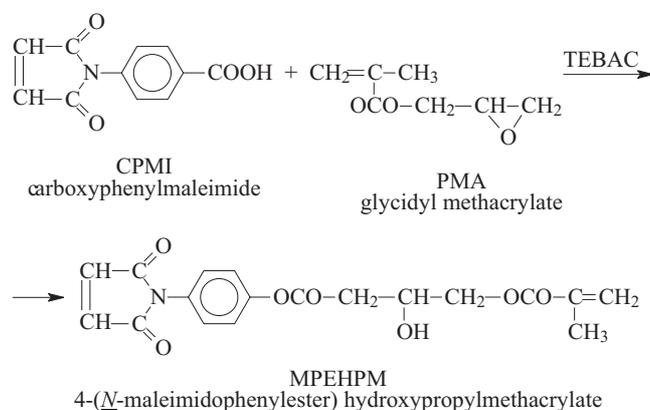
Scheme A. Reaction scheme for synthesis of CPMI

Synthesis of *N*-(4-carboxyphenyl)maleimide (CPMI)

0.5 mol (117.5 g) of amic acid was dissolved in 0.5 L of acetic anhydride and 25 g of sodium acetate in the same apparatus setup as described above and gradually heated to 85 °C and maintained for another 4 h under stirring. After cooling to room temperature, the reaction mixture was poured into a large amount of fresh snow to obtain fine gray-yellow precipitates, which was separated by filtration and dried under vacuum at 80 °C overnight. The yield was 92 %, the melting point after three recrystallizations from acetone/cyclohexane (1/1, v/v) 240–242 °C (see Scheme A).

Synthesis of 4-(*N*-maleimidophenylester) hydroxypropylmethacrylate (MPEHPM)

To a 0.5 L four-necked round bottomed flask fitted with a mechanical stirrer, a thermometer, a dropping funnel, and a reflux condenser, 0.1 mol (21.7 g) of CPMI and 100 mL THF were introduced and stirred under N₂ at reflux temperature until the solution become homogeneous. The temperature was reduced to 50 °C and 2 g of TEBAC and 0.1 mol (14.21 g) of glycidylmethacrylate (GMA) were added slowly for 30 min. Stirring of the reaction mixture was maintained under reflux after the addi-



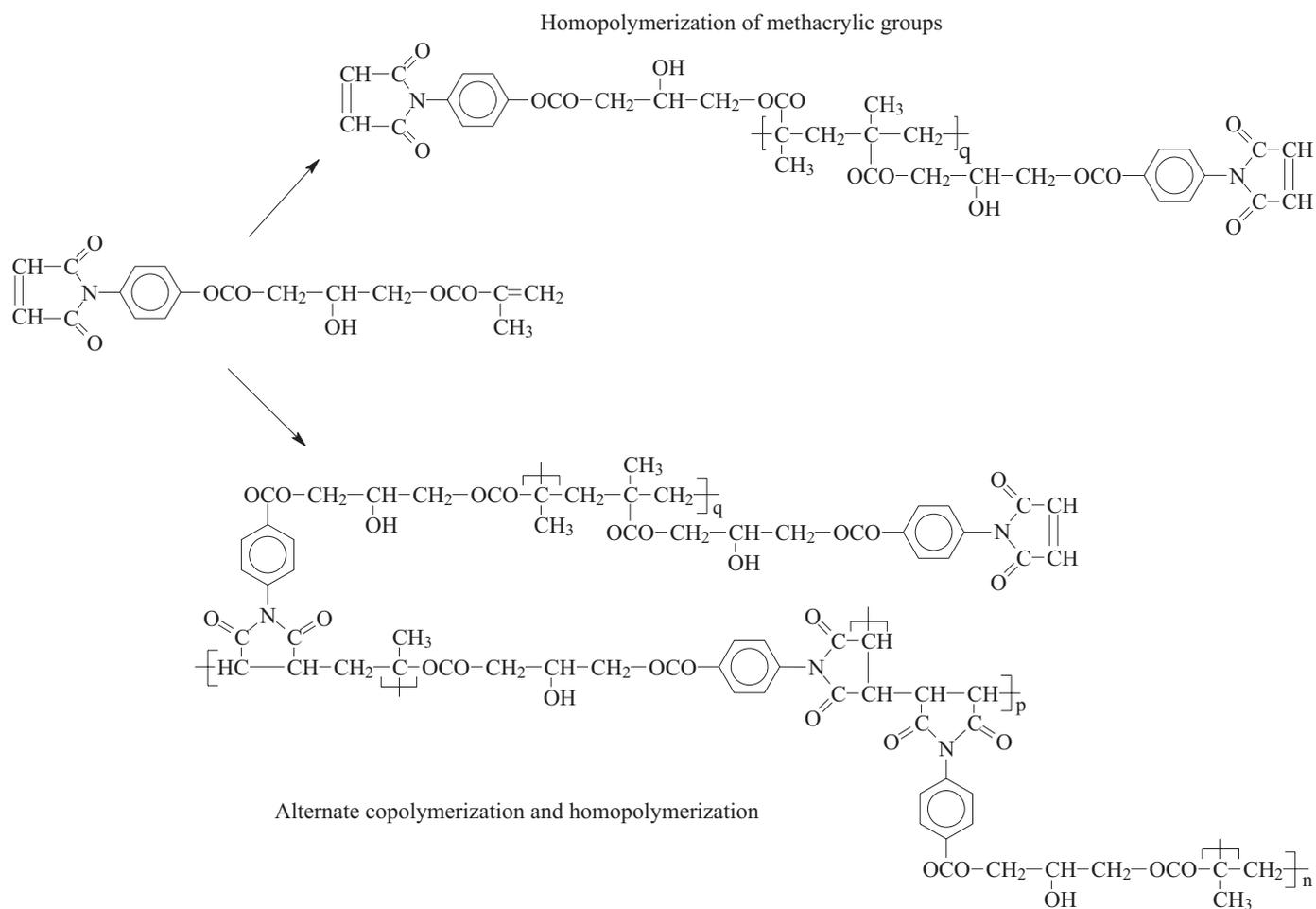
Scheme B. Reaction scheme for synthesis of MPEHPM

tion of reagents. The reaction solution turned grey violet and after some time a dark violet slurry developed. After the removal of 50 % of THF, the residue was poured into a large excess of fresh snow. The precipitate was filtered, washed twice with distilled water and dried under reduced pressure at 45 °C for 48 h (yield = 92 %, $N_{\text{calc}} = 3.899$ %, $N_{\text{found}} = 3.85$ %) (Scheme B).

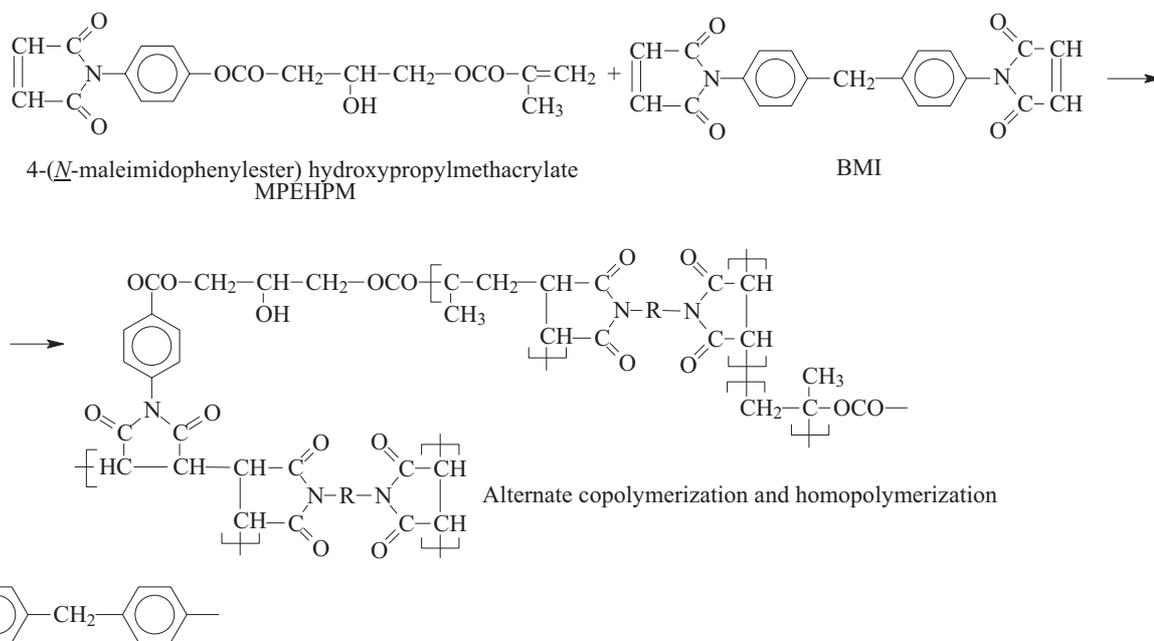
Crosslinking process of MPEHPM

Sample preparation for DSC and TGA studies

For calorimetric measurements, the obtained monomer and DGEBA, MDABMI, and MDA at stoichiometric



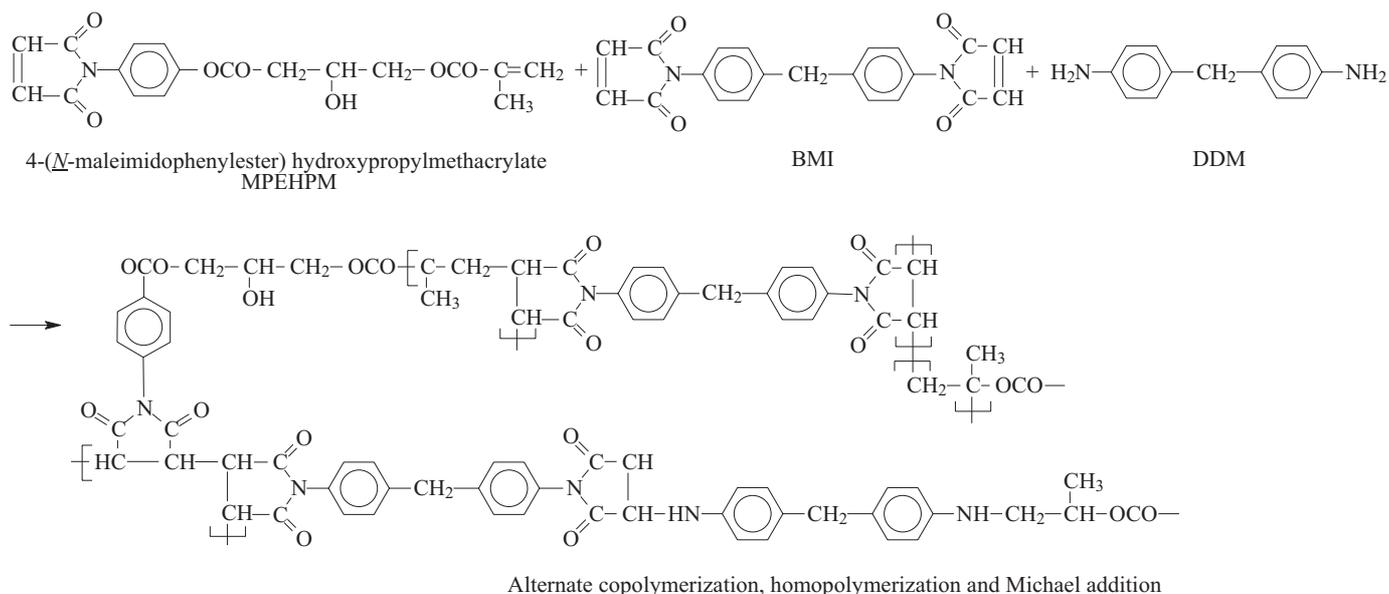
Scheme C. Probable crosslinking mechanism of MPEHPM



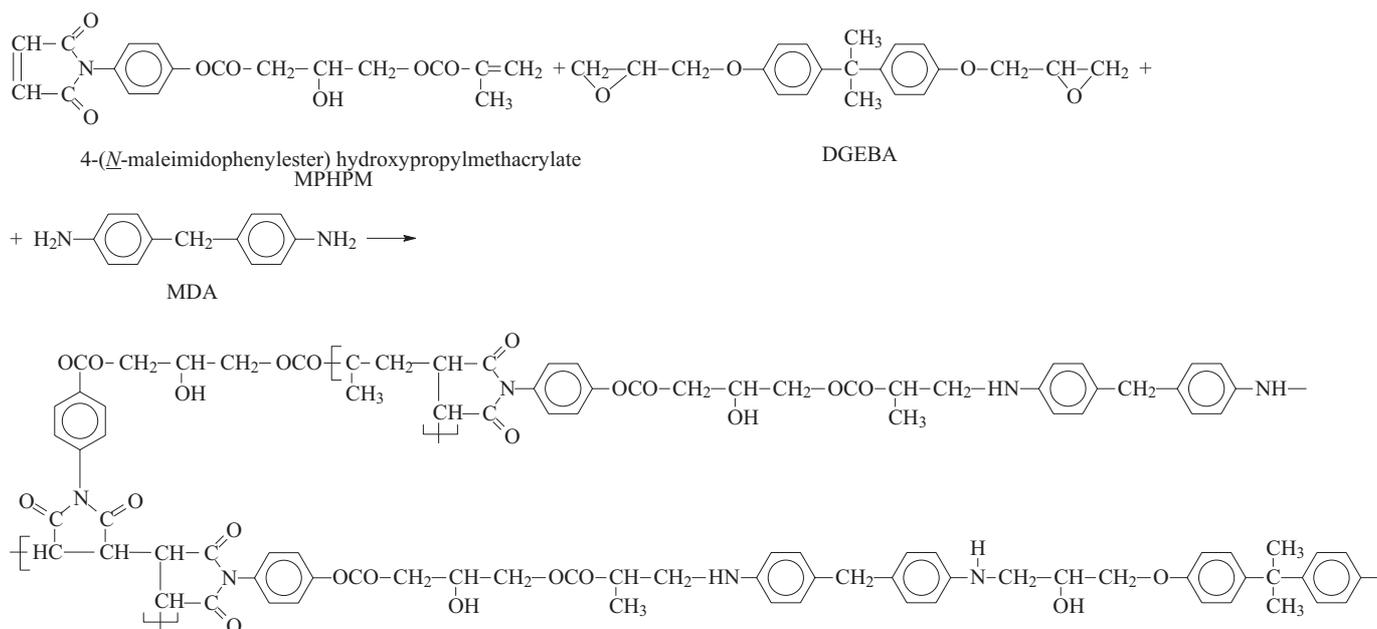
Scheme D. Probable crosslinking mechanism of MPEHPM/MDABMI system

ratio were carefully weighed, avoiding contact during this procedure. After commencing measurements, the products were immediately stirred vigorously to obtain a

homogeneous mixture subjected to vacuum for 15 min in order to remove trapped air. Curing cycles were determined by DSC thermograms (Scheme C–F).



Scheme E. Probable crosslinking mechanism of MPEHPM/MDABMI/MDA system



Scheme F. Probable crosslinking mechanism of MPEHPM/DGEBA/MDA system

Sample 1. 4–10 mg MPEHPM was used for the DSC studies and 1 g was cured at 140 °C for 1 h, and at 220 °C for 4 h was used for TGA studies.

Sample 2. 3.59 g MPEHPM (0.01 mol), 3.58 g (0.01 mol) MDABMI, and a small quantity of THF were mixed as above and a paste was obtained. The mixture was kept at 50 °C under vacuum for 1 h and cooled to 0 °C. 4–10 mg was used for DSC studies and a large part was cured at 140 °C for 1 h, at 220 °C for 4 h and used for TGA studies.

Sample 3. 3.59 g MPEHPM (0.01 mol), 0.99 g MDA (0.05 mol), and a small quantity of THF were mixed in a

beaker and stirred to obtain a paste. The mixture was kept at 50 °C under vacuum for 1 h and cooled at 0 °C. A small part of the mixture (4–10 mg) was used for the DSC studies and a large part was cured at 140 °C for 1 h, at 220 °C for 4 h and used for TGA studies.

Sample 4. 3.59 g MPEHPM (0.01 mol), 3.58 g (0.01 mol) MDABMI, 0.99 g MDA (0.05 mol), and a small quantity of THF were mixed in a beaker and stirred to obtain a paste. The mixture was kept at 50 °C under vacuum for 1 h and cooled to 0 °C. A small part of the mixture (4–10 mg) was used for the DSC studies and a

large part was cured at 140 °C for 1 h, at 220 °C for 4 h and used for TGA studies.

Sample 5. 3.59 g MPEHPM (0.01 mol), 1.485 g MDA (0.0075 mol) and 3.8 g (0.01 mol) DGEBA, were mixed in a beaker and stirred to obtain a paste. The mixture was kept at 50 °C under vacuum for 1 h and cooled at 0 °C. A small part of the mixture (4–10 mg) was used for the DSC studies and a large part was cured at 140 °C for 1 h, at 220 °C for 4 h and used for TGA studies.

Methods of testing

– The nitrogen content was determined in accordance with Kjeldhal method.

– The average epoxy equivalent weight was evaluated by pyridinium chloride-pyridine method (expressed in $\text{g} \cdot \text{eq}^{-1}$) [19].

– ^1H NMR and ^{13}C NMR spectra of the synthesized monomer were run on an Avance DRX 400 (BRUKER, Rheinstatten, Germany) at 50 °C with DMSO-d_6 as solvent.

– FT-IR spectra were obtained with a Bruker Vertex 70 FT-IR spectrometer on KBr pellets.

– The extent of curing was performed using a Pyris Diamond DSC, Perkin Elmer instruments at heating rates (5, 10, 15 °C \cdot min $^{-1}$), into the range of 20–400 °C in nitrogen atmosphere (3 l \cdot min $^{-1}$). The kinetic parameters of the crosslinking reactions were estimated from DSC thermograms using the variable peak exotherm method of Kissinger and Ozawa. The activation energies and the pre-exponential factor were also calculated. The activation energies and the kinetic parameters of the curing reactions of MPEHPM and MPEHPM systems were obtained from DSC thermograms measured at three heating rates according to Kissinger and Ozawa methods [20, 21]. Based on the obtained linear relationship between the reciprocal of exotherm peak temperature (T_p) and logarithm of the heating rate ($\ln \beta$) and $\ln (\beta/T_p^2)$, the activation energy of crosslinking reactions and the pre-exponential factor were calculated:

$$\ln (\beta/T_p^2) = E_a/RT_p - \ln (AR/E_a) \quad (\text{Kissinger equation}) \quad (1)$$

and

$$\ln \beta = C - 0.4567(E_a/RT_p) \quad (\text{Ozawa equation}) \quad (2)$$

where: A – the pre-exponential factor, C – a constant, E_a – the activation energy for the curing reactions, T_p – the peak of exothermic temperature, R – the gas constant, β – the heating rate.

– The thermal stability of the crosslinked polymers was evaluated by thermal gravimetric analysis (TGA) on a STA 449 F1 Jupiter apparatus (Netzsch-Germany) at a heating rate of 10 °C \cdot min $^{-1}$ in a temperature range of 25–700 °C under static air atmosphere. The kinetic parameters and activation energies of the degradation reactions for the obtained resins were calculated using Swaminathan & Modhavan and Coats & Redfern equations [22, 23]. The general equations used are:

$$d\alpha/dT = A \exp(-E_a/RT) [a^m(1-\alpha)^n] [-\ln(1-\alpha)]^p \quad (\text{Swaminathan \& Modhavan equation}) \quad (3)$$

and

$$\log [1 - (1-c)^{1-n}] / (1-n) \cdot T^2 = \log (AR/\beta E_a) - 2.303 (E_a/RT) \quad (\text{Coats \& Redfern equation}) \quad (4)$$

where: α – the conversion degree (ratio of the weight loss at time “ t ” and at the end of the process), A – the pre-exponential factor, c – the conversion, E_a – the activation energy of decomposition, n – the reaction order, m and p – the exponents of the conversion function, T – the temperature, β – the heating rate, R – the gas constant.

RESULTS AND DISCUSSION

Synthesis and structure of products

The hybrid monomer 4-(N -maleimidophenylester) hydroxypropylmethacrylate (MPEHPM) was obtained through the reaction between 4- N -carboxyphenylmaleimide (CPMI) and glycidylmethacrylate (GMA) in the presence of triethylbenzylammonium chloride (TEBAC) as a catalyst (see Scheme A). The reaction was conducted at low temperature to avoid the polymerization of the double bonds of the methacrylic type and the secondary reaction between the epoxy ring and the new secondary OH groups. The chemical structure of 4- N -carboxyphenylmaleimide (CPMI) and the hybrid monomer were identified by FT-IR, ^1H NMR and ^{13}C NMR spectroscopy. The reaction between the CPMI carboxylic group and the GMA epoxy ring was confirmed by the disappearance of the specific signal of epoxy ring in IR and NMR spectra. The IR spectrum of CPMI (Fig. 1a) showed a small absorption signal 3305 cm^{-1} , due to the carboxylic moieties. The absorption band specific to C=C double bonds in

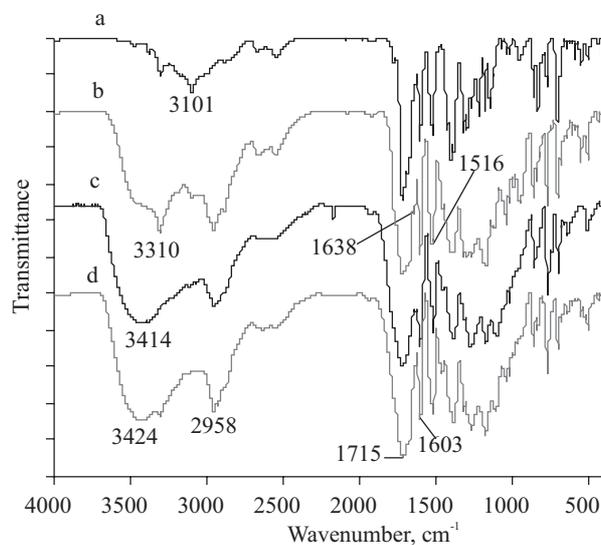


Fig. 1. FT-IR spectra for: a – CPMI, b – MPEHPM, c – cured MPEHPM at 150 °C 2 h, d – cured MPEHPM at 200 °C 2 h

maleic moieties is located at 3101 cm^{-1} . Also the strong absorption due to the presence of cyclic imide linkages is exhibited at 1780 cm^{-1} (C=O asymmetrical stretching), 1716 cm^{-1} (C=O symmetrical stretching), 1638 cm^{-1} (C=C double bonds), 1385 cm^{-1} (C-N stretching), 1250 , 1037 cm^{-1} (-Ph), 720 cm^{-1} (C=O bending).

In the ^1H NMR spectrum of CPMI given in Fig. 2, the specific signals for this product are those for the CH=CH protons at 7.22 ppm, in the range of 7.51 to 8.06 ppm for

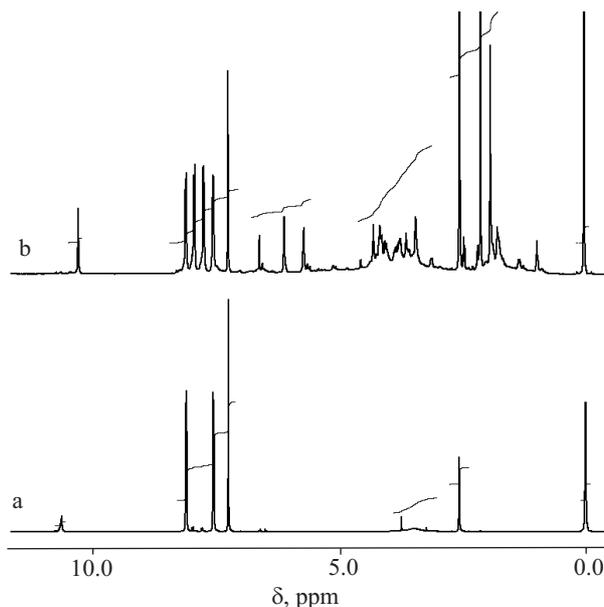


Fig. 2. ^1H NMR spectra for: a — CPMI, and b — MPEHPM

the aromatic protons and at 10.65 ppm for the carboxylic protons. Elemental analysis found 6.41 % for nitrogen. The chemical structure of 4-(*N*-maleimidophenylester) hydroxypropylmethacrylate (MPEHPM) was confirmed by FT-IR, ^1H NMR, ^{13}C NMR spectroscopy and elemental analysis. In the FT-IR spectrum (Fig. 1b), the characteristic absorption band of oxirane ring from GMA, located at 913 cm^{-1} was absent and a sharp signal appeared at 3310 cm^{-1} signifying an associated hydroxyl group, indicating that the reaction between epoxy ring and carboxylic proton has taken place. The absorption band specific to the ester group (C=O) is overlapped by the signal of the C=O group from imide ring and the signal specific to C-O- group, is presented in the 1173 to 1296 cm^{-1} range. The three signals located at 1607 , 1525 and 1455 cm^{-1} are assigned to the characteristic combined stretching and deformation of aromatic C=C bonds from *N*-(4-carboxyphenyl)maleimide moieties. The absorption bands specific to CH, CH_2 and CH_3 from GMA moieties are observed at 2960 cm^{-1} and the signals specific to double bonds are located at 3100 cm^{-1} for maleimide double bond and at 1638 cm^{-1} for methacrylic, respectively. Further characterization was performed with ^1H NMR and ^{13}C NMR. In ^1H NMR spectrum (Fig. 2), the

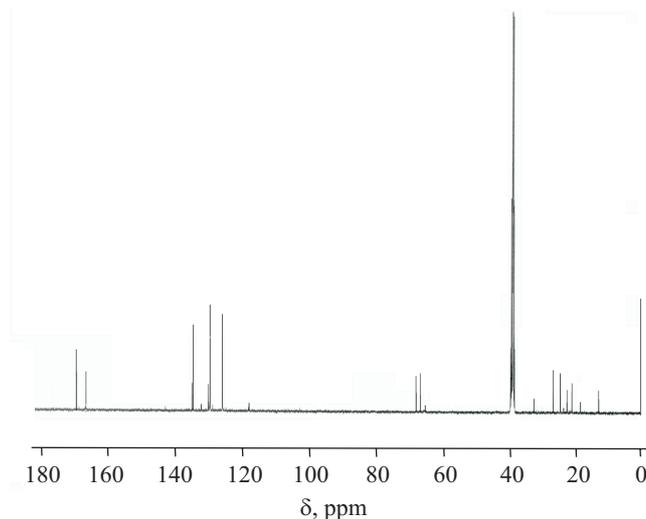


Fig. 3. ^{13}C NMR spectrum of MPEHPM

specific absorption bands characteristic to epoxy group at 2.6 and 2.8 ppm were not observed, but the signal specific to the new secondary OH group at 5.67 ppm appeared, indicating that the addition of the carboxylic group to the epoxy group was completed. The methacrylic double bonds are located at 6.1 ppm and the maleimide double bond is observed in the 7.21 ppm chemical shift range. This observation is confirmed by ^{13}C NMR spectrum (Fig. 3) by the disappearance of epoxy group signal, which is shifted to the CH and CH_2 signal in the low field (18–40 ppm), and appearance of the signal of isomers of secondary alcohols (68–70 ppm). The absorption bands specific to methacrylic and maleic double bonds are located in the 130–136 ppm chemical shift range and the signal specific to C-N bond are located at 126 ppm chemical shift. The absorption bands specific to C=O in the ester group are presented at 166 ppm while the peaks specific to C=O in the maleimide moieties are located at 170 ppm.

The curing process of MPEHPM

The polymerization reactions of MPEHPM and MPEHPM systems were studied by DSC. Simple MPEHPM monomer undergoes a limited number of reactions, homopolymerization of methacrylic or maleic moieties, and copolymerization of methacrylic and maleic double bonds, respectively. In MPEHPM/MDA, MPEHPM/MDABMI, MPEHPM/MDABMI/MDA and MPEHPM/MDA/DGEBA systems, several reactions can occur simultaneously depending on the reactivity of the components and temperature (homopolymerization of methacrylic or maleic moieties, oxirane ring-opening reaction with amine hydrogen, Michael-type reaction of $-\text{NH}_2$ protons to double bonds of maleimides, copolymerization of bismaleimides with methacrylic double bonds and a combination of them) [24–26]. The composition of these systems was established in such way as to determine all the amine hydrogen reacting with all double bonds of methacrylic and maleimide type (by

Michael-type reactions) and all oxirane rings. The possible chemical reactions are shown in Schemes A–F. The thermal behavior of the chemical reactions was monitored by DSC scanning experiments. For example, the thermograms of three heat rates of the MPEHPM system are presented in Fig. 4. It can be noticed that MPEHPM systems show two reaction exotherms depending on the reactivity of the two types of the double bonds and on temperature. The first exothermic peak might come from the homopolymerization of the methacrylic double bond and less probably from the copolymerization of the methacrylic double bond with maleimide moieties (the maximum peak temperature is situated at 123, 135 and 141 °C from 5, 10, 15 °C/min bears out by [27]). The second exotherm can be due to the homopolymerization of maleimide moieties (the maximum peak temperature is situated in the 201, 213 and 220 °C range from 5, 10, 15 °C/min, bears out by [24], too) (Scheme C). Fig. 1c represents the IR spectrum of the crosslinked product (MPEHPM crosslinked under 150 °C for 1.5 h), where the homopolymerization of methacrylic double bond (the absence of the signal of $\text{CH}_2=\text{C}$ at 1638 cm^{-1} and the presence of signal of $\text{HC}=\text{CH}$ maleic at 3105 cm^{-1}) can be observed the IR spectrum of the crosslinked MPEHPM after heating at 210 °C for 2 h, the absorption band of $\text{HC}=\text{CH}$ maleic type located at 3105 cm^{-1} is much attenuated and represents partially uncrosslinked maleimide $\text{HC}=\text{CH}$ double bonds (Fig. 1d).

In the case of MPEHPM/MDA system there are four main possible reactions: thermal homopolymerization of methacrylic double bonds, copolymerization of methacrylic and maleic double bonds, Michael-type reactions between amino groups and double bonds of MPEHPM and thermal homopolymerization of maleimide double bonds. The DSC curves show two exothermic peaks, in

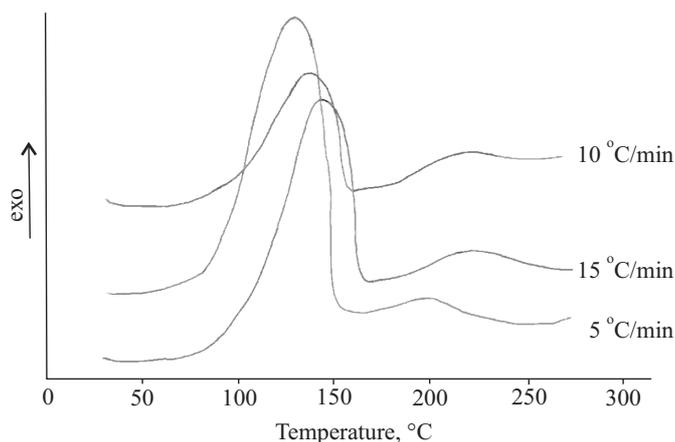


Fig. 4. DSC thermograms for MPEHPM at various heating rates

the 103, 111 and 114 °C range at 5, 10, 15 °C/min from the first exotherm specific to homopolymerization of methacrylic double bond and at 187, 204, 210 °C at 5, 10, 15 °C/min from the second exotherm caused from the Michael-type reactions and homopolymerization of the maleimide groups (Table 1). Results from the literature confirm that Michael-type reaction occurs at low temperatures in comparison with homopolymerization of maleic double bonds, but in this case the two chemical reactions occur simultaneously [27, 28]. From the IR spectrum of cured MPEHPM/MDA system (Fig. 5b), it can be seen that the double bond of the methacrylic type is absent (1638 cm^{-1}) and the maleic type presents a weak intensity (3100 cm^{-1}). The presence of a strong signal in the $1260\text{--}1265\text{ cm}^{-1}$ range and at 3377 cm^{-1} can be assigned to the C-N-C bond of the succinimide type and -C-NH amino bond, indicating the presence of Michael-type reaction.

Table 1. Kinetic parameters for cured MPEHPM systems from DSC scans

No	Sample	Heating rate, °C · min ⁻¹						Activation energy of curing reaction, kJ · mol ⁻¹				Pre-exponential factor, min ⁻¹	
		first exotherm			second exotherm			first exotherm		second exotherm		first exotherm	second exotherm
		5	10	15	5	10	15	Ozawa	Kis-singer	Ozawa	Kis-singer	Kis-singer	Kis-singer
		$T_M^{*)}$	T_M	T_M	T_M	T_M	T_M						
1	MPEHPM	123.5	135.3	141.6	201.1	213.6	220.7	97.31	90.41	117.37	109.20	14.52	14.35
2	MPEHPM/MDA (double bond group/amine proton molar ratio = 1/1)	102.7	111.5	114.3	187.5	203.8	210.6	111.51	104.92	95.85	87.87	21.40	10.85
3	MPEHPM/BMI	129.2	139.4	152.3	211.5	216.4	225.4	67.27	60.50	154.6	146.6	9.67	28.64
4	MPEHPM/MDA/BMI (double bond group/epoxy group/amine proton molar ratio = 1/1/1)	125.1	140.7	149.1	198.7	214.2	228.3	64.11	57.43	71.28	65.5	5.03	8.21
5	MPEHPM/MDA/DGEBA (double bond group/epoxy group/amine proton molar ratio = 1/1/1)	91.4	100.1	105.6	—	—	—	101.14	95.06	—	—	18.59	—

*) T_M — maximum peak temperature, °C.

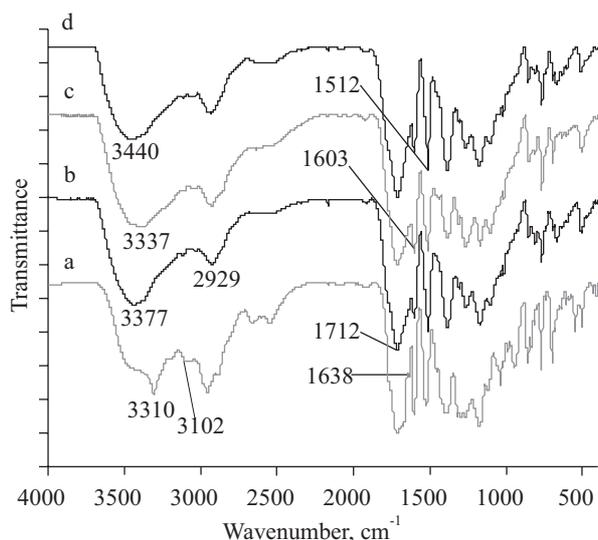


Fig. 5. FT-IR spectra for: a – MPEHPM, b – MPEHPM/MDA, c – MPEHPM/MDABMI, d – MPEHPM/MDABMI/MDA

The probable mechanism of the chemical reactions involved in the curing of MPEHPM/MDA/DGEBA system are presented in Scheme F. For this system only a single exotherm peak is observed. These peaks can be assigned to the following main reactions: oxirane ring opening with the amine hydrogen, Michael-type reaction of -NH_2 groups of MDA to the methacrylic and maleic double bonds and MPEHPM homopolymerization and copolymerization reaction. As a consequence of the MDA presence, the Michael-type reaction appears and a small shoulder to the main exotherm of all systems is observed, with the exception of the MPEHPM sample. The literature data for epoxy/BMI/MDA system shown that the homopolymerization is favoured over Michael-type reaction due to the formation of Zwitterions' adduct between the oxirane ring and BMI double bond, even at temperatures as low as 120 °C [29–31]. The absence of the signal around 915 cm^{-1} corresponding to the epoxy ring suggests that at this molar ratio there are no unreacted epoxy groups. This is also confirmed by the increase of the signal of OH groups situated in the 3337 cm^{-1} range. The characteristic ester absorption band has probably merged with the imide CO in the range of 1716 cm^{-1} . The signal situated in the 3100 cm^{-1} range, which can be attributed to the maleic double bonds, is absent due to the Michael-type reaction between the double bond of maleic type with NH_2 from MDA and new absorption bands appear in the 3413–3444 cm^{-1} range (Fig. 6a).

The activation energies and the kinetic parameters of the curing reactions of MPEHPM and MPEHPM systems were obtained from DSC thermograms measured at three heating rates according to Kissinger and Ozawa methods. This calculation mode of the activation energy of crosslinking reactions is possible without previous knowledge of the reaction order. The calculated activation energies of the curing reactions were listed in Table 1.

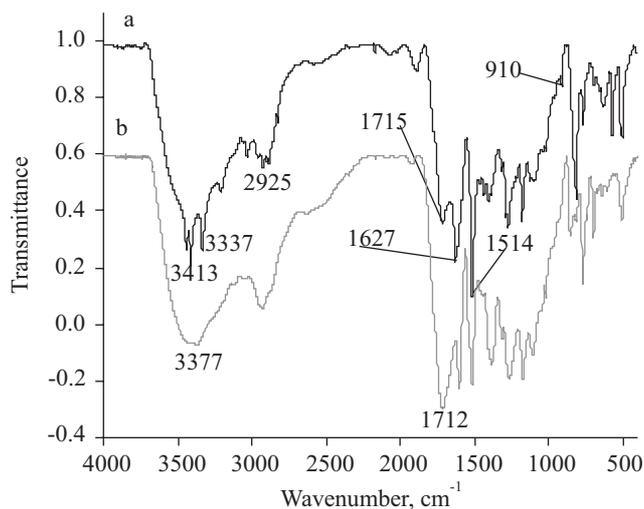


Fig. 6. FT-IR spectra for: a – MPEHPM/DGEBA/MDA, b – MPEHPM/MDA

The values of the activation energy obtained for the first reaction peak of the tested systems were in the 57 to 105 kJ/mol (Kissinger method) range, and were comparable with values presented in the literature [30–34]. The activation energy of the second reaction peak of the tested systems, presents was estimated to have values from 65 to 147 kJ/mol (Kissinger method), which are higher than those obtained for the first reaction peak. This can be attributed to the double bond polymerization of the maleic type [32, 35, 36]. The MPEHPM/MDA/DGEBA system presents only one reaction peak and the activation energy has a value situated between 95 and 101 kJ/mol. The presence of one-reaction peak with high values indicated that all curing reactions (oxirane ring/amine proton addition, Michael-type, homopolymerization of double bonds) took place at the same time interval and contributed to the exothermic value.

Thermal analysis of the cured resins

The thermal stability and thermal degradation behavior of the cured systems were examined by analysis of the thermogravimetric (TG) curves. Figure 7 and Table 2 show the thermal degradation curves and thermal parameters corresponding to dynamic experiments for the cured systems with MPEHPM in compositions. From Fig. 7 it can be observed that there is a slight and slow mass loss before 200 °C, probable due to the presence of readily degradable OH groups existing in the chemical structure of MPEHPM. The relative thermal stability of the different cured systems were evaluated using TG parameters (T_{10} – temperature at 10 % weight loss, T_{50} – temperature at 50 % weight loss, WL_{500} – weight loss at 500 °C) obtained from TG curves, the activation energies of the degradation process and the pre-exponential factor [obtained from equations (3) and (4)]. In Table 2, it is evident that the presence of MDA/BMI has a significant effect upon the activation energies of degradation process

Table 2. Thermal parameters of crosslinked MPEHPM systems at 200 °C, 2 h (in air)

Sample	MPEHPM systems	Temperature at characteristic weight loss, °C		Residue at 500 °C, WL_{500} , %	Reaction order	Decomposition activation energy, kJ/mol		Pre-exponential factor $\ln A$, A in s^{-1}
		T_{10} (10 %)	T_{50} (50 %)			Swaminathan and Modhavan	Coats and Redfern	
1	MPEHPM	310	420	31.2	0.77	45.56	43.10	1.15
2	MPEHPM/MDA	300	450	30.3	0.74	37.87	35.50	6.61
3	MPEHPM/BMI	360	500	49.6	0.72	46.12	43.41	7.66
4	MPEHPM/MDA/BMI	348	620	69	0.73	51.55	49.64	9.20
5	MPEHPM/MDA/DGEBA	364	600	61	1.03	93.45	91.29	6.97

and of coke residue. From Fig. 7, an improvement in the thermal stability of the Sample 4 and 5 is observed, the rate of decomposition being slowed down. This is attributed to an increase in imide and aromatic contents (when epoxy resin is used). Taking into consideration the T_{10} , T_{50} , WL_{500} and activation energies of degradation process as criteria for thermal stability, the crosslinked

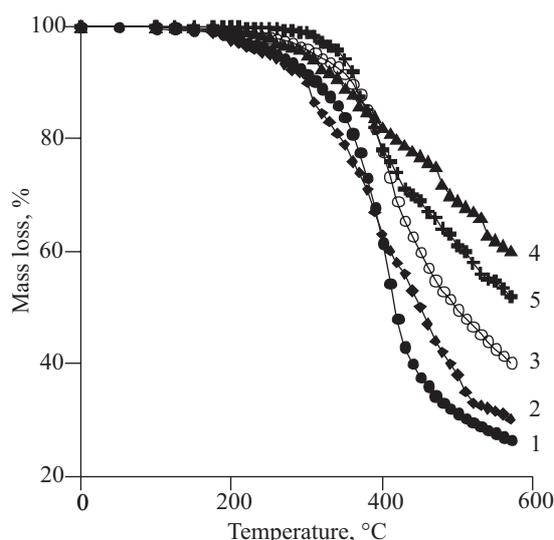


Fig. 7. TGA thermograms of crosslinked: 1 – MPEHPM, 2 – MPEHPM/MDA, 3 – MPEHPM/MDA/BMI, 4 – MPEHPM/MDA/BMI, 5 – MPEHPM/MDA/DGEBA in an air environment (heating rate 10 °C/min)

resins, which contain MDA/BMI, can be considered more stable in comparison with the system without MDA/BMI. The activation energies of the degradation process have values situated in the 36 to 91 $\text{kJ} \cdot \text{mol}^{-1}$ range. It can be observed in Table 2 that T_{10} is situated near 300 °C and T_{50} has values near 450 °C for the systems without MDA/BMI, whereas the resins with MDA/BMI in their composition have greater values with 50 °C for T_{10} and with 150 °C for T_{50} . This may be due to the thermally stable structure (more imide and aromatic nuclei in composition) present. The char yield for crosslinked systems also increases with an increase in the MDA/BMI content.

CONCLUSIONS

The crosslinkable product, which contains both double bond types, based on 4-(*N*-maleimidophenylester) hydroxypropylmethacrylate has been synthesized. The structure of this monomer was confirmed by IR, ^1H NMR, ^{13}C NMR and elemental analysis. The curing reaction of this bifunctional monomer with DGEBA, MDA/BMI, and MDA is a complex process due to the different functional groups present in the systems. The energies of crosslinking reactions obtained from DSC thermograms are situated in the 57–105 $\text{kJ} \cdot \text{mol}^{-1}$ range and are in good agreement with the literature. The cured resins possess good thermal stability; the apparent activation energies of degradation process having values situated in the range of 35–91 $\text{kJ} \cdot \text{mol}^{-1}$ and comparable with the those presented in the literature [31–33, 36, 37]. The crosslinked products can be used as moulding compounds and encapsulating materials in electric or electronic industry.

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