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Photo-crosslinking of multi-allylmaleate resins obtained from epoxy resins

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Some multiallylmaleate resins were synthesized by the chemical reaction between diglycidyl aniline (DGAN) diglycidyl hydroquinone (DGEHQ),diglycidyl ether of bisphenol A (DGEBA) and mono-allylmaleate in the presence of tetrabuthylbenzylammonium bromide (TBBAB) as catalyst. The new resins were characterized by FT-IR, ^{1}H-NMR, elemental analysis and analysis of the functional groups. An investigation on the photo-crosslinking reaction of diglycidyl aniline allylmaleate resins was also performed.

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1. Introduction

Presently, the epoxy resins and the unsaturated polyester resins are utilized for many applications due to the versatility imparted by the strained oxirane ring and the reactivity of the double bonds respectively.[1-3] The both resins can be crosslinked via homopolymerization in the presence of free radicals or by the reaction with crosslinking agents, to obtain polymers with network structures. The networks are widely used as polymer matrix for advanced composites manufacture, structural adhesives preparation or protective coatings because the above polymers combine the easy processing and the reduced manufacturing costs with their excellent mechanical properties, unreactiveness and thermal resistance. Also, the networks resulted from epoxy resins and unsaturated polyester resin find important applications in many industrial and domestic fields such as aeronautic, car, electrical and electronic industry as well as in building construction.[4-6] However, the crosslinked products are relatively brittle materials heaving low resistance to crack propagation. To solve the above problems one proceeds to the insertion of some flexible segments in the oligomer chains to decrease the crosslink densities of the networks.[7-21] Also, by using some modifiers such as synthetic elastomers (liquids rubbers-carboxyl terminated butadiene acrylonitrile elastomers, butadiene homopolymers, acrylic elastomers, etc.) or thermoplastic polymers (polyethers, polyether sulfone, polysulfone, polyether ketone, modified formaldehyde resin, polycarbonate) it can improve the toughness of the resulting networks [22].

The aim of this paper is to investigate the synthesis and the photo-crosslinking process of the new resin, obtained from the reaction between an epoxy resins and monoallylmaleate.

2. Experimental

2.1 Materials

The epoxy resins were diglycidyl aniline (DGAN)(epoxy equivalent weight of 174 g·eq^{-1}) diglycidyl hydroquinone (DGEHQ)(epoxy equivalent weight of 250 g·eq^{-1}) and diglycidyl ether of bisphenol A (DGEBA)(epoxy equivalent weight of 345 g·eq^{-1}). DGEBA was a commercial product supplied from Sintofarm, Romania, DGAN and DGEBA were synthesized after a procedure described elsewhere. [23,24] Other chemicals such as maleic anhydride (MA), allyl alcohol, hydroquinone (HQ), aniline (AN), epichlorohydrin (ECl), sodium and potassium hydroxide (NaOH, KOH), tetrabuthyl benzyl ammonium bromide (TBBAB), and the necessary organic solvents were analytical grade products, purchased from Aldrich, Germany.

2.2 Irradiation

The UV irradiation of the diglycidyl aniline alylmaleate resin was carried out by means of a middle-pressure mercury lamp, HQE-40 type, with a polychrome emission spectrum in the field 240-570 nm. The samples, as films, were mounted on a rotative device and positioned at 60 mm from the mercury lamp. The temperature inside the irradiation chamber was kept at 45°C with the aid of a fan.

The IR spectra of irradiated and unirradited samples were recorded on an M80 Specord spectrophotometer, using KBr pellets. The foto-crosslinked rate of DGAN/MAMAE was quantified by plotting A_t/A_0 versus the irradiation time, where the A_t and A_0 are the double bond surface signal of absorbances from 1640 cm^{-1} .

2.2 Measurements

Nitrogen content was determined in accordance with Kjeldhal method.[25] The epoxy equivalent weights were obtained using literature's method and expressed in $g\cdot eq^{-1}$.[26] Infrared spectra (FT-IR) were performed on a Bio-Rad Digi Lab Division (Portmann Instruments) and Specord M80 using KBr disk.

^{1}H-NMR and ^{13}C-NMR spectra were recorded on an Avance DRX 400 (BRUKER, Rheinstatten, Germany) at 50°C, using standard parameter, tetramethylsilane as internal standard and DMSO-d_6 as solvent (NMR chemical shift were expressed in ppm).

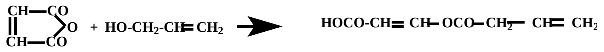
2.3 Synthesis of mono-allylmaleate acid ester (MAMAE)

MAMAE was synthesized starting from allyl alcohol and maleic anhydride according to Scheme 1.

A round-bottomed flask (500 –mL volume) equipped with condenser, mechanical stirrer, nitrogen inlet and thermometer was charged with a mixture containing allyl alcohol (58 g, 1mol), maleic anhydride (98g, 1mol) and 1.5g of hydroquinone. The flask was heated 15 minutes at 140°C with an oil bath under continuous stirring. The reaction mixture was maintained at this level for another 4 hours, under vigorous stirring in order to esterify all maleic anhydride. Mono-allyl maleate (1 mol) with 382 mg KOH $\cdot g^{-1}$ acid number value was the final product of the reaction.

2.4 Synthesis of diepoxy allylmaleate resins

Diallylmaleate resins were obtained starting from three kinds of epoxy resins in the presence of TBBAB as catalyst (3 % based of mono-allylmaleate acid ester weight) (Table 1).



Scheme 1. Synthesis of MAMAE.

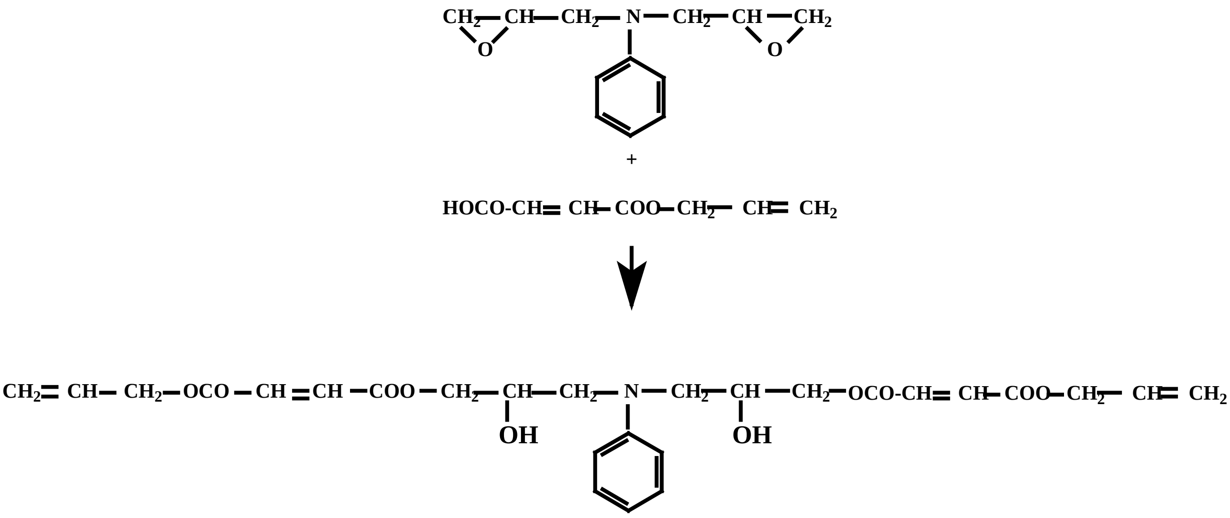
Table 1. Initial monomers composition and some physical-chemical properties of the epoxy resins modified with allylmaleate.

Sample	Monomer ratio (epoxy resin/MAMAE) (mol/mol)	Epoxy equivalent weight (calculated) ($g\cdot eq^{-1}$)	Nitrogen content (%)	Reaction time (h)	Inherent viscosity $^{a)}$	Yield (%)	Molecular weights $^{b)}$ (calculated/ experimental)	Aspect of the resin
1	DGEBA/MAMAE (1/1)	354	-	7	0.130	95	708/750	Pale brown
2	DGEHQ/MAMAE (1/1)	250	-	7	0.120	94	500/531	Brown
3	DGAN/MAMAE (1/1)	174	3.63	5	0.111	97	348/386	Dark violet

a) DMSO as solvent, c = 0.5w/w, 25°C
b) cryoscopic method, DMSO as solvent

The chemical reaction used for the synthesis of DGAN/MAMAE monomer is shown in Scheme 2.

In a representative experiment, a 1 L four necked round-bottom flask equipped with mechanical stirrer, oil bath, thermometer, nitrogen inlet, and Dean-Stark trap fitted with water condenser was charged with 1 equivalent of DGAN, 2 equivalents of MAMAE, 4 g of hydroquinone as polymerization inhibitor and 50 ml of DMF as solvent. Then, the temperature was raised to 100°C when TBBAB was added and was further increased to 140 °C with the heating rate of 10°C/h and held 5 hours while stirring. Finally, 50 mL of DMF was added, and the solution was cooled at room temperature. The polymer is separated by pouring the solution in a large excess of ice water mixture. The resulting polymer was purified by washing with a large amount of water and finally the material was dried by storing overnight in a vacuum oven at 50°C. The conversion of epoxy groups during the reaction with COOH groups was monitored following the evolution of IR peak from 915 cm^{-1}. This band can be attributed to the asymmetrical epoxy ring stretching of C-C bond during contraction of C-O bond [27].



Scheme 2. Synthesis of DGAN/MAMAE monomer.

3. Results and discussion

The reaction between epoxy ring and COOH groups was monitored by means of FT-IR spectroscopy. Fig 1 shows the FT-IR spectra recorded for MAMAE (a) and DGANMAMAE(b). In the DGANMAMAE spectrum (b) it can observe the decrease of the absorption peak intensity, which characterizes the epoxy ring (915 cm^{-1}). Therewith, in spectrum (b) one observes the increase of the peak intensity from 3450-3500 cm^{-1}, specific to O-H stretching vibration in alcohols (b) [27, 28]. This signal can be coupled with the shoulder from 1124 cm^{-1} which can be assigned to C-O stretching vibration in alcohol. The signal is overlapped over the C-O stretching vibration of C-O group in ester structure. The ester group in DGANMAMAE structure is characterized by the signals from 1724 cm^{-1} (symmetrical stretching vibration of C=O) and 1180-1280 cm^{-1} (-C-O stretching vibration). The signals from 3066 cm^{-1} and 1600 cm^{-1} characterize the C-H stretching vibration and –C=C- stretching vibration in aromatic ring. The signals can be coupled with the peaks appeared at 1000 cm^{-1} (characteristic to the C-H bending vibration in plane) and from 756 - 700 cm^{-1} region (proper to C-H bending vibrations out-of- plane) in aromatic structure. The two peaks from 756 and 700 cm^{-1} denote the presence of mono-substituted aromatic ring in the DGANMAMAE structure. The presence of the signal from 1370 cm^{-1} in the FT-IR spectrum (b) characterizes the C-N stretching vibration. The double bond stretching vibration from DGANMAMAE structure is presented in FT-IR spectrum (b) with the moderate band intensity from 1640 cm^{-1}. The characteristic absorption bands in the IR spectra of some multiallylmaleates are presented in Table 2.

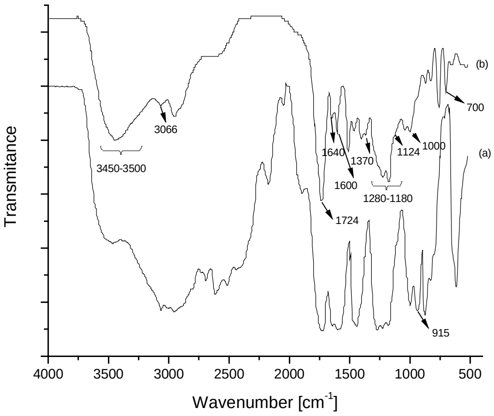


Fig.1. IR spectra of (a) MAMAE and (b) DGANMAMAE.

Fig. 2 shows the ^{1}H-NMR spectrum of DGANMAMAE. The correlation between proton chemical shifts from ^{1}H-NMR spectra with molecular structure of DGANMAMAE was made with the aid of literature data.[29-31] The structure of the monomer was confirmed by the presence in ^{1}H-NMR spectrum of the protons (a), assigned to H_2C=CH- final groups, at 5.9 and 5.3 ppm. The large signal from 2.88-4.82 ppm characterizes the b and d protons. The c protons, assigned to the double bond resulted from maleic acid moiety appeared in ^{1}H-NMR spectrum at 6.62 ppm and 7.25 ppm. The two signals characterize both the geometrical isomers of DGANMAMAE, cis- and trans- respectively.

The multiple peaks presented in the range of 6.67-7.16 ppm chemical shift are assigned to the aromatic protons. For other type of monomers the characteristic absorption bands in ^{1}H-NMR are tabulated in Table 3.

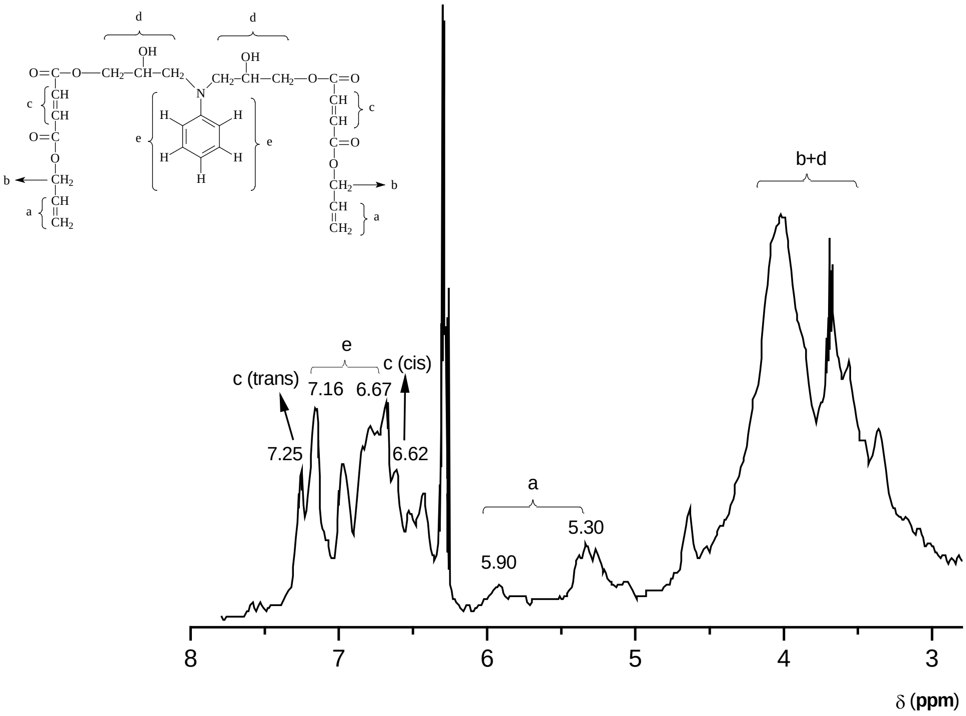


Fig. 2. H-NMR spectrum of DGEANMAMAE.

In the ^{13}C-NMR spectra (Fig.3) the signal presented at 64-68 ppm chemical shift can be attributed to the tertiary C where OH, appeared from the reaction between epoxy ring and MAMAE protons are linked. The double bonds of allylic type are presented in the range of 112-119 and 134-ppm chemical shift and are probable overlapped by the C-H signals of aromatic rings.

Maleic double bounds and CO group from MAMAE are presented in the range of 129.3-130.4 and at 167.5 ppm chemical shift.

The UV radiation assures the photo-crosslinking of DGANMAMAE (Fig. 4). From Fig. 4 one can observe the displacement of carbonyl stretching band from 1724 cm^{-1} to 1740 cm^{-1} during UV treatment. Simultaneously it found the gradually decrease of the double bonds characteristic signal from 1640 cm^{-1}. The decrease of double bonds signal and displacement of the carbonyl absorbance to higher wavenumber after UV irradiation are changes argumentative of the conversion of unsaturated polyester structures resulted from maleic acid into cross-linked polyester structure [32] (Scheme 2).

Table 2. The IR characteristic bands of DGEBA and DGEHQ multiallylmaleates.

Group	Wavenumber (cm^{-1})	Characteristic group	Origin
OH	3450,1080-1039	hydroxyl	multiallylmaleate resins
C=C	3080,825	maleic double bonds	multiallylmaleate resins
CH_2,CH_3	2960-2937	methylene, methyl	allyl maleate acid ester epoxy resin
$C(CH_3)_2$	2960-2937	isopropyl	DGEBA
CO	1728	ester	allylmaleate acid ester
C-O-C	11247-1178	ester	multiallylmaleate resins allylmaleate acid ester
C_6H_4	1600 766-775	aromatic ring p- disubstituted benzene	epoxy resin
C=C	1650,928	allylic	multiallylmaleate resins

Table 3. The ^{1}H-NMR characteristic bands of DGEBA and DGEHQ multiallylmaleates.

Group	δ(ppm)	Characteristic group	Origin
$C(CH_3)_2$	0.65	isopropyl methyl	DGEBA resin
$CH_{2,}$	1.25-2.15	methylene	allylmaleate acid ester
CH_2	2.85-3.85	methylene	glycidyl
OH	4.45	hydroxyl	glycerol moieties
CH_2=CH	5.45-5.81	allylic	allylmaleate acid ester
CH=CH	6.26-5,81	maleic	allylmaleate acid ester
C_6H_4	6.65-7.25	aromatic proton	epoxy resins
C_6H_4	7.95-8.15	aromatic proton	epoxy resins

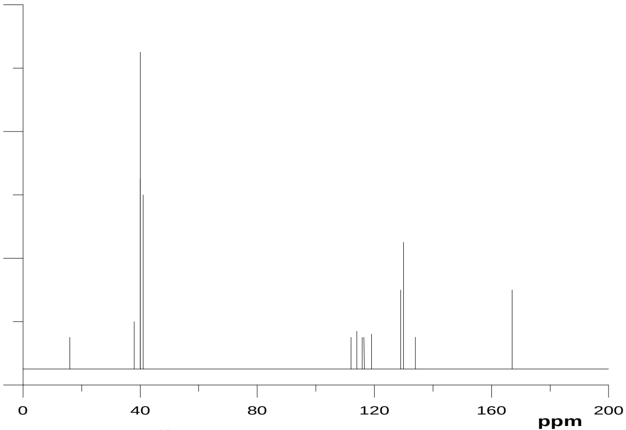


Fig. 3. ^{13}C-NMR spectrum of DGEANMAMAE.

The increase of carbonyl absorbance with the irradiation time and the enlargement of the signal at 1800 cm^{-1} can be explained through the formation of some peroxide liaisons and the appearance of some photo oxidative crosslinkings [32], such as presented in Scheme 3. The kinetic of photo-crosslinking reaction was measured by following the conversion of double bonds using the absorbance from 1640 cm^{-1}. The increase of the irradiation time leads to the lower amount of -C=C- groups in the sample compared with unirradiated DGANMAMAE (Fig. 5). This behaviour confirms the crosslinking process of the resin.

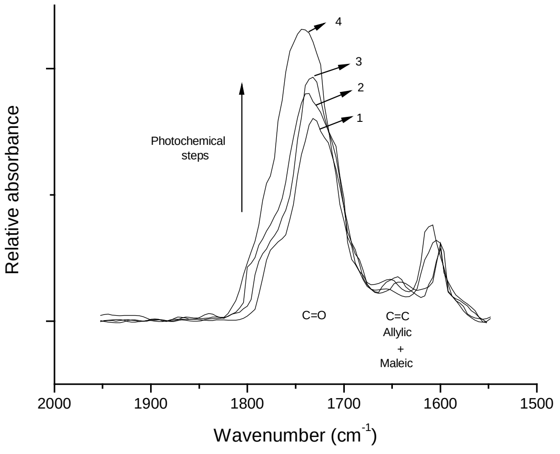
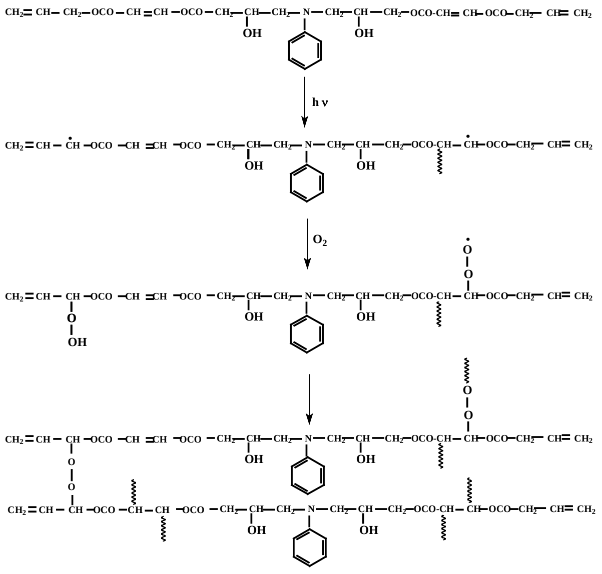


Fig. 4. Changes in IR spectrum of DGANMAME with UV irradiation time: 1-unirradiated sample; 2-after 2 hours irradiation time; 3-after 4 hours irradiation time; 4-after 6 hours irradiation time.

4. Conclusions

Unsaturated monomers containing maleic and allylic double bonds were synthesized. Chemical structure of the obtained monomers were confirmed through IR and NMR spectroscopy as well as with elemental analysis. The samples were irradiated with UV light (λ > 240 nm) up to 7 hours.



Scheme 3. The photo-crosslinking mechanism of DGANMAMAE.

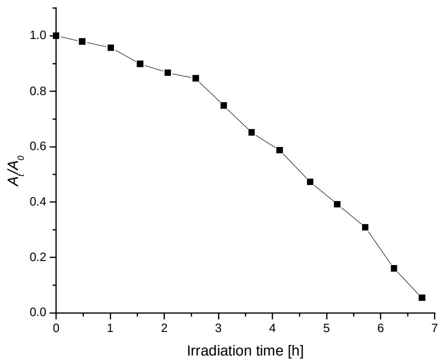


Fig. 5. Changes of -C=C- groups amount in DGANMAMAE during UV- irradiation, where A_o, A- integral intensities of the double bound band (1610-1660 cm^{-1} range) in sample before and after determined irradiation time.

The double bonds located in the molecular structure of these monomers permit of crosslinking during the exposure to ultraviolet and visible radiation and in the presence of oxygen from air.

The most important photoreactions took place at the double bonds appertaining to the maleic moieties while the allylic structure generated photo-oxidative crosslinking.

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