Lactic Ester of Maleoabietic Acid as Crosslinking Agent for Epoxy Resins

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Lactic ester of maleoabietic acid (RAMALA) was obtained by chemical reaction between Diels-Alder adduct of resin acids with maleic anhydride (RAMA) and lactic acid (LA). The obtained product was characterized by elemental analysis and by spectroscopic methods (IR and NMR). Curing reaction of three epoxy resins (diglycidylether of bisphenol A (DGEBA), diglycidyl ether of hydroquinone (DGEHQ) and diglycidylaniline (DGAN), with (RAMALA) in the presence of triethylbenzylammonium chloride (TEBAC) as catalyst was examined by differential scanning calorimetry (DSC) at different heating rates. Using the literature methods the kinetic parameters of crosslinking reactions were obtained. The activation energies of the curing reaction varied in the range of 48 to 85 kJmol⁻¹ depending on epoxy systems. The thermal behaviour of cured products was also investigated using dynamic thermogravimetric analysis (TGA) technique. The cured products present good thermal stability and the activation energies of the degradation process exhibit values between 82 to 155 kJxmol⁻¹.

Keywords: Diels-Alder adduct of resin acids, lactic ester of Diels-Alder adduct of resin acids with maleic anhydride, epoxy resin, crosslinking reactions, thermal properties

In recent years, as a consequence of the increase of the pollution with polymer waste materials (polyethylene bags, polyester bottles, etc.), various biodegradable polymers (polyactic acid, polyhydroxybutirate, polyvinyl alcohol, polyvinyl pyrrolidone, polyethylene oxide) have been extensively investigated [1-4]. These raw materials are obtained from renewable resources (cellulose, turpentine, resin, natural rubber, vegetable and animal oil, sugar saccharide and so on) from petroleum derivatives or by blending of synthetic polymers with natural polymers. Thermosetting resins as epoxy resins and unsaturated polyester resins are the most important group of polymers, which when are cured display good thermal and chemical resistance, excellent mechanical strength, good bonding to substrate and are used in numerous industrial fields such as: fibers composites, metal coating compositions, friction moulding materials, insulation materials for electric and electronic devices, etc. The above polymers exhibit good bonding properties but are not environmentally friendly because they are not biodegradable.

Rosin, raw material obtained from oleoresin of conifer trees is mainly constituted from resin acids and can be considered as possible biodegradable material [5-8]. In the last decade, the Diels-Alder adducts of resin acids with the dienophile (maleic anhydride, fumaric acid, acrylic acid, β-propiolactone etc.) have been used as raw materials in synthesis of polymers (polyesters, unsaturated polyesters, polycarbonates, polyamides, polyamid-imides, alkyd resins, epoxy resins and so on.) [9-33]. There are some reports regarding the use of the resin acids and their derivatives as raw materials in the formulation of epoxy resin synthesis [34-42].

The aim of this work was the synthesis of Diels-Alder adduct resin with maleic anhydride modified with lactic acid as possible biodegradable compounds, and using them as curing agents for three epoxy resins. The kinetic of curing and the thermal stability of cured products were also emphasized.

Experimental part

Materials
Maleic anhydride (MA), resin acids (RA) (a.n. =181 mg KOH×g⁻¹), triethylbenzylammonium chloride (TEBAC), hydroquinone (HQ), aniline (AN), lactic acid (LA) and organic solvents were analytical grade products. Diels Alder adduct of resin acids in levopimaric form with MA (RAMA) was obtained as described in previous published [43] article. Epoxy resins: a) diglycidylether of bisphenol A (DGEBA) (Sintofarm, Bucharest), was a commercial product with an average epoxy equivalent weight of 345 g x eq⁻¹; b) diglycidyl ether of hydroquinone (DGEHQ) and diglycidylaniline (DGAN) (6.75 %N), were synthesized according to the procedure described in our previous article and have an average epoxy equivalent weight of 205 g x eq⁻¹ and 130 g eq⁻¹ [21,41,42] respectively. Resin acids (RA) were obtained from commercial rosin by twice recrystallization from acetone.

Measurements
Nitrogen content was determined in accordance with Kjeldhal method [44]. Acid number for resin acids and for (RAMA) was obtained from direct titration of the samples dissolved in acetone (to make a 5% (w/v) solution) with 0.1 N ethanolic KOH solutions in presence of phenolphthalein to the end point. The epoxy equivalent weights were obtained using literature method and expressed in g×eq⁻¹ [45]. Infrared spectra (FTIR) were registered on a Bruker Vertex 70 (Germany) apparatus, using KBr pellets. The curing thermal data and the glass transition were obtained by means of a Mettler DSC-12E type apparatus. All the experiments are performed in nitrogen atmosphere (3 l×min⁻¹) under dynamic condition. For the kinetic characterization, the tests were run from 20 to 350 °C with different heating rates (5,10,15 °C×min⁻¹). The kinetic parameters of the curing reactions were calculated from DSC measurements using the variable exothermic peak method of Kissinger taking in consideration three heating rates [46]. The following equation is used:

\[ T_p = T_0 + \frac{k}{E_a} \ln \left( \frac{R T_0^2}{\alpha A} \right) \]
ln(β/\(T^2\)) = \(E_a/R \cdot T\) - ln (Z/R\(E_a\))  

(1)

were: β is the heating rate (°C×min⁻¹), \(T\) is the exothermic peak temperature (°C), \(E_a\) is the activation energy for the curing reactions (kJ/mol⁻¹), \(R\) is the gas constant (kJ×mol⁻¹×°K⁻¹), \(Z\) is the frequency factor (min⁻¹). From the graph ln(\(β/\(T^2\)) versus 1/\(T\)) the activation energy of curing and frequency factor were obtained. Also, the activation energies for the presented epoxy systems were determined by the Ozawa method (equation 2)[47,48]:

\[ \ln \beta = B - 1.052E_a/RT \]  

(2)

where the parameters are similar with those from eq.1. This method is valuable only for curves consisting of single unit process. Plotting log β versus reciprocal absolute temperatures of \(T\) one can estimate from the slope of the straight lines, the activation energies of the curing process.

Thermal stability of the cured products was evaluated by TGA measurements and was obtained on a MOM-Budapest of Paulik, Paulik-Erdey type derivatograph at heating rate of 10 °C×min⁻¹ in air on the temperature range of 25-700°C. The TG parameters, \(T_\alpha\) (temperature for 10% weight loss), \(T_{50}\) (temperature for 50% weight loss) \(W_{L,500}\) (weight loss at 500°C) and the activation energy of decomposition reaction were used in order to determine the thermal stability of the crosslinked polymers. Kinetic analyses of TG data were performed using the main peak of degradation reaction, by applying the Swaminatham & Modhavan and Coats & Redfern methods [49,50]. The general equations are used:

\[ \log(1- (1-c)^{\alpha})/(1-n) \times T^2 = \log(\alpha/\beta E_a/RT) - 2.303 (E_a/RT) \]  

(3)

and

\[ \Delta \alpha/\Delta T = \alpha \exp(-E_a/RT)(\alpha^\alpha(1-\alpha)^n) \times \ln(1-\alpha)^p \]  

(4)

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

**Synthesis of Diels-Alder adduct of resin acids with maleic anhydride (RAMALA)**

Diels-Alder adduct of resin acids with maleic anhydride (RAMALA) was prepared as follows: 0.1 mol of RAMA, 0.1 mol of anhydrous LA and 20 mL of acetone, were mixed 20 min into the reaction flask equipped as above, at room temperature, when the mixture becomes homogenously. Then, the reaction mass was heated to reflux and acetone was removed. The heating was continued and the temperature was raised up to 200°C in 30 min. This level of the temperature was maintained for 2 h, when was raised to 230°C and maintained for another 4 h. Finally, the mixture was poured into a porcelain dish, cooled at room temperature and powdered as fine grains, dissolved in ethyl ether and precipitated with petroleum ether (b.p. 20-60 °C). A yellow brownish product was obtained (54% yield) (scheme 1).

**Samples preparation for DSC and TGA studies**

The epoxy resins and lactic ester of Diels-Alder adduct of resin acids with maleic anhydride (RAMALA) (powdered as fine grains) accurately weighed were vigorously mixed in a proportion corresponding to a molar ratio \(r = 1\) where “\(r\)” represents the carboxyl group/epoxy ring ratio. A small quantity of the mixture was taken for DSC studies. The dynamic scans were performed at heating rates 5,10,15 °C×min⁻¹ in the range of 20-400°C. The remaining samples were cured at 120°C for 1 h, at 140 °C for 2 h and post cured at 180°C for another 3h. The cured products were powdered and used for TGA studies in the dynamic scan. (scheme 2)
Results and discussion

Resin acid (RA) in levopimaric acid form, as dienic monomer, reacts with dienophile monomer (MA) under Diels-Alder reaction. The chemical reactions and the overall structure of the obtained products can be represented as in scheme 1. The structure can be confirmed by the FT-IR and NMR spectra. The results for RAMA and RAMALA are shown in figures 1-3. In figure 1c, (IR spectra for RAMA), the presence of the peaks in the domain of 2870-2960 cm⁻¹ specific to CH, CH₂, and CH₃ aliphatic groups can be assigned to these groups located in the hydrophenanthrene and hydroxypropyl groups (fig.1). The absorption bands located at 3450 –3500 cm⁻¹ and at 1700 cm⁻¹ reveal the presence of COOH groups while the peaks situated at 1776 and 1845 cm⁻¹ are specific to anhydride groups. The band characteristic to the double bond into the hydrophenanthrene moiety is observed at 1460 cm⁻¹. As a consequence of the reaction between lactic acid and maleic anhydride groups (scheme 1), the specific peaks of anhydride moieties (1776 and 1845 cm⁻¹) disappeared and appeared a new absorption band located at 1725 cm⁻¹, which evidences the presence of ester groups.

In the ¹H-NMR spectra of RAMA and RAMALA (fig. 2) one can observe a lot of peaks situated in the range of 0.67-1.75 ppm chemical shift that represent the major signals assigned to aliphatic protons from hydrophenanthrene moieties. The peaks located in the range of 0.71 ppm chemical shift are probably the protons from isopropyl methyl group and from CH₃ groups bonded to the hydrophenanthrene units of RA, and the peaks occuring in the range of 0.9-1.75 ppm chemical shift represent the CH and CH₂ protons groups from hydrophenanthrene units. The olefinic protons located in the RA ring, appear as weak peaks in the range of 5.45 ppm chemical shift. The aromatic pattern presented as a weak peak in the chemical shift range 7.1 to 7.3 ppm represents the condensate ring of hydrophenanthrene nuclei. The carboxylic acid protons appear as a broad band with a chemical shift of about 12.09 ppm. In figure 3, (¹³C NMR spectra for RAMALA), the characteristic signal attributed to CH₃ bonded to hydrophenanthrene ring appears in the range of 14 to 19 ppm while the peaks assigned to the CH₂ group situated...
into hydrophenanthrene ring appear in the range of 22 to 35 ppm. The peaks specific to CH= groups of the olefin link can be seen in the range of 120 ppm and at 135 ppm for C= groups into the hydrophenanthrene ring. The signal presented in the range of 165 ppm can be attributed to the CO ester type and the peak located in the range of 186 ppm can be assigned to COOH groups.

The oxirane group easily reacts with carboxylic and carboxylic acid anhydride groups in the presence of catalysts (metal derivatives, quaternary ammonium salts, tertiary amines, lithium halide) at high temperatures (180 °C) to form crosslinked products with infinite molecular weight [51-55]. The methods used for the study of the curing behaviour and kinetic parameters of these systems are: IR, NMR, UV and DSC spectroscopy and chemical analysis.

In the present work, we obtain the networks by crosslinking of DGEBA, DGEHQ and DGAN with RAMALA as crosslinking agent. The used method here for the estimation of crosslinked parameters, was DSC technique. The curable systems were obtained by mixing these epoxy resins with RAMALA at the molar ratio 1/1 (epoxy group/carboxylic proton) and crosslinked under the action of temperature. The reaction between carboxylic proton and epoxy ring in the presence of catalysts involves a complex mechanism [51-53]. In scheme 2 the crosslinking reaction and the network formation are shown. The dynamic DSC scans of the systems presented above were registered at different heating rates and the curing exotherms were recorded. From the figure 4 it may be seen that the systems exhibit three exotherms. The RAMALA shows, three kinds of carboxylic groups with the probability to react at three different temperatures. The first exotherm at relatively low temperature may be due to the opening of epoxy ring in the presence of carboxylic group of lactic ester type (more flexible chain). The second peak can be due to the reaction of the original carboxylic group bonded to the hydrophenanthrene moieties of resin acid that presents higher steric hindrance. The third exotherm can be attributed to the reaction between the third carboxylic group appeared from the opening of maleic moieties by the lactic acid with more steric hindrance. Finally, it is possible, with the increase of the temperature the esterification reactions between hydroxyl and carboxylic groups to occur. All four kinds of reaction can exist simultaneously and induce the formation of crosslinked structures. These chemical reactions between carboxylic and epoxy groups can be evidenced from IR spectra of crosslinked products (fig 1b), where it can be seen that the peaks located in the range of 915 cm⁻¹ (specific to

![Fig 3. 13C-NMR spectrum of RAMALA](image)

<table>
<thead>
<tr>
<th>Table 1</th>
<th>KINETIC PARAMETERS OF EPOXY SYSTEMS FROM DSC SCANS (EQUIVALENT OF CARBOXYL PROTON/EPOXIDE GROUP=1/1)-CALCULATED FROM FIRST EXOTHERM</th>
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<tbody>
<tr>
<td>Epoxy resin</td>
<td>Curing agent</td>
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<tr>
<td></td>
<td></td>
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<tr>
<td></td>
<td></td>
</tr>
<tr>
<td>DGEBA</td>
<td>RAMALA</td>
</tr>
<tr>
<td>DGEHQ</td>
<td>RAMALA</td>
</tr>
<tr>
<td>DGAN</td>
<td>RAMALA</td>
</tr>
<tr>
<td>DGAN</td>
<td>DDM</td>
</tr>
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</table>

* a) Blank test; b) T_m- maximum peak temperature °C; c) E_Oscans, E_Kissenger Activation energy of curing calculated with eqs. 1 and 2; d) calculated with Kissinger equation; e) measured after crosslinked at 200 °C, 3h

<table>
<thead>
<tr>
<th>Table 2</th>
<th>KINETIC PARAMETERS OF EPOXY SYSTEMS FROM DSC SCANS (EQUIVALENT OF CARBOXYL PROTON/EPOXIDE GROUP=1/1)-CALCULATED FROM SECOND EXOTHERM</th>
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<td></td>
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<tr>
<td></td>
<td></td>
</tr>
<tr>
<td>DGEBA</td>
<td>RAMALA</td>
</tr>
<tr>
<td>DGEHQ</td>
<td>RAMALA</td>
</tr>
<tr>
<td>DGAN</td>
<td>RAMALA</td>
</tr>
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</table>

* Tm- maximum peak temperature °C
Table 3

<table>
<thead>
<tr>
<th>Epoxy resin</th>
<th>Curing agent</th>
<th>Heating rate (°C min⁻¹)</th>
<th>Activation energy of curing (kJ mol⁻¹)</th>
<th>Frequency factor ( \ln A ) (min⁻¹)</th>
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<tr>
<td></td>
<td></td>
<td>5</td>
<td>10</td>
<td>15</td>
</tr>
<tr>
<td>DGEBA</td>
<td>RAMALA</td>
<td>294</td>
<td>318</td>
<td>342</td>
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<tr>
<td>DGEHQ</td>
<td>RAMALA</td>
<td>265</td>
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<td>300</td>
</tr>
<tr>
<td>DGAN</td>
<td>RAMALA</td>
<td>190</td>
<td>229</td>
<td>241</td>
</tr>
</tbody>
</table>

b) \( T_m \) - maximum peak temperature °C

Table 4

<table>
<thead>
<tr>
<th>No</th>
<th>Molar ratio (Epoxy resin/RAMALA) (mol/mol)</th>
<th>Temperature corresponding to 10% ( T_{10} ) and 50% ( T_{50} ) weight loss (°C)</th>
<th>Weight loss at 500°C (WL₅₀₀°C) (%)</th>
<th>Decomposition activation energy ( E_{\text{decomp}} ) (kJ mol⁻¹)</th>
<th>Reaction order ( a )</th>
<th>Pre-exponential factor ( \ln A ) (min⁻¹)</th>
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<tbody>
<tr>
<td>1</td>
<td>DGEBA/RAMALA</td>
<td>350</td>
<td>475</td>
<td>60</td>
<td>109.7</td>
<td>105.6</td>
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<tr>
<td>2</td>
<td>DGEHQ/RAMALA</td>
<td>310</td>
<td>358</td>
<td>67</td>
<td>154.6</td>
<td>178.9</td>
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<tr>
<td>3</td>
<td>DGAN/RAMALA</td>
<td>315</td>
<td>375</td>
<td>80</td>
<td>107.4</td>
<td>109.5</td>
</tr>
<tr>
<td>4</td>
<td>DGEBA/DDM</td>
<td>360</td>
<td>480</td>
<td>54</td>
<td>81.9</td>
<td>76.1</td>
</tr>
</tbody>
</table>

a) \( E_{\text{decomp}} \) - activation energies of decomposition reaction calculated with Coats and Swaminathan equation

b) calculated with Swaminathan equation

Thermal properties of the cured resins

The thermal stability of crosslinked resins was evaluated by the thermogravimetric analysis, TGA curves and the main parameters of degradation process, obtained in air atmosphere are shown in figure 5 and listed in table 4. The epoxy ring, disappeared and the new obtained groups (tertiary OH and ester) occur in the range of 3450-3500 cm⁻¹, 1710-1730 cm⁻¹ and 1100-1280 cm⁻¹ respectively. As it can be seen in figure 4 and in tables 1-3, the epoxy resin/RAMALA systems show (at 10°C/min heating rate) a first maximum exotherm peak centered in the range of 143-200°C, a second maximum exotherm peak centered in the range of 200-260°C and third maximum exotherm peak centered in the range of 229-318°C. These temperatures are specific to each system and have the minimum values for the DGAN/RAMALA system (tables 1-3). This fact can be explained by the liquid state of DGAN with low viscosity, that permits easy contact between reactive groups. The data presented in the table 1-3 show that the \( T_m \) has different values, depending of the chemical structure of epoxy resins and these data are shifted to high values with the increase of heating rate. From the tables 1-3, it can be seen that the crosslinking energies are different, depend of chemical structure of epoxy resins and are situated in the range of 40 - 67 kJ mol⁻¹ (calculated from the first exotherm) and between 44-91 kJ mol⁻¹ (calculated from the second exotherm). The influence of the structure of cured epoxy resins has also been examined by measuring the glass transition temperature \( T_g \). As it can be seen from Table 1, the \( T_g \) of the DGEHQ/RAMALA system is enhanced in comparison with the DGEBA/RAMALA and DGAN/RAMALA systems. This can be explained by the rigid structure of DGEHQ in comparison with DGAN and DGEBA.
activation energy and the pre-exponential factor were obtained by applying the equation 3 and 4. In order to quantitatively estimate the relative thermal stability, activation energy and TG parameters such as $T_{10}$ (temperature for 10% weight loss), $T_{50}$ (temperature for 50% weight loss) and weight loss at 500°C($WL_{500}$) were measured. Accepting $T_{10}$, $T_{50}$ and $WL_{500}$ as the criteria of relative thermal stability, the ordering of thermal stability is $\text{DGEBA/RAHALA > DGEHQ/RAHALA > DGAN/RAHALA.}$

As can be seen in Table 4, the activation energy of thermal degradation process exhibit a value situated in the range of 107 - 155 kl/mol.

Conclusions

The lactic acid ester of Diels-Alder adduct with maleic anhydride was successfully used as crosslinking agent for epoxy resins. The curing reaction of the three epoxy resins in presence of RAHALA is a complex process because the three carboxylic groups have different reactivities. The cured resins with moderately glass temperatures and good thermal stability were obtained. The cured resins, can be used as potentially matrix resins in the field of electrical and electronic industries, especially as environmentally friendly materials, because they have lactic ester groups in their structure, potentially biodegradable.

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