FANICA MUSTATA[*)], IOAN BICU

"P.PONI" Institute of Macromolecular Chemistry
Aleea Gr. Ghica Vodã nr. 41 A
Iasi — 700487, ROMANIA

Hydroxyesters of resin acids modified with *o*-cresol/*p*-nonylphenol/formaldehyde resins

Summary — Hydroxyesters of resin acids (ERA) were obtained by the esterification of resin acids (RA) with diglycidyl resins, such as diglycidyl ether of bisphenol A (DGEBA), diglycidyl ether of hydroquinone (DGEHQ) or diglycidyl aniline (DGAN), in the presence of triethylbenzylammonium chloride as a catalyst. The preparations of heat reactive *o*-cresol (*o*-Cz)/*p*-nonylphenol (*p*-NP)/formaldehyde resins (FR) by basic catalyzed polycondensation at various molar ratios of *o*-Cz, *p*-NP and *p*-formaldehyde (*p*-FA) were carried out. ERA were reacted with obtained heat reactive FR giving hydroxyesters of resin acids modified with formaldehyde resins (ERAFR). The chemical structures of all the products were determined by FT-IR, ^{1}H NMR, ^{13}C NMR spectroscopy and elemental analysis. ERAFR exhibit properties that make them useful in formulations of vehicles for gravure or printing inks.

Key words: hydroxyesters of resin acids, diglycidyl resin, phenol-formaldehyde resins, modification, printing inks vehicles.

HYDROKSYESTRY KWASÓW ŻYWICZNYCH MODYFIKOWANE ŻYWICAMI *o*-KREZOLOWO/*p*-NONYLOFENOLOWO/FORMALDEHYDOWYMI

Streszczenie — Hydroksyestry kwasów żywicznych (ERA) otrzymywano w wyniku estryfikacji tych kwasów (RA) związkami diglicydylowymi, mianowicie diglicydylowym eterem bisfenolu A (DGEBA), diglicydylowym eterem hydrochinonu (DGEHQ) bądź diglicydyloaniliną (DGAN) (tabela 1). Na drodze katalizowanej zasadowo polikondensacji *o*-krezolu (*o*-Cz), *p*-nonylofenolu (*p*-NP) oraz *p*-formaldehydu (*p*-FA) użytych w różnych stosunkach molowych, otrzymano serię odpowiednich żywic formaldehydowych (FR, tabela 2). Opracowano optymalne warunki reakcji ERA z FR prowadzącej do wymienionych w tytule produktów (ERAFR, tabela 3). Budowę chemiczną ERA, FR i ERAFR potwierdzono metodami FT-IR (rys. 1), ^{1}H NMR (rys. 2) oraz ^{13}C NMR (rys. 3). Ponadto scharakteryzowano odporność cieplną ERAFR (tabela 4, rys. 4), a także rozpuszczalność ERA i ERAFR (tabela 5). Właściwości opisanych ERAFR wskazują na możliwość ich wykorzystania w charakterze nośników farb drukarskich.

Słowa kluczowe: hydroksyestry kwasów żywicznych, modyfikacja, związki diglicydylowe, żywice fenolowo-formaldehydowe, nośniki farb drukarskich.

Rosin is a natural material obtained from the oleoresin exudates of conifer trees, containing resin acids (abietic, levopimaric, neoabietic acids *etc*.). Lately, resin acids and their Diels—Alder adducts with *e.g.* maleic anhydride, acrylic acid, acrylonitrile, or acrylamide have been widely used as intermediates for the syntheses of polymers such as unsaturated and saturated polyesters [1—6], polyesterimides [7—10], polyimidamides [11—14], epoxy resins [15—19], formaldehyde resins [19, 20], allylic polymers [21, 22], ketonic resins [23, 24], or acrylic polymers [25, 26].

Formaldehyde resins (an important group of polymers) obtained in acid or basic catalysis, are used in numerous industrial fields such as: wood and fibres composites, metal coating compositions, adhesives, abrasive and friction molding materials, insulation materials for electric and electronic devices and vehicles for printing and gravure inks [27—30].

Presently, raw natural materials have attracted considerable attention for syntheses of various chemicals and monomers for polymer syntheses, due to their compatibility with the environment and their degradability under the environmental conditions. Owing to the great development of printing arts, a lot of modified rosin resins are synthesized to obtain the inks of valuable properties (high speed of printing, high gloss, quick drying, continuous and resistant film surface, solubility in the solvents which do not attack rubber rollers, *etc*.). Maleic

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[*)] Author for correspondence; e-mail: fmustata@icmpp.ro rosin esters modified with phenol-formaldehyde resins are characterized by many of the above mentioned properties. Typically, these esters are synthesized at high temperatures and often these severe reaction conditions cause very broad molecular weight distribution and undesired dark color of the products obtained [31—34]. The known methods to produce light color esters are expensive and the yields are poor.

In this work, hydroxyesters of resin acids ERA were synthesized starting from diglycidyl resins and resin acids. These new hydroxyesters have potential for the development of a new method of the production of formaldehyde resins (FR) with hydrophenanthrene moieties in their structures, which allow them to be the vehicles for printing inks.

EXPERIMENTAL

Materials

— Resin acids (RA, acid number = 180 mg KOH · g^{-1}) were separated from a rosin commercial product by double recrystallization from the concentrated solutions in acetone.

— *p*-Nonylphenol (*p*-NP, d^{15} = 0.955 g · cm^{-3}; n_D^{20} = 1.511) and paraformaldehyde (*p*-FA, 98 % of purity) were purchased and used as received.

— Epoxy resins: diglycidyl ether of bisphenol A (DGEBA, epoxy equivalent weight = 345 g · eq^{-1}) was a commercial product (SC Sintofarm SA, Romania), diglycidyl ether of hydroquinone (DGEHQ, epoxy equivalent weight = 250 g · eq^{-1}) and diglycidylaniline (DGAN, epoxy equivalent weight = 175 g · eq^{-1}) were synthesized as described in [11, 35].

— *o*-Cresol (*o*-Cz), sodium hydroxide (NaOH), triethylbenzylammonium chloride (TEBAC) and organic solvents were analytical grade products or purified by distillation before the use.

Syntheses

Syntheses of hydroxyesters of resin acids

A set of three ERA was obtained by polyaddition reaction of RA with DGEBA, DGEHQ or DGAN, in the presence of TEBAC as a catalyst, in solution or in bulk (Scheme A where RA = abietic acid).

A typical experiment for the synthesis in solution of the polymer (sample 1, see Table 1) was carried out as follows: a four-necked reaction flask equipped with a mechanical stirrer, N_2 inlet, an ascendent condenser, a thermometer and heating devices was charged with 60.4 g (0.2 mol) of RA, 70 g of DGEBA (0.1 mol) and 50 g of toluene and the mixture was mixed at room temperature until it became homogeneous. While stirring, the mixture was heated up to 110 °C and the temperature was maintained at this level for 15 minutes. Then, 0.6 g (1 wt. % referred to RA weight) of TEBAC was added and the reaction mass was then heated to 140 °C for 1 h and to 160 °C for several hours (according to the chemical structure of the epoxy resin) (see Table 1). The solvent was extracted under vacuum and after cooling down, the reaction mass was powdered as fine grains, extracted with a large amount of petroleum ether (b.p. 20—60 °C), and dried under vacuum at 80 °C overnight. After purification, a yield equal to 92 % was registered.

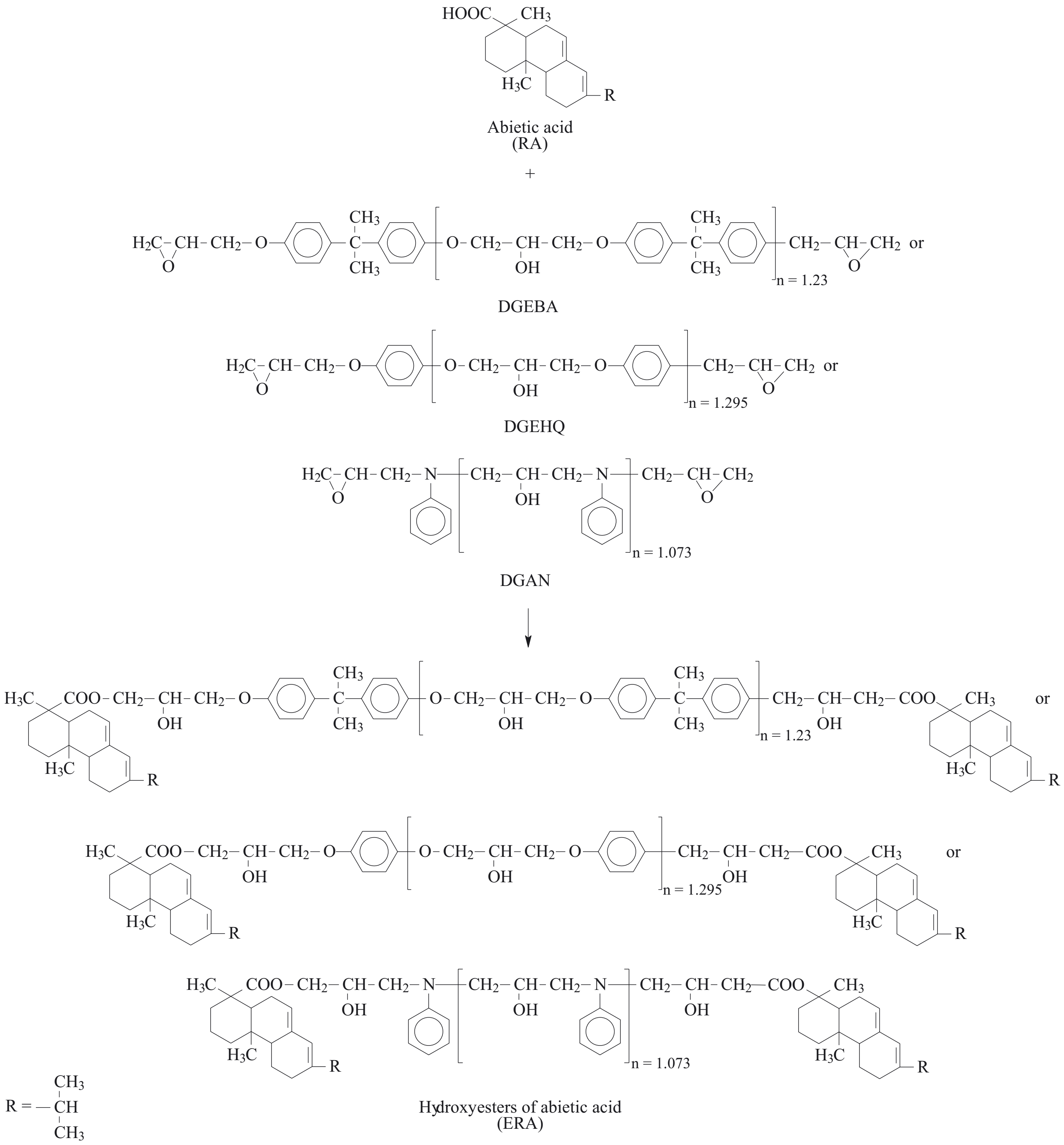
The bulk condensations were performed at the same molar ratios and in the same reaction conditions as the condensations in solution. The obtained polymers were processed by pulverization and extraction with warm petroleum ether. This time, the yields were somewhat higher in comparison with those registered for the condensation in solution.

Syntheses of formaldehyde resins

FR resins were obtained from *p*-NP, *o*-Cz (at different molar ratios), and *p*-FA at the molar ratio phenols/formaldehyde = 1:1.07 under alkaline conditions (4 % NaOH as aqueous solution, based on monomer weights, Scheme B). An exemplary experiment (sample FR 1, see Table 2) was carried out as follows: 0.5 mole of *p*-NP, 0.25 mole of *o*-Cz, and 0.8 mole of *p*-FA were added into a four-necked flask and heated at 60 °C, stirring continuously. Then 6.4 g of NaOH (50 % aqueous solution) was added in three equal portions. An exothermic effect was observed (temperature increase 14 °C). The temperature was increased up to 85—90 °C and the mixture was left while stirring at this temperature for 90 min, for methylolization. Then, 30 mL of DMF/cyclohexane (2/1, v/v) was added and a Dean Stark separator was fitted to the top of the water condenser. The mixture was heated to reflux and the generated water was extracted by azeotropic distillation with cyclohexane. After 1.5 h the reaction was completed. Finally, a large amount of DMF and cyclohexane was extracted under vacuum, and the formaldehyde resin was taken out from the flask, cooled at room temperature and powdered as fine grains. Then, the resin was extracted twice with petroleum ether (b.p. 28—60 °C). The final mass was filtered and the cake was placed under light vacuum at 60 °C to remove the volatile components (yield 91 % of pale brown resin).

Syntheses of modified hydroxyesters

The best procedure to obtain the modified hydroxyesters is cooling of ERA produced in the first step while stirring at 120 °C, and mixing with the powdery FR in molar ratio 1:1 under the nitrogen atmosphere (Scheme C). The reaction was carried out in the presence of 0.1 mole of *p*-FA and 0.01 mole of TEBAC as a catalyst, at 180 °C, for 1 h, and then at 220—230 °C for another 5 h. Finally, the water and solvent traces were extracted under vacuum, the reaction mixture was cooled and powdered as fine grains. The obtained product had a pale brown color.



Scheme A. Syntheses of hydroxyesters of resin acids (ERA)

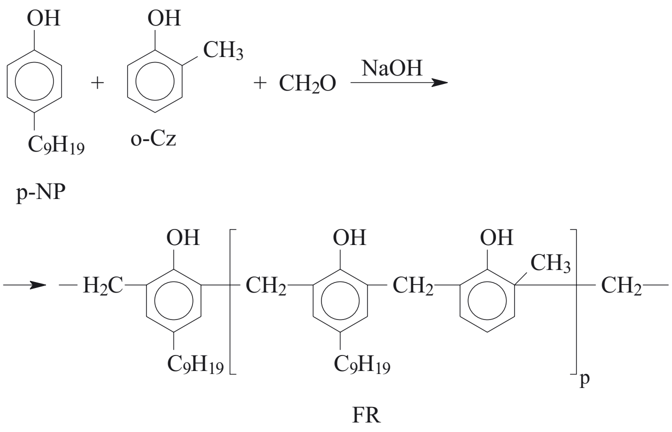
Methods of testing

— Acid number was determined by titration with 0.1 N ethanolic KOH solution in the presence of phenolphthalein up to the pink end point.

— The epoxy equivalent weights and hydroxyl number values were determined using the literature method and were expressed as g · eq^{-1} and (%) OH, respectively [36].

— Average number molecular weights were determined by the cryoscopic method using DMSO as a solvent [37].

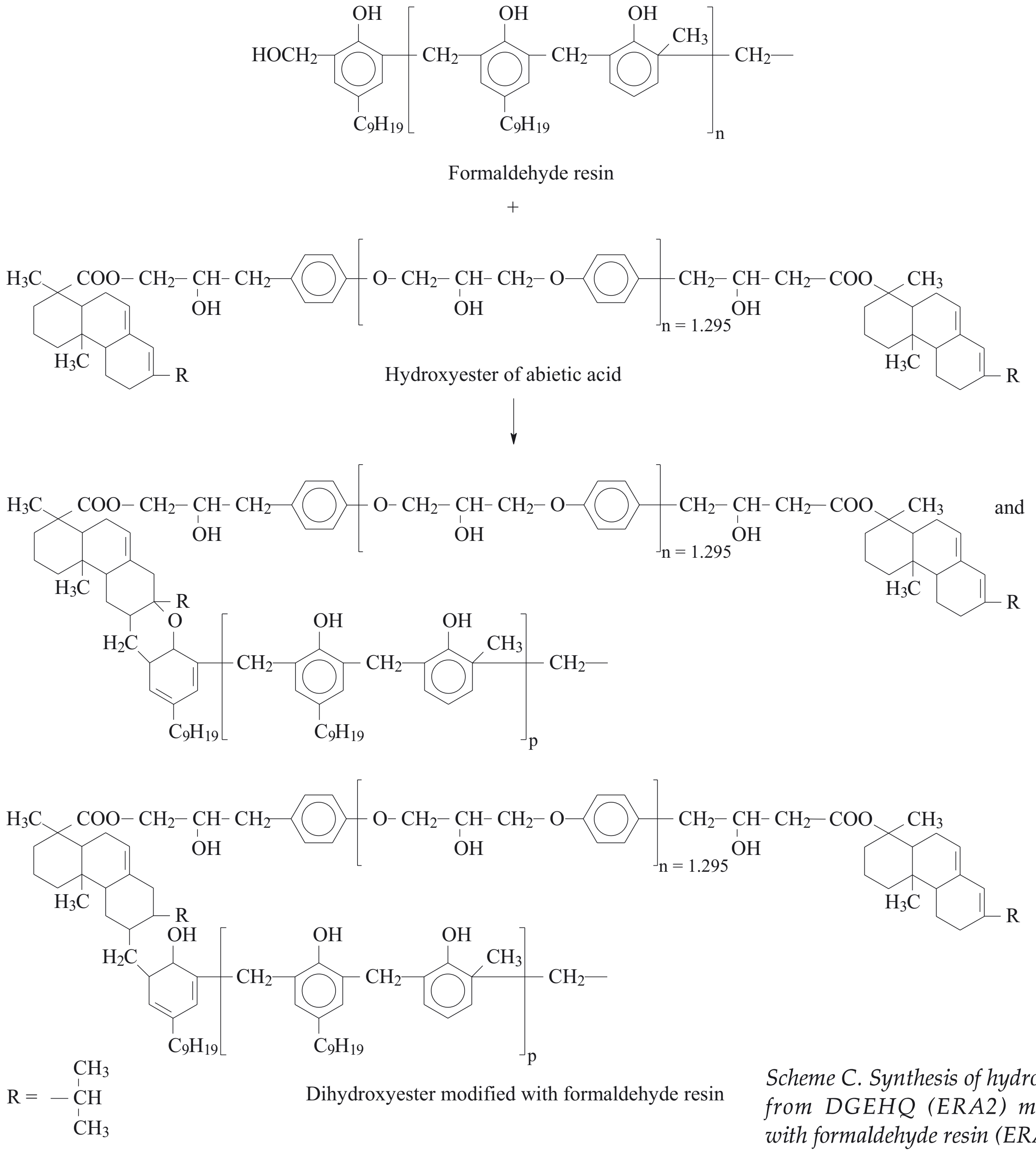
— The chemical structures of FR and ERA were identified using FT-IR (Bruker Vortex 70, Germany, KBr pellets) and ^{1}H NMR and ^{13}C NMR [Avance DRX 400, Bruker, Rheinstatten, Germany, 50 ^{o}C, d$_6$-DMSO as a solvent, tetramethylsilane (TMS) as internal standard] spectroscopic methods.



Scheme B. Synthesis of formaldehyde resin (FR)

Thermal stability of cured products was evaluated by thermogravimetric measurements. TG curves were recorded on a MOM-Budapest of Paulik, Paulik-Erdey type derivatograph at heating rate of 10 °C · min^{-1} in air between 25—700 °C. The TG parameters, namely T_{10} (temperature for 10 % weight loss), T_{50} (temperature for 50 % weight loss) and WL_{500} (weight loss at 500 °C) as well as the activation energy of decomposition reaction (E_a) were used in order to determine the thermal stability of the crosslinked polymers. The kinetic parameters were calculated using Coats & Redfern and Swaminatham & Modhavan methods [38, 39]. The general equation used are:

$$\log\,[1-(1-c)^{1-n}]/(1-n)\cdot T^2 = \\ = \log\,(AR/\beta E_a) - 2.303(E_a/RT) \qquad (1)$$



Scheme C. Synthesis of hydroxyester from DGEHQ (ERA2) modified with formaldehyde resin (ERA2FR) and

$$d\alpha/dT = A\exp(-E_a/RT)[\alpha^m(1-\alpha)^n][-\ln(1-\alpha)^p] \quad (2)$$

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, β — the heating rate, 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, R — the gas constant.*

RESULTS AND DISCUSSION

Chemical structures

Hydroxyesters (ERA)

The obtained hydroxyesters (Table 1) are low tacky, solid, brittle products, with the color varying from pale yellowish to pale red brownish as a consequence of their chemical structures well, soluble by heat in different organic solvents, except petroleum ether (b.p. 20—60 °C). The probable chemical reactions and possible structures of the synthesized products were confirmed by FT-IR, ^{1}H NMR and ^{13}C NMR spectroscopy as well as by elemental analysis (the results are not presented in this paper). The fact that the obtained values of nitrogen content and OH contents are in good agreement with the calculated values confirm the proposed structures of the synthesized hydroxyesters (see Scheme A). IR spectra (Fig. 1a) show an intense unresolved band in the range of 3450—3500 cm^{-1}, which is typical for tertiary OH groups, resulting from the reaction between the epoxy ring and COOH groups. In the range of 2880—2980 cm^{-1}, the specific bands of symmetric and asymmetric vibrations of CH, CH_2, CH_3 groups bonded to the hydrophenanthrene moieties and the specific peaks assigned to CH_2 groups located in the glycerol moieties (resulting from the reaction between the epoxy ring and COOH groups) appear. The peaks typical for ester groups are placed at 1725 and 1705 cm^{-1} (C=O group) and in the range of 1230—1180 cm^{-1} (C-O-C). The presence of the peaks situated in the range of 1504 cm^{-1}, 821, 748 and 693 cm^{-1} is typical for aromatic ring introduced by the epoxy resins. An absence of the peak at 910—915 cm^{-1} (typical for epoxy ring) confirms the extinction of terminal epoxy groups, as a consequence of molar ratio 1/2 of the epoxy and carboxyl groups.

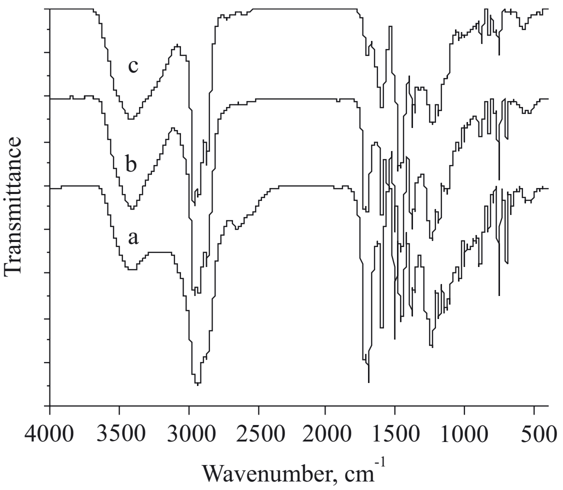


Fig. 1. FT-IR spectra of: (a) DGAN/RA hydroxyester (ERA3); (b) DGAN hydroxyester modified with formaldehyde resin (ERA3FR2); (c) formaldehyde resin (FR2)

T a b l e 1. Reaction conditions and some physicochemical characteristics of hydroxyesters

Sample	Monomer molar ratio (epoxy resin/RA)	Reaction time, h	Number average molecular weight	Softening point, °C	Nitrogen content, %	Yield, %	Color
ERA1	DGEBA/RA (1/2)	6	1380	65	—	93	pale brown
ERA2	DGEHQ/RA (1/2)	6	1150	67	—	96	pale brown
ERA3	DGAN/RA (1/2)	4	1080	50	1.29	94	pale red brown

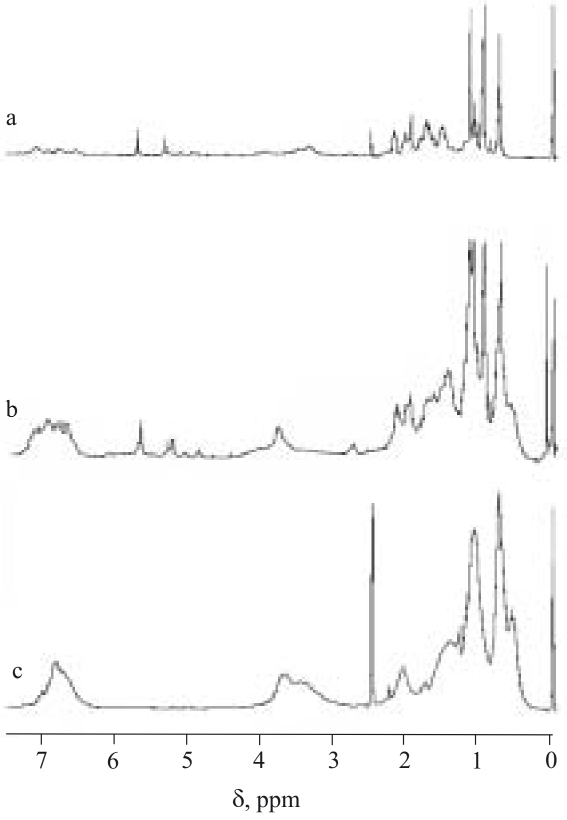


Fig. 2. ^{1}*H NMR spectra of (a) DGAN/RA hydroxyester (ERA3); (b) DGAN hydroxyester modified with formaldehyde resin (ERA3FR2); (c) formaldehyde resin (FR2)*

The ^{1}H NMR and ^{13}C NMR spectra also confirm the structures of the hydroxyesters obtained. Thus, in Fig. 2a (^{1}H NMR), the major signals located in the range of 0.9—2.15 ppm chemical shift represent the vibrations of CH, CH_2 and CH_3 groups presented in the hydrophenanthrene and DGAN moieties. The CH, CH_2 protons of the glycerol groups and the methylene bridges are situated in the range of 2.7—2.78 and 3.3—3.7 ppm, while the newly formed OH protons appear in the range of 3.9—4.12 ppm. The olefinic double bonds situated in the hydrophenanthrene ring resonate as weak peaks in the range of 5.5—5.76 ppm chemical shift and the aromatic protons introduced by the epoxy resin are presented as multiple peaks in the range of 6.8—7.6 ppm.

In Fig 3a, b (^{13}C NMR), the major signal situated in the range of 14—52 ppm chemical shift represents the vibrations of carbon atoms from CH, CH_2, CH_3 groups presented in the hydrophenanthrene and glycerol moieties. The tertiary carbon atom linked to OH group is presented at 67—69 ppm chemical shift and the double bonds of olefinic type are presented in the range of 120—144 ppm. The peaks situated in the range of 156—157 ppm chemical shift can be attributed to the ether linkage located in the glycidyl and glycidol moieties. The presence of low peaks situated in the range of 176—177 ppm chemical shift is typical for unreacted residual carboxylic groups of RA.

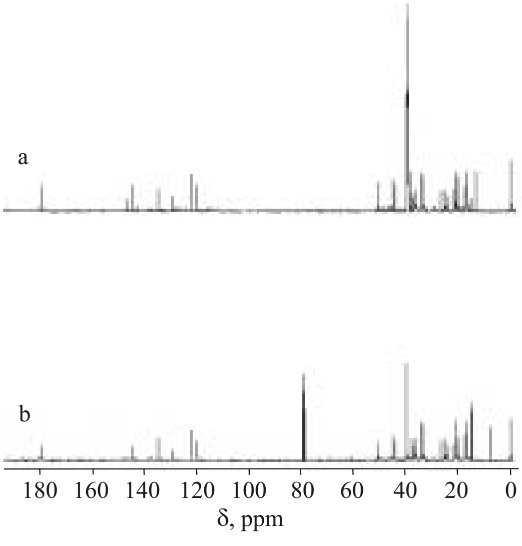


Fig. 3. ^{13}C NMR spectra of (a) DGAN/RA hydroxyester (ERA3); (b) hydroxyester modified with formaldehyde resin (ERA3FR2)

Formaldehyde resins (FR)

The condensation conditions and the main characteristics of the obtained formaldehyde resins are presented in Table 2. The reactant monomers/formaldehyde ratio (1/1.07) was kept constant for all experiments. In the first step, in base catalysis, the monomers react with formaldehyde and form methylol groups. In the second step, under the action of temperature and in the presence of cyclohexane, the water was split off and the methylol groups were transformed into dimethylene ether and methylene linkage between the aromatic and aliphatic rings. Finally, majority of dimethylene ether turns out into methylene bridges typical for formaldehyde resins. The chemical reaction involved in this synthesis is presented in Scheme B. The possible structures of the obtained resins are confirmed by FT-IR and NMR spectroscopy. In Figure 1c a broad unresolved absorption peak at 3424 cm^{-1} corresponding to the vibration of -OH groups from *p*-NP can be seen. The symmetric and asymmetric vibrations of CH_2 and CH_3 groups from the nonyl fragments, and as methylene bridges between the aromatic rings, are presented in the range of 2870—2960 cm^{-1}. The peaks typical for the aromatic rings from *p*-NP are presented in the range of 1600 cm^{-1}. Also, in the ^{1}H NMR spectra (Fig. 2c) the main peaks of CH, CH_2, CH_3 protons derived from *o*-Cz and *p*-NP are presented in the range of 0.568—2.26 ppm. The peaks located in the range of 2.23—2.27 ppm can be attributed to CH_3 groups from *p*-NP and *o*-Cz. The protons located in the methylene bridges between the aromatic rings are presented in the range of 3.34—3.75 ppm chemical shifts. The signals of aromatic protons appear at 6.5—7.1 ppm. The signals observed at 4.54—4.75 ppm could be attributed to OH groups located in *p*-NP and *o*-Cz. ^{13}C NMR spectra (not presented here) also confirmed the FR structures.

Table 2. Reaction conditions and some physicochemical characteristics of prepared formaldehyde resins (FR)

Sample	Monomer molar ratio (*p*-NP/*o*-Cz/*p*-FA)	Number average molecular weight	Softening point, °C	Yield, %	Color
FR1	0.5/0.25/0.8	1400	78	96	pale brown
FR2	0.25/0.25/0.535	1100	90	95	pale brown
FR3	0.25/0.5/0.8	1200	102	91	hue brown

Modified hydroxyesters (ERAFR)

The modified ERA are solid materials, brittle, with pale brown color. They are soluble in majority of aromatic solvents and insoluble in petroleum ether and partially soluble in cyclohexane and dioxane. The structures of ERAFR (see Scheme C) are confirmed by FT-IR and

Table 3. Some physicochemical characteristics of hydroxyesters modified with formaldehyde resins FR2 (ERA:FR2 = 1:1)

Sample	Hydroxyester	Inherent viscosity*)	Softening point, °C	N, %	Yield, %	Colour
ERA1FR2	DGEBA	0.23	83	—	96	pale brown
ERA2FR2	DGEHQ	0.22	125	—	94	pale brown
ERA3FR2	DGAN	0.20	103	0.66	95	pale red brown

*) DMSO as a solvent, c = 0.5 w/w, 25 °C.

NMR spectroscopy and also elemental analyses results not given in this paper. In the IR spectra (Fig. 1b) the peak typical for ester groups (CO) in hydroxyesters is presented in the range of 1723 cm^{-1}. In the ^{1}H NMR spectra (Fig. 2b) CH_2 groups located in the vicinity of COO groups are presented in the range of 3.55 to 3.84 ppm. In the ^{13}C NMR spectra (Fig. 3b) the COO groups are presented in the range of 179 ppm chemical shift. Also, for the modified hydroxyesters obtained from DGAN hydroxyesters and formaldehyde resins (sample ERA3FR2) N % content confirms these transformations (Table 3).

ERAFR characteristic

The thermogravimetric analyses curves of modified hydroxyesters are shown in Fig. 4. The relative thermal stability was assessed by recording the metioned in Experimental part decomposition parameters (namely T_{10}, T_{50}, WL_{500} values) and also the pre-exponential factor

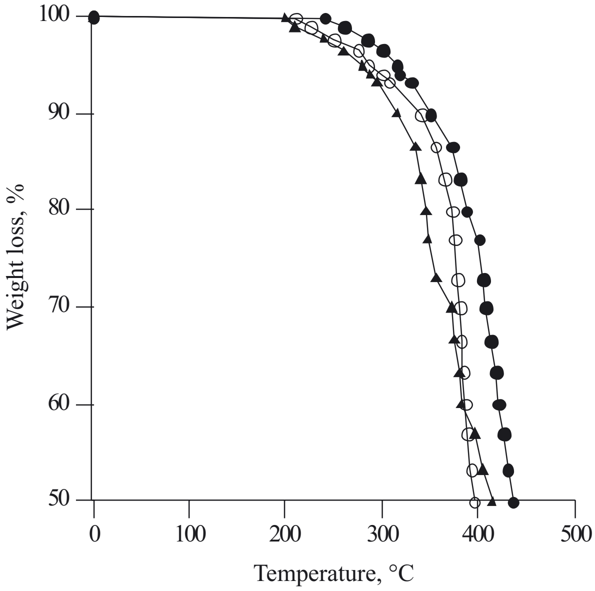


Fig. 4. Weight loss of the systems: ERA1FR2 (●), ERA2FR2 (o) and ERA3FR2 (▲)

Table 4. Thermal parameters of ERAFR

Sample	$T_{10\%}$, °C	$T_{50\%}$, °C	Weight residue at 500 °C %	Decomposition activation energy, kJ · mol^{-1}		Order of reaction	Frequency factor lnA, min^{-1}
				according to Coats & Redfern method	according to Swaminathan & Modhavan method	according to Swaminathan & Modhavan method	
ERA1FR2	350	435	40	77.75	87.67	1.21	15.26
ERA2FR2	315	395	37	66.86	80.65	0.93	13.27
ERA3FR2	305	415	20	61.22	68.68	0.97	10.62

Table 5. Solubility of ERA and ERAFR (room temperature, g/100 cm^3)

Solvent	DGEBA hydroxyester (ERA1)	DGEHQ hydroxy-ester (ERA2)	DGAN hydroxy-ester (ERA3)	ERA1FR2	ERA2FR2	ERA3FR2
Cyclohexane	soluble by heat	soluble by heat	soluble by heat	soluble by heat	soluble by heat	soluble by heat
Petroleum ether	insoluble	insoluble	insoluble	insoluble	insoluble	insoluble
Acetone	>60	>70	>60	>45	>55	>40
Methyl alcohol	>50	>60	>45	>40	>50	>40
Ethyl alcohol	>55	>65	>50	>45	>55	>45
Dioxane	soluble by heat	soluble by heat	soluble by heat	soluble by heat	soluble by heat	soluble by heat
CCl_4	>40	>45	>40	soluble by heat	soluble by heat	soluble by heat
Chloroform	>65	>70	>60	>55	>60	>50
Benzene	>60	>65	>60	>50	>55	>45
Toluene	>65	>75	>60	>55	>60	>50
Diethyl ether	>60	>70	>55	>50	>55	>45
DMSO	>55	>60	>55	>45	>50	>40
DMF	>60	>70	>60	>50	>60	>50
DMAc	>65	>75	>60	>60	>65	>50

and the activation energy of degradation process. The results of TG studies are collected in Table 4. It can be observed that the thermal stability depends on the nature of epoxy resin and formaldehyde resin. The T_{10} temperature in an air is located in the range of 305 °C and 350 °C and the T_{50} temperature between 395 °C and 435 °C. Accepting the above parameters as criteria of thermal stability, we can conclude that the products obtained from DGEBA hydroxyester (ERA1FR2) are more stable in comparison with DGEHQ or DGAN hydroxyesters. This observation may be explained on the basis of chemical structures of epoxy resins, which give a high rigidity to the cured resins.

The solubility behaviors of the ERAFR are presented in Table 5. As can be seen, the obtained products are soluble at room temperature in most of polar solvents and insoluble in petroleum ether, dioxane, carbon tetrachloride and cyclohexane.

Hydroxyester of DGEHQ modified with the formaldehyde resin (ERA2FR2) exhibits properties that make it useful in formulations of vehicles for gravure and printing inks with pale and warm colors. The presence of hydrophenanthrene and nonyl moieties in chemical structures of hydroxyesters gives them hydrofobicity and good adhesion to the substrate (paper or polymeric films).

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