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Physical and chemical characterization of new pressure sensitive adhesives containing abietic acid formaldehyde resins

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Formaldehyde resins containing resin acid derivatives in their structure were synthesized. The insertion of resin acid derivatives into molecular chains was carried out to improve the cohesive strength of pressure sensitive adhesives. IR, ^{1}H-NMR spectroscopy and other physical-chemical methods were used to characterize the monomers, polymers and obtained pressure sensitive tapes. The hydrophenanthrene moieties presented in the chemical structure of these polymers confer them, high solubility in common organic solvents, high adhesiveness, hydrophobicity and water resistance. The presence of formaldehyde resins with hydrophenanthrene moieties (up to 10 wt-% referred to the adhesive composition) into pressure sensitive formulation used as insulting materials for electrical and electronic devices, coffers them an increase of cohesive strength without affecting the adhesive strength.

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1. Introduction

Formaldehyde resins, which contain in their structure para substituted alkyl phenols, obtained in acid or basic catalysis, generically named "oil soluble" resins, are used as curing agents and as tackifiers in pressure sensitive adhesive formulations. The presence of these resins confers to pressure sensitive formulations, good chemical resistance, superior thermal stability but low adhesive behaviour [1-10]. In the last years, as a consequence of oil crisis, a lot of natural raw materials (cellulose, oils, rosin and natural waxes, natural rubber, sugars) were used as intermediary in chemical synthesis. Rosin, a natural product obtained from exudates oleoresin of pine trees, contain in principal abietic and levopimaric acids. These acids are used as raw materials for synthesis of alkyd resins, epoxy resins, printing inks, polymers, varnishes and as paper sizing agents [11-33]. The presence of the hydrophenthrene moieties into or on the polymeric chains confers to them high adhesiveness, hydrophobicity and water resistance. In this communication we report the synthesis and characterization of the formaldehyde resins with hydrophenathrene moieties in chemical structure. Our interest in these resins result from their applications as tackifiers in pressure sensitive compositions. The influence of these resins on the adhesive properties was investigated.

2. Experimental

2.1. Materials

p-Nonyl phenol (p-NP) (d^{15}= 0.955 g·cm^{-3}) and p-formaldehyde (p-FA)(98%) are commercial products and are used as received. 2-Ethylhexyl acrylate (2-EHA), acrylic acid (AAc), vinyl acetate (AcV),and benzoyl peroxide were analytical grade products. Resin acids (RA) were obtained from a commercial rosin by recrystallization from acetone and have acid number = 178 mg KOH☺g^{-1}. Epoxy resins: diglycidylaniline (DGAN) (epoxy equivalent weight = 174g☺eq^{-1}) and diglycidyl ether of hydroquinone (DGEHQ) (epoxy equivalent weight = 256g☺eq^{-1}) were synthesized as in literature [35,34]. Diglycidyl ether of bisphenol A (DGEBA) (SC Sintofarm SA, Romania) (epoxy equivalent weight = 380g☺eq^{-1}) was a commercial product and was used as received. Acrylic adhesives at weight ratio (2-EHA/AAc/AcV, 75/20/5) was obtained as in literature [29] Triethylbenzylammonium chloride (TEBAC) was used as catalyst for reaction between epoxy ring and resin acids. The organic solvents were analytical grade products, or were distilled before use.

2.2. Measurements

The average epoxy equivalent weights were obtained using literature method and were expressed as g☺eq^{-1} [36]. Nitrogen content was determined in accordance with Kjeldahl method [37]. The acid number (a.n.) was obtained by titration with 0.1N alcoholic KOH, in the presence of phenolphthalein as indicator, to the pink endpoint. FTIR spectra were taken on a Bio-Rad Digi Lab Division (Portmann Instruments) using KBr disks. Thermogravimetric analyses (TGA) were carried out on a MOM-Budapest of Paulik, Paulik-Erdey type derivatograph at heating rate of 10^{o}C☺min^{-1}, in air, in the temperature range from 25 to 600 ^{o}C. The kinetics parameter was calculated using literature equations [38,39]. Viscosity measurements were performed with 0.5g/dL solution in DMF as solvent at 25^{o}C using an Ubbelhode.

Williams plasticity as measure of cohesive strength, was determined as fallows: a film of the adhesive solution is cast on the siliconated paper and was dried at room temperature for 25 minutes and for another 25 minutes at 100 ^{o}C in a circulation air oven. The adhesive layer is removed from the silicone paper and exact 2g were weight and formed as sphere ball. The ball is placed between two films of polyethylene terephthalate (25 μm) and inserted into the plastometer under a 5000 g load at 50 ^{o}C for 15 minutes. The Williams plasticity is expressed by the thickness in millimetres of the pellet. The adhesive strength was recorded using 180 ^{o} angle peel test. In conducting this test, films of the adhesives being evaluated are applied to a PVC film baking in a 25 μm dry thickness. The test samples, which have 20 mm in width and 300 mm in length, are securely adhered by thumb pressure to a polished stainless steel plate (treated with chromic acid, washed with acetone and distilled water and dried). After 20 min wetting out period, the top of the plate was clamp vertically in the upper jaw of the testing machine, tape was extended downward and secured in the lower jaw. The driven jaw shall move at a rate of 100 mm/min. The adhesion values were measured in g/cm width. The test of the cumulative adhesion and cohesion strength (0^{o} angle hold test) was conducted as fallows: at the bottom of a steel plate treated as above, a test sheet (width= 25 mm) was applied with an area of 625 mm^{2}, pressed twice with a 2000 g rubber-covered roller and maintaining at 25^{o}C for 20 min. Then the plate was fixed vertically and 1000 g weight was attached on the lower end of the test sheet. The time until the test sheets fall down from the substrate was measured as the value of the adhesive stability.

2.3. Obtaining of the pressure sensitive adhesive tapes

The adhesive tapes are made as follows: PVC films, 140 μm, are coated in the usual manner with a 50% adhesive solution and the coating was dried at 80 ^{o}C for 20 minutes in a circulation air oven. The resulting adhesive films are cut into adhesive tapes of 20 and 25 mm width and the obtained tapes are tested.

2.4. Synthesis of formaldehyde resins

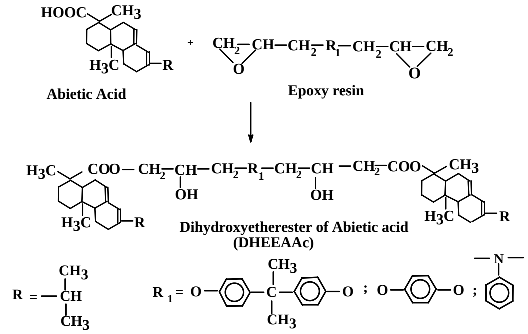
The raw materials used in these syntheses were epoxy resin, RA, p-NP and p-FA. The chemical reactions were conducted in two steps:

-synthesis of hydroxyetheresters of RA;

-synthesis of formaldehyde resins.

2.4.1. Synthesis of hydroxyetheresters of resin acids

Hydroxyetheresters of RA were obtained as in literature [40]. Into a 1L, 3-necked round-bottomed reaction vessel, equipped with mechanical stirrer, water reflux condenser, oil bath and temperature controller, was charged 1 mol of epoxy resin and 2mol of resin acids. The reaction mixture was heated at 100^{o}C and 0.05 mol (15.5g) of TEBAC was added and maintained at this level of temperature under stirring until the acid number is 30 or less. Then the reaction mass was cooled at room temperature, divided as fine grain and extracted twice with petroleum ether. It was resulted a pale brown resin. (Scheme 1)

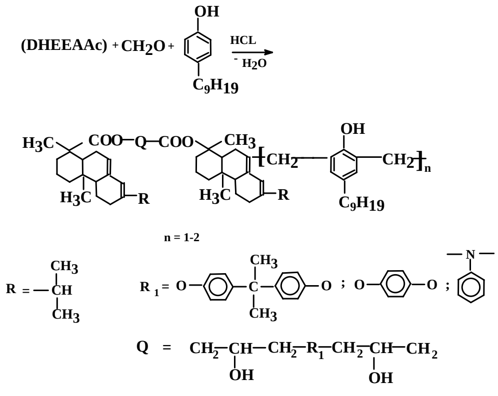


Scheme 1. Synthesis of dihydroxyesters of resin acids.

2.4.2. Synthesis of formaldehyde resins

Synthesis of formaldehyde resins was conducted in acid catalysis (HCl 35 %) at molar ratio 1/0.95 (monomers/formaldehyde). Reaction conditions are presented in Table 1.

In a representative experiment, into a 1L reaction vessel equipped as above, was added 1 mol of hydroxyetheresters of RA, 1mol of p-NP, 1.9 mol of p-FA and 150 ml of toluene, heated at 80 ^{o}C and 45ml of catalyst (HCl) were added in three portions. A weak exotherm effect (5 ^{o}C) was observed, and mixture becomes transparent. After the temperature stabilization, the reaction mass was heated at reflux and maintained under stirring, 1.5 h (step of creation of CH_2OH groups). After this, a Dean-Stark trap was attached to the water condenser and the water was extracted azeotropically with toluene under a slowly vacuum. To further hasten the dehydration step, the temperature increased at 140-150 ^{o}C, and methylene bridges appeared (total reaction time-3h). Finally, the formaldehyde resins are cooled, ground as fine powder, extracted with petroleum ether (b.p. 30-60 ^{o}C) and dried under vacuum at 80 ^{o}C, 16 hours. It resulted a pale brown colour resins (Scheme 2).



Scheme 2. Synthesis of formaldehyde resins.

3. Results and discussion

The formaldehyde resins were obtained in two steps. In the first step, RA in presence of TEBAC as catalyst reacts with epoxy rings and hydroxyetheresters appear. In the second step, formaldehyde reacts with p-NP and hydroxyetherester and CH$_2$OH groups appear. By raising the temperature, the reaction water split off and the methylol groups are transformed in methylene bridges between hydrophenanthrene rings and aromatic ring of p-NP, resulting the formaldehyde resins. (Scheme 2). The resulting resins are solid, brittle, with colour varying from pale brown (for resin with DGEHQ) to reddish brown colour (for resin with DGAN), as a consequence of their chemical structure.

The probable structure of the synthesized resins was confirmed by FT-IR and ^{1}H-NMR spectroscopy. IR spectra (Fig. 1) show an intense unresolved band in the range of 3450-3500 cm^{-1} that is specific to tertiary OH groups resulted from the reaction between epoxy ring and COOH groups. The peaks specific to symmetric and asymmetric vibration of CH, CH$_2$, CH$_3$, groups presented in the hydrophenanthrene, nonylphenol and in the glycerol moieties (resulted from the reaction between epoxy ring and COOH groups) appear in the range of 2280-2960 cm^{-1}. The peaks specific to ester groups are placed at 1725 cm^{-1} (CO group) and in the range of 1280-1160 cm^{-1} (C-O-C). The multiple peaks located in the range of 680- 840 cm^{-1}, indicated the presence of aromatic ring of p-substituted benzene introduced by the epoxy resins and p-NP. The ^{1}H-NMR spectra (Fig. 2) also confirm the structure of obtained polymers, the major signals located in the range of 0.9-2.15 ppm chemical shift represent the vibration of CH, CH$_2$, CH$_3$, groups presented in the hydrophenanthrene, p-NP and DGEBA moieties. The CH, CH$_2$, protons of the glycerol groups and methylene bridges are situated in the range of 2.8-3.8 ppm chemical shift and the newly formed OH protons appear in the range of 3.9-4.6 ppm chemical shift. The aromatic protons introduced by the epoxy resin are present as a multiple peaks in the range of 6.8-7.6 ppm chemical shift.

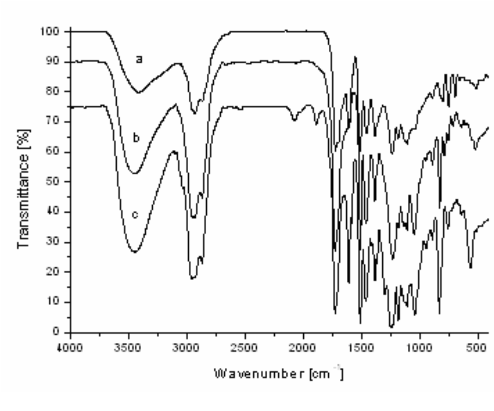


Fig. 1. IR spectra of formaldehyde resins: (a) with DGEHQ, (b) with DGEBA and (c) with DGAN.

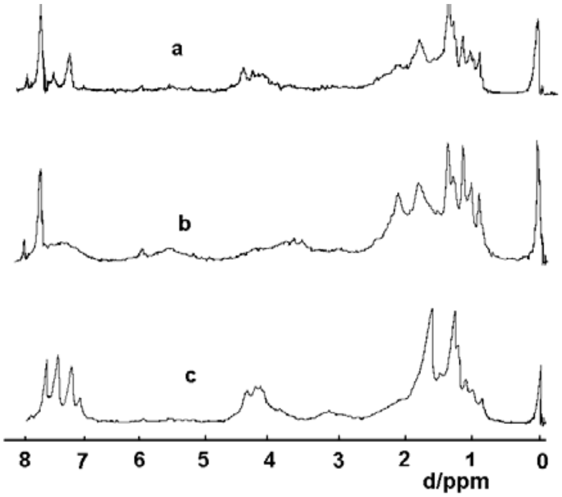


Fig. 2. H-NMR spectra of formaldehyde resins: with DGEBA, (b) with DGEHQ and with DGAN.

The obtained resins are tacky materials and were submitted to the detailed studies regarding their behaviour in pressure sensitive formulation used in fabrication of pressure-sensitive tapes. Table 2 shows various formulae for adhesive composition and some characteristics of obtained pressure sensitive tapes. These tapes are compared with similar tape obtained from other pressure sensitive composition without formaldehyde resins in structure. As can be see in Table 2, the pressure sensitive tapes obtained with pressure sensitive formulation which contain formaldehyde resins, have high values for times obtained using the 0^o angle hold test (measure of cohesive strength) in comparison with the values for the tapes obtained from adhesive composition without formaldehyde resins in their formula. This can be due to the fact that the formaldehyde resins which have residual CH$_2$OH groups can react with natural rubber or with acrylic polymer and a partially crosslinked structure can be obtained. On the other hand these conclusions can be confirmed by the Williams plasticity. The values of Williams plasticity increase from 1.65 for acrylic adhesive to 2.53 for the adhesive with formaldehyde resin in composition. All the adhesive tapes show acceptable adhesion, but only the tapes that contain up to 10wt-% formaldehyde resin present a equable balance between cohesive and adhesive strength. When the quantity of formaldehyde resin exceeds 10 wt-%, the cohesive strength increases very much but the adhesive strength decreases up to approximately 40 % from the value of acrylic adhesive.

Table 1. Reaction conditions and some physical-chemical characteristics of the obtained resins.

Sample	Monomer ratio (mol/mol)	Catalyst	Yield (%)	Number[a)] average molecular weight	Inherent[b)] viscosity dL/g	Nitrogen content (%)	Colour
1	(DGEBA/RA/p-NF/p-FA) (1/2/1/2)	HCl	95	2240	0.18	-	pale brown
2	(DGEHQ/RA/p-NF/p-FA) (1/2/1/2)	HCl	96	2020	0.15	-	pale brown
3	(DGAN/RA/p-NF/p-FA) (1/2/1/2)	HCl	93	2050	0.16	1,44	pale red brown

a) cryoscopic, DMSO as solvent
b) DMSO, 25 °C, 0.5% g/g

Table 2. The composition of adhesives used for the production of adhesives tapes and some of their characteristics.

Sample	Adhesive formula (Formaldehyde resin/Acrylic adhesive) (g/g)	Williams plasticity (mm)	Tape substrate	Adhesive tape characteristics	
				0° Hold test (h)	180° peel test (g · cm^{-1})
A	0/100	1.65	PVC film	0.25	740
B	5(Sample 1)/95	1.82	PVC film	0.34	650
C	10(Sample 1)/90	2.02	PVC film	0.45	610
D	20(Sample 1)/80	2.35	PVC film	1.09	500
E	5(Sample 2)/95	1.93	PVC film	0.39	590
F	10(Sample 2)/90	2.20	PVC film	0.53	610
G	20(Sample 2)/80	2.48	PVC film	1.11	450
H	5(Sample 3)/95	1.91	PVC film	0.41	600
I	10(Sample 3)/90	2.25	PVC film	0.50	510
J	20(Sample 3)/80	2.53	PVC film	1.04	400

The thermal properties of obtained formaldehyde resins were evaluated by thermogravimetric analysis (TGA). As can be seen in the Fig. 3, the formaldehyde resins have a weight loss of 10% between 200 and 300 °C. The ordering by thermal stability is; resins with bisphenol A.> resins with aniline> resin with hydroquinone in its structure. The activation energy of degradation process for formaldehyde resins calculated for the main peak of degradation process have values situated between 120 to 150 kJ/mol.

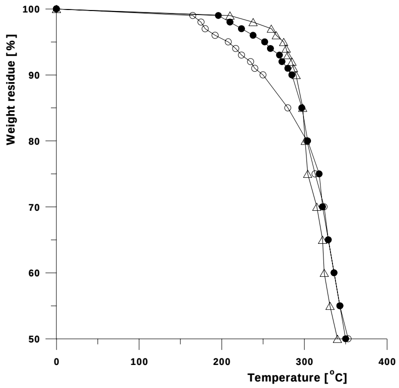


Fig. 3. TGA curves of formaldehyde resin obtained with(△) DGEHQ; (O) DGEBA; (●) DGAN.

The variation of the activation energy with conversion degree (Fig. 4) shows dramatically changes in the decomposition process only in the initial stage of degradation up to 0.1 for all polymers, and remains approximately constant for the conversion degree between 0.1-0.8. This fact denotes that the nonyl group situated in 2-EHA structures is most easily degradable in the fist stage of degradation process and affects negatively the thermal stability of the obtained resins.

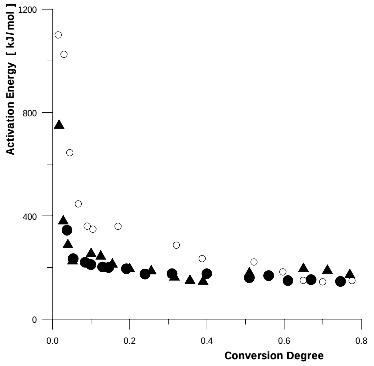


Fig. 4. Activation energy of degradation reaction versus conversion degree for formaldehyde resin obtained from: (▲) DGEHQ; (O) DGEBA; (●) DGAN.

4. Conclusion

The formaldehyde resins, which contain hydrophenanthrene moieties in their structure, were obtained and characterized. These resins are solid materials, brittle, with brown colour, and soluble in a large variety of organic solvents. Used as tackfier agents in pressure sensitive adhesive formulation, they induced an important increase of the cohesive strength.

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