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p-Nonylphenol/*o*-cresol/cyclohexanone/formaldehyde resins as modifiers in pressure sensitive compositions

Summary — The preparation, in basic catalyzed polycondensation, of heat reactive *p*-NPh/*o*-CR/CHX/*p*-FA resins at various molar ratios of monomers has been described. The resins thus obtained were characterized by ^1H NMR and infrared spectroscopy and were used as crosslinking components in pressure sensitive formulae. The presence of these polymers in PSA's composition of rubber or acrylic type, imparted after curing a high cohesive strength, without affecting significantly the adhesive strength. Such compositions are useful for the laminates working at high temperature.

Key words: *p*-nonylphenol/*o*-cresol/cyclohexanone/formaldehyde resins, synthesis, binding agents, pressure sensitive adhesives, adhesive properties, thermal properties.

Formaldehyde resins (obtained in basic or acid catalysis) compose an important class of polymers used in many industrial fields such as: adhesives, metal coating compositions, structural composites, insulating materials for electric and electronic devices, because of their excellent thermal and chemical stability, superior electrical and mechanical properties, in addition to low cost [1—4].

The resins of *para* substituted alkyl phenols (*para*-*n*-propylphenol, *para*-*n*-butylphenol, *para*-*n*-octylphenol, *para*-*n*-nonylphenol, *para*-*tert*butylphenol, *para*-*tert*amylphenol, *para*-phenylphenol, *etc.*) obtained in a basic catalysis, are heat-reactive, "oil-soluble" and are used as curing agents in adhesive compositions [5—14]. These resins containing active hydroxymethyl groups were developed to cure unsaturated elastomers (natural rubber, chloroprene rubber, butyl rubber, nitrile rubber, *etc.*) or acrylic polymers used in pressure sensitive adhesive (PSA) compositions. The presence of these resins in these compositions gives them chemical resistance, good strength of the bond, superior thermal stability and high cohesive strength, before or after curing.

In the present paper we present the results of the synthesis and characterization of *p*-nonylphenol/*o*-cresol/cyclohexanone/formaldehyde resins. Our interest in these resins results from their applications as crosslinking agents for adhesive compositions. The influence of these resins on the adhesive and cohesive strength was also investigated.

EXPERIMENTAL

Materials

p-Nonylphenol, (*p*-NPh) ($d^{15} = 0.955 \text{ g} \cdot \text{cm}^{-3}$; $n_D^{20} = 1.511$) and *p*-formaldehyde (*p*-FA) (98% purity) were obtained from commercial sources and were used as received.

Cyclohexanone (CHX), *o*-cresol (*o*-CR), 2-ethylhexyl acrylate (2-EHA), acrylic acid (AAc), vinyl acetate (VAC), sodium hydroxide and organic solvents were analytical grade products, or were purified by distillation, before use. Natural rubber (RSS-1 Thailand) was milled before use at Mooney value (ML-4 at 100 °C) 24. Petroleum resin (Pentacol —CP Brazi, Romania, m.p. 75 °C), was a commercial product and was used as received. Pressure sensitive adhesive of acrylic type (2-EHA/VAC/AAc-72/23/5) was obtained the way as in literature [10].

Synthesis

Synthesis of formaldehyde resins

The condensation reactions were conducted at different molar ratio of *p*-NPh/*o*-CR/CHX and at monomers/formaldehyde molar ratio of 1/1.1, in the presence of 4% sodium hydroxide as a catalyst (based on the weight of reactants, Table 1).

In conclusion it is worth to note that the specific behaviors observed for monomeric electron acceptor-electron donor bridged molecules and for the polymeric initiator-coinitiator systems are more likely not controlled by the back electron transfer process. The observed phenomena come probably from a possibility of different proton transfer between Rose bengal radical anion and tertiary aromatic amine radical cation. This property can be deduced on the basis of Marcus theory, describing the kinetics of photoinduced intermolecular and intramolecular electron transfer processes, and the laser flash photolysis measurements.

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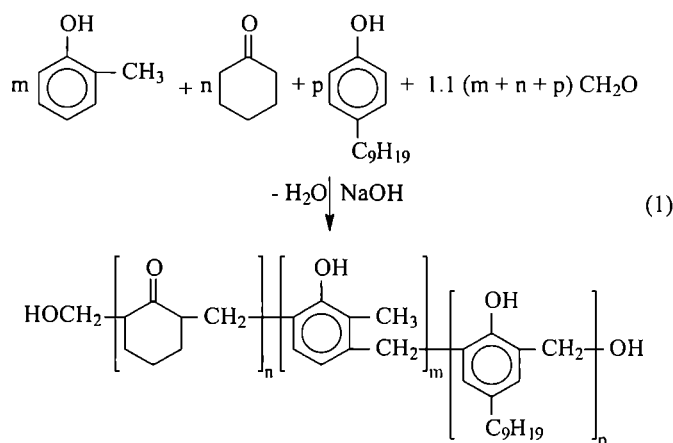
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Table 1. Synthesis and some physico-chemical characteristics of *p*-nonylphenol/*o*-cresol/cyclohexanone/formaldehyde resins (*p*-NPh/*o*-CR/CHX/FA)

Sample	Molar ratio <i>p</i> -NPh/ <i>o</i> -CR/ CHX/FA	Number average molecular weight	Melting point °C	Yield %	Color
1	0.5/0.25/0.25/1.1	1400	78	93	pale brown
2	0.25/0.5/0.25/1.1	1100	120	95	pale brown
3	0.25/0.25/0.5/1.1	980	81	91	pale brown
4	0.33/0.33/0.33/1.1	1250	110	97	pale brown

p-NPh/*o*-CR/CHX random copolymer

A typical synthesis of the formaldehyde resin is presented, as follows [equation (1), sample 1, Table 1]: A 0.5 L, 4-necked round-bottomed reaction flask equipped with a thermometer, heating device, dropping funnel,



mechanical stirrer and water condenser was charged with 110 g (0.5 mol) of *p*-NPh, 27.03 g (0.25 mol) of *o*-CR, 24.53 g (0.25 mol) of CHX and 33 g (1.1 mol) of *p*-FA and mixed at room temperature. Then, the reaction mixture was slowly heated at 60 °C, maintained at this level for 15 minutes and then 50 wt. % aqueous solution of NaOH (catalyst) was added slowly in three portions. A vigorous exothermic effect (about 40 °C) was observed and the reaction mixture became transparent. After the temperature stabilization, the mixture was maintained stirred under reflux 1.5 hour (step of the creation of hydroxymethylene groups -CH₂OH). Then, a Dean Stark trap was attached to the top of the water condenser, and the reaction water was removed under vacuum (step of the condensation of -CH₂OH groups with methylene bridges -CH₂- creation). To further hasten the dehydration step, the temperature may be raised to 145–150 °C. The product was washed twice with warm distilled water to free it from a catalyst. The total resin preparation can be completed in 3 hours. Finally, the reaction mixture was cooled, fine grains divided and extracted

with petroleum ether (boiling range 35–60 °C). It resulted 214 g (yield 93%) of pale brown resin.

Additionally, the separate polycondensation reactions of the other three monomers with *p*-formaldehyde were carried out in the following conditions molar ratio monomer: *p*-FA = 1:1.1, temperature 100 °C, time 1 hour, 50 wt. % aqueous NaOH as a catalyst. The aim was to obtain the samples useful for IR spectra identifications.

Synthesis of the pressure-sensitive adhesives

It was realized by mixing of acrylic copolymer (as 25 wt. % solution in ethyl acetate) or a milled natural rubber (as 15 wt. % solution in aliphatic fraction of petroleum, boiling range 60–105 °C) with the formaldehyde resins (sample 1–4 as 50 wt. % solution in toluene). The concentrations of these mixtures were corrected to 20 wt. % value by dilution with adequate quantities of ethyl acetate or toluene.

Obtaining of the pressure sensitive tapes

The adhesive tapes (see Table 3, sample A–E) were prepared by conventional coating technique. Containing compositions was spread upon on side of an impregnated paper sheet, which previously was coated on the other side with a release silicon coating composition. The acrylic pressure sensitive compositions (see Table 3, sample G–J) were coated on the polyester nonwoven fabrics (50 g · m⁻² basic weight). The both obtained kinds of pressure sensitive tapes were maintained at room temperature for 15 minutes, and dried at 120 °C for another 5 minutes. Then, the pressure sensitive tapes were cut into 25 mm wide strips and they were tested from the view point of adhesive properties.

Measurements

Melting points were measured by means of a microscope with a heated plate (Böetius type). Average number molecular weights were determined by cryoscopic method using dioxane as a solvent [15].

The chemical structures of *p*-NPh/*o*-CR/CHX/FA resins were identified using ¹H NMR (JEOL-JNMC 60 HL, 50 °C, CDCl₃ as a solvent, tetramethylsilane as internal standard) and IR (Specord M80 Carl Zeiss, KBr disk) spectroscopic methods. Thermogravimetric analyses (TGA) of the resins discussed were done with MOM Budapest derivatograph of Paulik, Paulik-Erdey type at a heating rate of 12 °C · min in air. Activation energies of decomposition reactions were determined using Siwaminthan and Modhavan, and Coats and Redfern methods [16, 17]. The general equations used were:

$$\frac{d\alpha}{dT} = A \exp\left(\frac{-E_a}{RT}\right) [\alpha^n (1-\alpha)^n] \cdot [-\ln(1-\alpha)]^p \quad (1)$$

$$\frac{\log[1-(1-\alpha)^{1-n}]}{(1-n) \cdot T^2} = \log\left(\frac{AR}{\beta E_a}\right) - 2.303 \left(\frac{E_a}{RT}\right) \quad (2)$$

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

The adhesive strength was recorded using the standard adhesion test (180° angle peel test) — ASTM D-1000. The test of the cumulative adhesion and cohesion strength was conducted as follows: an area of 25×25 mm (625 mm²) at one of the end of the test sheet was applied to the bottom side of a polished stainless steel plate (treated with chromic acid, washed with distilled water and dried) and was pressed twice with a 2000 g rubber-covered roller. After maintaining at tested temperature for about 25 minutes, the plate was fixed vertically and 1000 g load was attached to the lower end of the test sheet. The time until the test sheet fall down from the substrate was measured as the value of the adhesive stability.

Williams plasticity is determined as follows: a film of the adhesive solution is coated on the silicon paper to produce a dry film of approximately 50 μ m thickness. It is dried at room temperature for 15 minutes and for another 5 minutes at 100 °C in an air circulation furnace. Then, the adhesive layers are removed from the silicone paper, are divided exactly into 2 g weight samples and were formed in the shape of a ball. The ball is placed between two films of poly(ethylene terephthalate) (25 μ m) and it is conditioned at 50 °C for 15 minutes. Finally, the sample was placed in the plastometer under 5000 g load at 50 °C for another 15 minutes. The Williams plasticity is expressed as the thickness of a pellet in millimeters.

RESULTS AND DISCUSSION

The obtained resins are solid, brittle with the color varying from pale brown to red brown as a consequence of their chemical structures, they are soluble in a major-

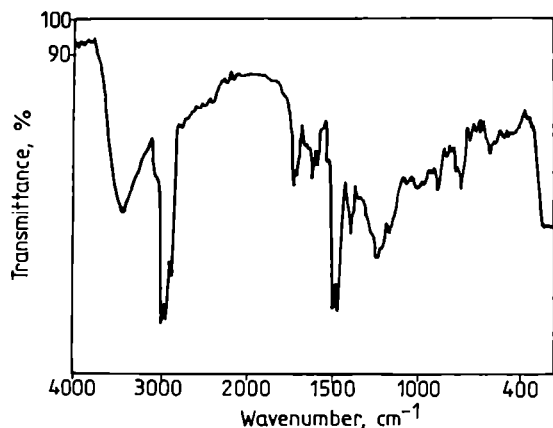


Fig. 1. IR spectra of *p*-NPh/*o*-CR/CHX/FA resin (sample 4 in Table 1)

ity of organic solvents with the exception of petroleum ether (boiling range, 35–60 °C). The IR spectra of the resins (Fig. 1) show a strong absorption peak specific to each monomer. The peaks at 1720 and 1780 cm⁻¹ are attributed to C=O group of cyclohexanone fragment while the band in the range 3400–3550 cm⁻¹ is characteristic for methylol groups. In the range of 3400–3600 cm⁻¹ the signals related to the vibrations of OH groups from *p*-nonylphenol or *o*-cresol appear. In the range 740–860 cm⁻¹ the substituted benzene rings vibrations are observed. The symmetric and asymmetric vibrations specific to CH₂ and CH₃ groups located in the cyclohexanone ring and in the aliphatic structures bonded to benzene ring are identified at the 2880–2980 cm⁻¹, while the peaks attributed to aromatic ring are located in the range of 1610–1640 cm⁻¹.

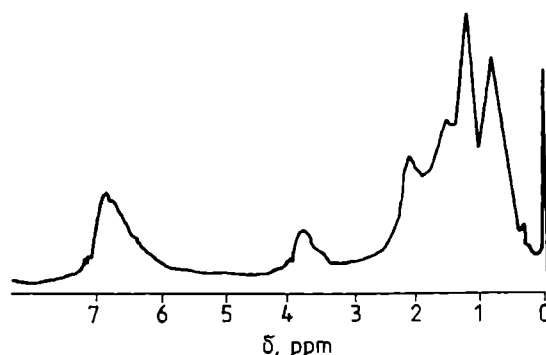


Fig. 2. ¹H NMR spectra of *p*-NPh/*o*-CR/CHX/FA resin (sample 4 in Table 1)

In the ¹H NMR spectra (Fig. 2) the main peaks of CH₂ protons located in the cyclohexanone ring and in the aliphatic nonyl group are presented at the 1.2–2.25 ppm

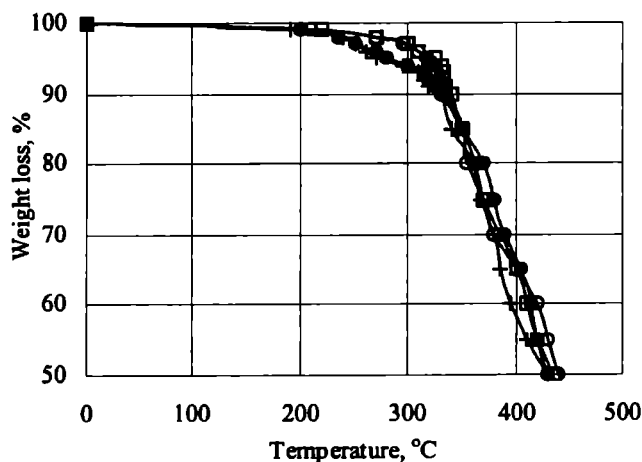


Fig. 3. TGA curves of *p*-NPh/*o*-CR/CHX/FA resin: ● — sample 1, ○ — sample 2, + — sample 3, □ — sample 4 (samples numbers according to Table 1)

chemical shift. The peak centered at 0.81 ppm chemical shift represents the CH₃ protons located in the nonyl aliphatic groups. The methyl protons bonded directly to the aromatic ring (in *o*-cresol) appear as singlets at 1.11 and 1.32 ppm chemical shift. The protons specific to CH₂ groups from cyclohexanone which is not adjacent to C=O groups are located at 1.52 ppm, while the protons adjacent to C=O groups are situated at 2.05–2.25 ppm. The aromatic protons from phenols appear as a large complex pattern in the range of 6.6–7.2 ppm. The protons of the methylene bridges attached to the aromatic and/or aliphatic rings, specific to the formaldehyde resins, are presented as large peak in the range of 3.6–3.7 ppm chemical shift.

Table 2. Thermal parameters of *p*-NPh/*o*-CR/CHX/FA resins

Sample	Temperature corresponding to 10% (T_{10}) and 50% (T_{50}) weight loss, °C		Weight loss at 500 °C (WL_{500}) %	Decomposition activation energy (E_a), kJ/mol		Pre-exponential factor ($\ln A$) min ⁻¹
	T_{10}	T_{50}		acc. [17]	acc. [16]	
	1	330	430	60	38.80	
2	335	440	59	72.95	88.90	18.49
3	330	430	70	50.30	52.20	7.73
4	340	435	65	78.01	82.64	16.57

The TGA curves (Fig. 3, Table 2) indicate that the polymers undergo up to 2–5% weight loss at temperature up to 340 °C. The resin with more *o*-CR in the structure (sample 2) is more stable than the resins with more

T_{50} , WL_{500}). Accepting these parameters as the criteria of thermal stability one can conclude that the synthesized resins are reasonable thermostable products.

The resulting formaldehyde polymers, as heat reactive resins, were submitted to the detailed studies regarding their behavior in pressure sensitive tapes (Table 3). These tapes are compared with a similar tapes obtained with a pressure sensitive composition without formaldehyde resin in its structure. So two groups of the tapes were investigated namely with a milled natural rubber, but without acrylic adhesive (samples B–E) and without a milled natural rubber but with acrylic adhesive (samples G–J). The same rubber and acrylic adhesive were used in all the tests, to make sure the differences in the adhesive properties could be attributed to formaldehyde resins only. The data presented in Table 3 evidenced the adhesive samples B–E and G–J impart approximately the same degree of adhesion in comparison with sample A (composition without formaldehyde resin and acrylic adhesive) and F (acrylic adhesive only), while the cohesive strength and Williams plasticity increase significantly. This can be due to the fact the reactive formaldehyde resin reacts with rubber and acrylic adhesive and a partially cross-linked polymer was obtained. The values of the Williams plasticity increase from 1.65 to 2.15 for rubber based adhesives and from 1.60 to 3.5 for the acrylic ones. The cohesive strength shows a high increase from 0.25 h to 24 h. All the tapes show acceptable adhesion but only the tapes which contain formaldehyde resins in their formulae show good, strong cohesive behaviors. An interesting property of the tapes obtained from the compositions with these for-

Table 3. Characteristics of pressure sensitive adhesive compositions and tapes

Sample	Adhesive compositions (milled natural rubber/petroleum resin/formaldehyde resin/acrylic adhesives)	Williams plasticity mm	Tape substrate	Adhesive tape characteristics	
				0° hold test, h	180° peel test g/cm
A	100/100/0/0	1.65	paper sheet	0.25	740
B	100/80/20 (sample 1)/0	2.15	paper sheet	>22	1000
C	100/80/20 (sample 2)/0	1.95	paper sheet	>22	1050
D	100/80/20 (sample 3)/0	1.87	paper sheet	>22	710
E	100/80/20 (sample 4)/0	2.00	paper sheet	>22	740
F	0/0/0/100	1.60	polyester nonwoven fabric	1	610
G	0/0/15 (sample 1)/100	2.90	polyester nonwoven fabric	>24	540
H	0/0/15 (sample 2)/100	3.50	polyester nonwoven fabric	>24	500
I	0/0/15 (sample 3)/100	2.40	polyester nonwoven fabric	>24	510
J	0/0/15 (sample 4)/100	3.00	polyester nonwoven fabric	>24	550

p-NPh in their compositions (sample 1). This fact denotes that the nonyl group bonded to the aromatic ring is most easily degradable and affect negatively the thermal stability of the resin. The relative thermal stabilities of the resins were quantitatively estimated using the activation energy of decomposition and TG parameters (T_{10} ,

maldehyde resins is the thermal stability. When the tape adhered to the steel surface was heated at 140 °C for 0.5 h it showed no dimensional change or wrinkling and the adhesive was not transferred to the steel surface. This facts recommend these tapes for work at elevated temperatures. A possible disadvantage of pressure sensi-

tive tapes containing formaldehyde resins may be the light dark color, restrictive such resins using for the light colored tapes.

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W kolejnym zeszycie ukaza się m.in. następujące artykuły:

- Nowy sposób syntezy hydrofobowo modyfikowanego poli(kwasu akrylowego)
- Wpływ promieniowania gamma na udarność i właściwości cieplne polistyrenu wzmacnianego dodatkiem SBR (*j. ang.*)
- Badanie wpływu modyfikacji mineralnych napelnaczy proszkowych silanami na wybrane właściwości mechaniczne liniowego polietylenu małej gęstości
- Wpływ wybranych środków pomocniczych na właściwości warstwy wierzchniej wytłaczanego polietylenu
- Badanie trwałości układów mikrokrystalicznego chitozanu z wybranymi niesteroidowymi substancjami przeciwzapalnymi (*j. ang.*)
- Kryteria podobieństwa przepływów tworzyw polimerowych w zimnych kanałach form wtryskowych
- Symulacja przemieszczania się cząsteczek polietylenu w tarczowej strefie wytłaczarki
- Badanie stabilności modyfikowanej żywicy mocznikowo-formaldehydowej (*j. ang.*)