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MACROMOLECULAR CHEMISTRY AND POLYMERIC MATERIALS

Polyurethane Varnish Materials Based on Diphenylolpropane

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Abstract—Polyurethane varnish materials based on diphenylolpropane were synthesized. The properties of the varnishes and coatings obtained were studied in relation to the nature and ratio of the starting compounds.

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The modern paint-and-varnish industry offers a wide assortment of coatings, among which a particular place is occupied by compounds based on polyurethane (PU) film-forming components. The volume of production and consumption of these materials is lower compared to other types of varnishes and paints, but the production growth rate is higher by a factor of almost 2. According to experts' forecast, in the nearest future the demand for these materials will increase, on the average, by 4–6% annually [1].

Such a demand for PU varnish materials (VMs) is due to a unique set of service properties characteristic of PU coatings. They exhibit extremely high wear resistance, excellent adhesion to metal and nonmetal surfaces, high strength, and resistance to atmospheric factors, water, chemicals, benzine, and oil [2].

At the same time, the available assortment of VMs allows preparation of coatings that either have high hardness but are brittle and therefore have poor impact resistance or, vice versa, are insufficiently hard and therefore have poor abrasive resistance. There are virtually no formulations ensuring formation of films that would combine hardness and elasticity. Furthermore, in most cases the raw materials used in the synthesis are expensive and toxic and are in short supply. This particularly concerns such compounds as 1,4-butanediol and methylenebis-*o*-chloroaniline (MOCA) acting as chain-extension and curing agents.

The goal of this study is the preparation of high-quality coatings using new raw materials and evaluation of the properties of these coatings.

EXPERIMENTAL

In our study we used polyoxypropylenetriols of molecular weights 3000, 3600, and 5000 derived from glycerol: Laprol 3003 [TU (Technical Specification) 6-05-1513–75], 3603 (TU 6-05-2033–87), and 5003 (TU 6-55-62–93) grade, with OH group content of 1.70, 1.42, and 1.02 wt %, respectively; diphenylolpropane (DPP), bp 250–252°C/13 mm Hg, mp 155°C (TU 2423-172-00203335–2007); 1,4-butanediol (BD), mp 20.9°C, bp 203°C/759 mm Hg (TU 64-5-105–86); polyisocyanate (PIC), NCO group content 30 wt %; distilled phenyl isocyanate (PhIC), bp 343°C/3 mm Hg, n_D^{20} 1.5367; distilled triethylamine (TEA), bp 89.5°C, n_D^{20} 1.4044; pure grade acetone.

The model compounds, product 1 (DPP + 2PhIC) and product 2 (BD + 2PhIC), were synthesized by the reaction in acetone of DPP or BD with 2 mol of PhIC in the presence of catalytic amounts of TEA [3]. The products obtained were analyzed by IR spectroscopy on a Vector 22 Fourier spectrometer (Bruker) with a resolution of 4 cm^{-1}, and also on an SDT Q 600 thermal analyzer at a heating rate of 2 deg min^{-1} in the temperature range 25–300°C.

Polyurethane varnish was synthesized at room temperature. The reactant amounts were taken so as to ensure the molar ratio NCO : OH = 1 : 1. Coatings were prepared by casting a varnish compound onto glass, steel, or tin plates.

The conventional viscosity of VMs was determined as outflow time from a VZ-4 viscometer in accordance

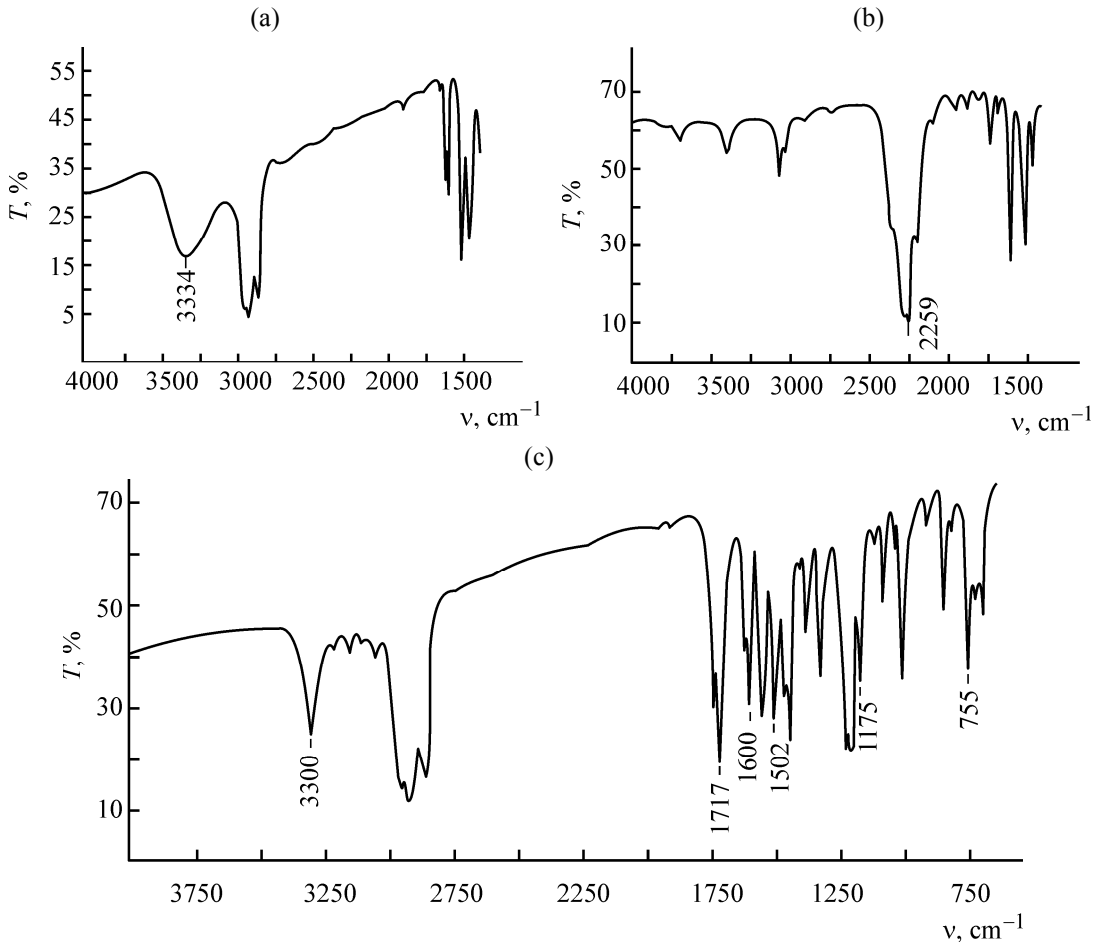


Fig. 1. IR spectra of (a) DPP, (b) PhIC, and (c) reaction product (DPP + 2PhIC). (*T*) Transmission and (ν) wavenumber.

with GOST (State Standard) 8420–74. Free films were prepared according to GOST 14243–78. The drying time of the coatings was determined as the time in which the film lost stickiness.

Physicomechanical tests of coatings were performed in accordance with the following standards: bending strength, GOST 6806–73; impact strength, GOST 4765–73; hardness, GOST 5233–67; and

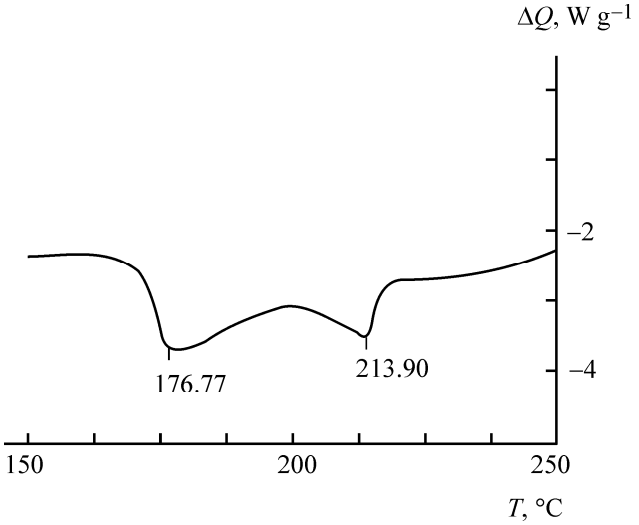


Fig. 2. DSC diagram of the DPP + 2PhIC reaction product. (*T*) Temperature and (Δ*Q*) heat flux; the same for Fig. 3.

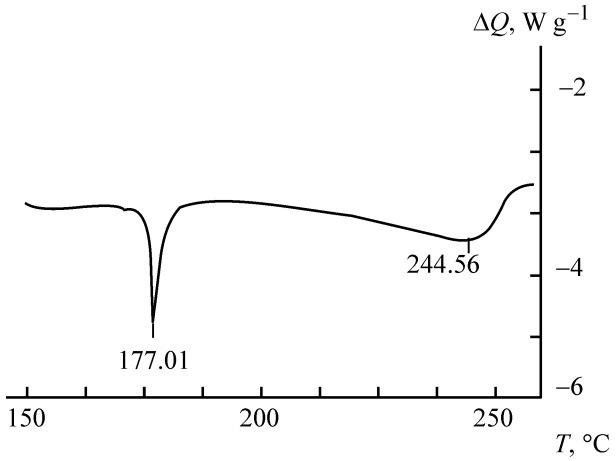


Fig. 3. DSC diagram of the BD + 2PhIC reaction product.

adhesion, GOST 15140–78. The water and full resistance was evaluated according to GOSTs 6594–73 and 21064–75, respectively.

In this study, we suggested for the first time to use DPP for preparing PU varnishes. The choice of DPP is governed by the presence in its molecule of two hydroxy groups, which allows the use of this compound as a chain-extension agent in PU compounds. The presence of aromatic rings in DPP gives grounds to expect that PUs prepared with this component will exhibit increased hardness, compared to BD-based analogs. Comparison of DPP with carcinogenic MOCA demonstrates the advantages of DPP from the viewpoint of toxicity. Furthermore, synthesis of PU with MOCA is performed via preparation of an isocyanate prepolymer, whereas in preparation of PU with DPP this step is unnecessary. The other factors in favor of choosing DPP are its availability (DPP is produced by Kazan'orgsintez Joint-Stock Company, whereas MOCA and BD are imported) and relatively low cost.

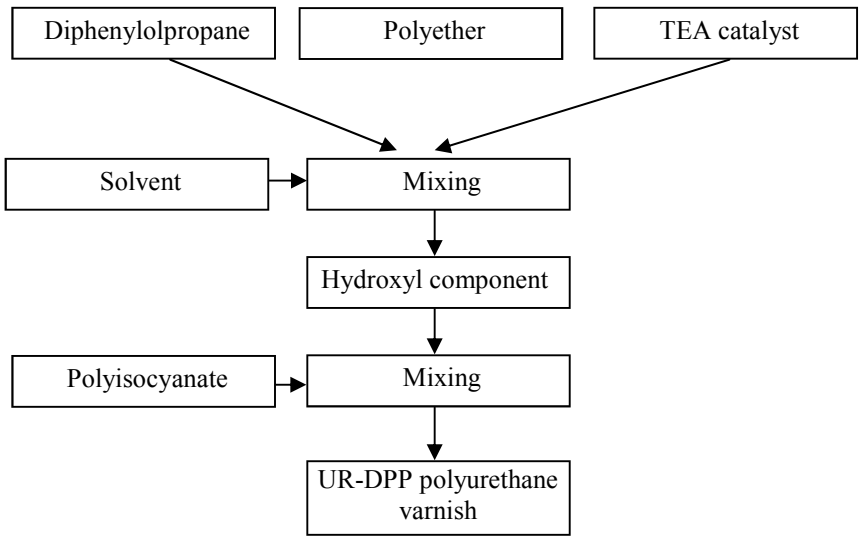
To confirm the formation of a urethane bond via chemical reaction of phenolic hydroxyl in DPP with the isocyanate group, we examined by IR spectroscopy model product 1, DPP + 2PhIC. Comparison of the spectra of the starting compounds (Figs. 1a, 1b) with that of product 1 (Fig. 1c) revealed the presence in the latter of absorption bands (cm^{-1}) characteristic of urethane group [1717 (C=O stretching vibrations), 1175 (C–O stretching vibrations), 1502 (N–H bending vibrations), 3300 (N–H stretching vibrations), and 755 (out-of-plane C=O bending vibrations)] and of aromatic ring (1600, C=C stretching vibrations), whereas the bands of NCO group at 2259 cm^{-1} and phenolic hydroxyl at 3334 cm^{-1} were absent. Thus, the IR data confirm the presence of urethane groups in the sample.

Then we evaluated the heat resistance of product 1 with the aim to determine the temperature of decomposition of the urethane bond. The thermogram shown in Fig. 2 has two endothermic peaks. The first of them corresponds to melting of product 1 at 177°C, and the second, to its decomposition into DPP and PhIC at 214°C.

Under the same conditions we performed an experiment on thermal decomposition of product 2, BD + 2PhIC. Figure 3 shows that, as in the former case, the thermogram has two endothermic peaks corresponding to melting of product 2 (177°C) and its decomposition (244°C). As can be seen, product 2 degrades at 30°C higher temperature than product 1.

This fact is associated with higher resistance to elevated temperatures of the urethane bond formed by an alcoholic hydroxyl, compared to the bond formed by a phenolic hydroxyl. Despite this fact, the use of DPP in PU synthesis is quite possible, because the operation temperature of these materials in most cases does not exceed 100°C.

The next step of our study was the development of a PU varnish compound based on DPP (UR-DPP). As shown in the scheme below, initially we prepared the



Scheme of preparation of UR-DPP polyurethane varnish.

Table 1. Influence of catalyst concentration on the properties of coatings based on UR-DPP varnish

Property	Value at indicated TEA concentration, wt %					
	0	0.0085	0.017	0.034	0.068	0.136
			Varnish			
Viscosity (outflow time from VZ-4), s		11	13	17	20	32
			Coating			
Impact strength, N m		5	5	3	3	3
Bending strength, mm	"Wet film"	1	1	5	5	5
Hardness, arb. units		0.87	0.87	0.85	0.86	0.85
Adhesion, point		1	1	2	2	2
Drying time, min		54	32	17	8	4

hydroxyl component by dissolving in acetone DPP, Laprol, and catalyst.

Then, to the resulting solution we added polyisocyanate. The varnish was allowed to stand for 10–15 min prior to applying onto a support. This procedure is necessary for the removal of air inclusions formed in the course of mechanical mixing of the components and for the release of CO_2 formed by the reaction of the isocyanate with the residual moisture present in the reactants.

The properties and performance of the coatings largely depend on the process parameters and formula of the varnish compound. Therefore, we examined how the concentration of the reactants in the solvent, catalyst amount, time and temperature of curing, and structure and ratio of the reactants affect the properties of the varnish and coatings thereof.

An important process parameter of VMs is the viscosity, which directly depends on the catalyst concentration (Table 1). In turn, the catalyst concentration affects the strength and adhesion properties of the coating (Table 2). Without TEA and at its low content, a "wet" film is formed, because cross-linking is extremely slow. As the catalyst amount is increased, the drying time becomes shorter, and the strength and adhesion properties of the film are improved, reaching a maximum at a TEA concentration of 0.017 wt %. Further increase in the catalyst amount leads to worsening of the physicomechanical characteristics of the film, apparently due to too fast curing, preventing formation of an adhesion contact in the polymer–metal system.

The viscosity of a varnish compound depends not only on the catalyst content, but also on the concentration of the reactants in the solvent. As their concentration is increased, the viscosity of the system increases, and the film formation is accelerated (Table 2). As for the dependence of the physicomechanical characteristics on the concentration of the reactants, the concentration variation in the interval 30–50% does not appreciably affect the properties of the coatings. At the same time, its increase over 50% leads to deterioration of the coating quality.

In view of the requirements to VMs, we recommend the concentration of the reactants in acetone of 40% and the catalyst concentration in the varnish of 0.017%. This formula ensured good spreadability of the varnish, its sufficiently long

Table 2. Influence of the concentration of the reactants on properties of UR-DPP varnish and coatings thereof

Property	Value at indicated concentration, wt %			
	30	40	50	70
		Varnish		
Viscosity (outflow time from VZ-4), s	–	11	–	36
		Coating		
Impact strength, N m	5	5	5	3
Bending strength, mm	1	1	1	5
Hardness, arb. units	0.86	0.87	0.87	0.86
Adhesion, point	1	1	1	2
Drying time, min	43	32	28	15

Table 3. Influence of curing time at 24°C on the properties of coatings based on UR-DPP varnish

Property	Value at indicated curing time, h				
	5	10	24	48	72
Impact strength, N m	50	50	50	50	50
Bending strength, mm	1	1	1	1	1
Hardness, arb. units	0.65	0.72	0.85	0.87	0.87
Adhesion, point	1	1	1	1	1

Table 4. Influence of Laprol structure on the properties of coatings based on UR-DPP varnish

Property	Value for indicated Laprol grade		
	L 3003	L 3603	L 5003
Impact strength, N m	50	50	50
Bending strength, mm	1	1	1
Hardness, arb. units	0.89	0.87	0.82
Adhesion, point	1	1	1

working life (105 min), and high levels of strength, elasticity, and adhesion of the coatings. A study of curing of coatings based on UR-DPP varnish showed that the film formation was complete at room temperature in 2 days, after which the physicomechanical parameters did not change noticeably (Table 3).

The properties of the coatings can be varied by varying the Laprol structure (Table 4). An increase in the molecular weight of Laprol led to the formation of a more elastic coating, as indicated by a decrease in the hardness and an increase in the bending strength, which is apparently due to a decrease in the density of the chemical network of the PU film. Evaluation of the swelling resistance showed that the coatings are resistant to hexane, oil, gasoline, and water. The swelling of the films in these media did not exceed 1%.

The application characteristics of UR-DPP varnish and the physicomechanical properties of coatings thereof are given in Table 5 in comparison with commercial PU VMs. Thus, the use of DPP allowed preparation of a coating that was not inferior to commercial analogs in the main properties and even surpassed them in the hardness. An advantage of the suggested compound is a decreased power consumption (curing at room temperature) compared to UR-231 VM and lower cost compared to UR-SKU-PFL.

CONCLUSIONS

(1) A process was developed for preparing polyurethane varnish material using diphenylolpropane. The coatings obtained are not inferior to the commercial analogs in the strength, elasticity, and adhesion and even surpass them in hardness. The

Table 5. Properties of various PU VMs and coatings based on them

Property	Value for indicated polyurethane VM			
	UR-DPP	Lapteks	UR-SKU-PFL	UR-231
Varnish				
Color	Pale yellow	Pale yellow	Pale yellow	Pale yellow
Viscosity (outflow time from VZ-4), s	11	–	–	11
Curing temperature, °C	24	24	24	80
Drying time, h	1	36	6	3
Coating				
Impact strength, N m	5	5	5	5
Bending strength, mm	1	1	1	1
Hardness, arb. units	0.87	0.50	0.50	0.50
Adhesion, point	1	1	1	1

coatings exhibit excellent resistance to water, gasoline, and oil and have relatively low production cost.

(2) Regular trends in the influence of the catalyst concentration, molecular weight of the polyetherpolyol, and synthesis and curing conditions on the application, physicomechanical, and service characteristics of polyurethane varnish prepared with diphenylolpropane and of coatings based on it were revealed.

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