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MACROMOLECULAR CHEMISTRY AND POLYMERIC MATERIALS

Fluorinated Paint-and-Varnish Compounds and Coatings Prepared from Them

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Abstract—The possibility of developing a wide range of paint-and-varnish compounds based on fluorinated oligomers, fluorohydrocarbons, and fluoropolymers for preparing strongly adhering coatings with improved properties on supports with various surface energies was examined.

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Fluorinated polymeric materials exhibit unique resistance to various actions. Therefore, it seems attractive to use them in paint-and-varnish compounds for preparing coatings for various purposes: with long service life, protective, chemically resistant, hydrophobic, and wear-resistant.

The main property of paint-and-varnish coatings distinguishing them from other polymeric materials is good adhesion to a support. However, fluoropolymers are adhesion-inactive toward high-surface-energy supports, among which are the main structural materials whose surface energy amounts to hundreds of millijoules per square meter. Therefore, until recently fluorinated paint-and-varnish compounds were of limited use, although studies have been made [1, 2] and epoxy–Ftorlon lacquers [3] based on polyvinylene fluoride copolymers have been developed on the basis of the incompatibility principle [4].

It is well known that the driving force of migration and orientation of substances composing a multicomponent system is the tendency to decrease the surface energy. In coatings that are thin films with a well-developed surface, surface interactions on phase boundaries should play an important role in their formation. The weakness of intermolecular interaction in fluorine compounds, providing their low surface energy, should facilitate the component segregation in compounds with traditional paint-and-varnish film-forming agents exhibiting good adhesion to high-surface-energy supports.

Based on this approach, we examined the possibility of developing a wide range of fluorinated paint-and-varnish compounds for various purposes.

EXPERIMENTAL

In the experiments we used fluorinated oligomers (FO), fluorohydrocarbons (perfluoro acids, polyfluorinated telomeric alcohols), and fluoropolymers (F-42L, F-62L, F-40D, F-4D) in combination with widely used commercially available paint-and-varnish film-forming agents such as epoxy, alkyd, and melamine–formaldehyde oligomers. As model systems we used compounds of ED-20 epoxy–4,4'-isopropylidenediphenol oligomer with its fluorinated analog prepared by the reaction of 2,2-bis(p-hydroxyphenyl)-1,1,1,3,3,3-hexafluoropropane with epichlorohydrin [5]. The characteristics of the oligomers are given in Table 1.

The fluorinated oligomer, being an analog of ED-20, does not, however, form a strongly adhering coating on a steel support. Therefore, we examined the possibility of its compounding with ED-20, followed by joint curing. As curing agents we used triethylenetetramine (TETA) and polyethylenepolyamine (PEPA).

Table 1. Properties of oligomers

Oligomer	Molecular weight	Self-ignition temperature, °C	Epoxy number, %	Viscosity, Pa s
ED-20 (EO)	420–650	470	20–22	0.126
FO[a]	550–720	620	15–18	0.112

[a] (FO) Fluorinated oligomer derived from 2,2-bis(*p*-hydroxyphenyl)-1,1,1,3,3,3-hexafluoropropane

To compare the reactivity of FO and EO with amine curing agents, we used DSC. Thermograms were recorded with a Mettler DSK 20 device [6] in a helium atmosphere. The samples were prepared by a common procedure [7]. Scanning was performed at different heating rates in the range 288–398 K, with the temperatures of the reaction onset and peak determined.

Thermomechanical curves (TMCs) were taken with a UIP-70M device at a constant compression load of 1.2 MPa and heating rate of 5 deg min^{-1}.

Coatings on steel, glass, and fluoroplastic were prepared from solutions by pneumatic spraying. The physicomechanical and protective characteristics of coatings were measured by standard procedures used in paint-and-varnish industry [8].

To study the structure and morphology of coatings and the elemental composition of coatings across their thickness, we used electron-probe spectral microanalysis in combination with scanning electron microscopy [9] using a Philips SEM-500 scanning electron microscope with a probe diameter of 2–10 nm.

The surface energy of the coatings on the boundary with air was calculated by the Elton equation [10–12] $\gamma_s = 0.5\gamma_l(1 + \cos\theta)$, where γ_s is the surface energy; γ_l, surface energy of the test liquid; and θ, contact angle of the solid surface with the test liquid.

The contact angles were determined by the sessile drop technique [11]. The measurements were performed at 20°C with an optical horizontal microscope with a goniometric scale, using a set of test liquids [10].

From the thermograms we plotted the dependences of the logarithm of the heating rate on the reciprocal temperature in the point corresponding to the reaction maximum and then, using the Arrhenius equation, calculated the apparent activation energy of curing of FO and EO with amine curing agents [12]. The results are given in Table 2.

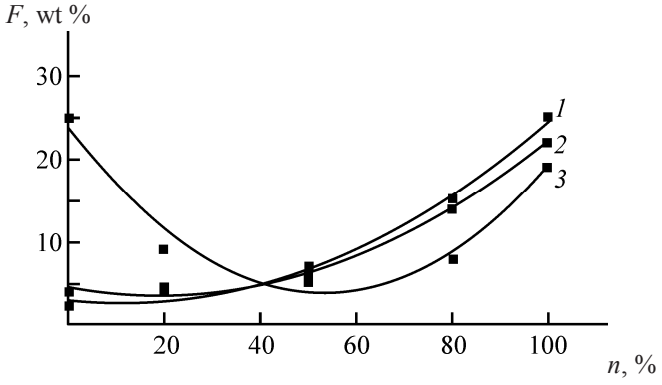
Table 2. Results of determining the activation energy of oligomer curing

Components and their weight ratio	E_a, kJ mol^{-1}
ED-20	49
PEPA	54.7
FO	45
TETA	50

It can be seen that in all the cases the apparent activation energy in reactions with FO is somewhat higher than with EO, but the difference is minor. This fact suggests the possibility of joint curing of EO–FO mixture with amine curing agents. Mixtures of FO and EO and their solutions in organic solvents were transparent in a wide concentration range.

The results of testing the properties of FO–EO coatings on steel are given in Table 3. It can be seen that addition of even small (1–5%) amounts of FO into compounds based on ED-20 oligomers positively affects the hydrophobicity, hardness, and water absorption of coatings, exerting virtually no effect on the adhesion.

To understand the cause of such properties of coatings, we examined the physicochemical properties, composition, and morphology of the coatings obtained. From the thermomechanical curves we determined the



Distribution of bound fluorine as a function of the distance from the support n (fraction of film thickness) in coatings prepared from mixtures of ED-20 (EO) and 2,2-bis(*p*-hydroxyphenyl)-1,1,1,3,3,3-hexafluoropropane (FO) oligomers in 1 : 1 ratio. (*1*) Steel, (*2*) glass, and (*3*) polytetrafluoroethylene.

Table 3. Properties of coatings

Compound	Contact angle, deg	Adhesion, points	Impact resistance, cm	Hardness (TML-2124)	Water absorption in 24 h, %
ED-20 + TETA	68–70	1	30	0.76	3
ED-20 + FO (1%) + TETA	84–85	1	30	0.82	2
ED-20 + FO (5%) + TETA	85–86	1	30	0.86	1.5
ED-20 + FO (10%) + TETA	90–92	1	30	0.88	1

glass transition point T_g, which for cured films of the oligomers mixed in 1 : 1 ratio is in good agreement with that given by the Fox equation for the condition of compatibility [10].

It was shown by electron-probe spectral microanalysis in combination with scanning electron microscopy that there was no phase segregation in the systems. All these facts show that the components in the cured films are compatible in a wide range of component ratios in the starting mixture. Nevertheless, the coatings obtained on various supports (glass, Teflon, 08KP steel) are nonuniform in composition across the film thickness.

As seen from the figure, in the case of high-surface-energy glass (surface energy 640 mJ m^{-2}) and steel (surface energy 1220 mJ m^{-2}) supports, the fluorinated component is concentrated on the boundary with air, and the layer on the boundary with the support is depleted of it (curves *1, 2*). With Teflon used as support (surface energy 18 kJ m^{-2}), the fluorinated component is concentrated near the support (to even a greater extent than on the boundary with air in the previous cases), and the middle layer is significantly depleted of this component (curve *3*). The results of the tests (Table 3) confirm the nonuniformity of the coatings across the thickness.

Table 4. Contact angles θ and surface energies γ_s of composite coatings

Compound	θ, deg	γ_s, mJ m^{-2}
Cured ED-20 oligomer	72	46.8
Cured FO	94–95	34.7
ED-20 + FO, wt fraction:		
0.01	84–85	37.8
0.05	86–87	37.2
0.1	90–92	36.1
0.5	92	36

Thus, concentration of the nonfluorinated component of the mixture near the high-surface-energy support provides good adhesion of the composite coatings, and the upper fluoroplastic layer imparts to the coating hydrophobicity, moisture resistance, and increased hardness. Thus, the required properties of coatings can be provided by using minimal amounts of the fluorinated component.

The nonuniformity of the coatings across the thickness may be due to low surface tension of the fluorinated component and its low affinity for high-surface-energy surfaces of steel and glass. In their formation, the decisive effect is exerted by surface interactions rather than the density of the components and the curing rate.

From the data on the contact angles, we determined the surface energies of the composite coatings on the boundary with air using the Elton equation (Table 4).

The factor responsible for the coating nonuniformity across the thickness is the tendency of the surface energy to decrease. Formation of the structure of the surface layers of paint-and-varnish coatings is also due to a decrease in the surface energy. Since the coatings were prepared from very dilute solutions, the translation mobility of the oligomers is high, and the diffusion hindrance after applying the system onto the support is insignificant. Proceeding from the assumption that in a thin layer the mass transfer processes occur immediately after applying the solution onto the support, we can assume that these processes are mainly governed by the thermodynamic factor. In this process, the decisive role should belong to the adsorption. To confirm the adsorption mechanism of the mass transfer, we estimated the adsorption in accordance with the Gibbs equation [11]

$$G = \frac{(1 - c)c}{RT} \frac{d\gamma}{dc},$$

where $d\gamma/dc$ is the surface activity of FO in the compound.

Since the surface energy was determined for the cured coating, it can be assumed that the use of adsorption relationships valid for the systems occurring in an equilibrium is quite acceptable in this case. As a criterion of the surface activity we took $\lim \Delta c/c$ at $c \to 0$ and determined this quantity graphically from data of Table 4 [11]. Its absolute value appeared to be 3.4. In accordance with the Gibbs equation, we calculated the weight fraction of the fluorinated component in the surface layer for the 2 : 1 weight ratio of EO and FO in the mixture. It appeared to be 0.85, which corresponds to the 22.5% content of fluorine in the surface layer (the theoretical fluorine content of FO is 26.5 wt %). The experimental fluorine content is 24.5%. This fact proves that the surface energy is a decisive factor responsible for nonuniformity of the coatings across the thickness.

Thus, a specific feature of the chemical composition of the surface of coatings formed from a mixture of EOs with their fluorinated analogs is enrichment of the surface layer at the film–air interface with the component having the lowest surface energy.

Phenomena observed on the coating|support boundary also depend on the surface energy of the support and can be accounted for on the basis of the wetting concept.

It is known that wetting of a solid surface with a liquid depends on the nature of the liquid–solid interaction. It is characterized by the equilibrium contact angle θ and is described by the Young equation [12]

$$\cos \theta = (\gamma_s - \gamma_{sl})\gamma_l,$$

where θ is the contact angle; γ_s, surface energy of the solid surface; γ_{sl}, energy of interphase interaction of the solid surface with the wetting liquid; and γ_l, surface energy (surface tension) of the wetting liquid.

Thus, to enhance the wetting (increase cos θ), it is necessary for the surface energy (surface tension) of the wetting liquid γ_l to be minimal, and this is possible only if the surface and the wetting liquid are similar in molecular nature. Hence, the gain in the free energy is attained at the expense of variation of the wetting. The fluorinated oligomer whose surface energy is lower than that of EO better wets the low-surface-energy surface of poly(tetrafluoroethylene).

With high-surface-energy glass and steel supports, better wetting and correspondingly larger gain in the interphase interaction energy are attained in the case of wetting with EO. This fact accounts for the observed distribution of the components at the support|coating phase boundary.

Thus, by the example of epoxy film-forming agents we demonstrated the possibility of modifying the properties of paint-and-varnish compounds by using minimal amounts of fluorinated products, owing to the coating nonuniformity across the thickness.

To obtain such paint-and-varnish coatings, the components in the initial compound should form a single-phase system in a common solvent. The cured coating itself can be single-phase or heterogeneous. In all the cases, the fluorinated component will be always concentrated at the boundary with air. The component segregation in the course of coating formation will ensure a combination of good adhesion of the coating to a metal support, provided by the paint-and-varnish component at the film|support boundary, with high levels of hydrophobicity, wear resistance, protective properties, and chemical resistance, provided by the fluorinated component at the coating surface.

Similar nonuniformity across the thickness, caused by energetic interactions in the coating–support and coating–air systems, was also reported for other fluorinated paint-and-varnish systems: oligomer–fluorohydrocarbon [14–17] and fluoropolymer–oligomer [18–21].

CONCLUSIONS

(1) Nonuniformity across the thickness of thin-layer coatings prepared from fluorinated paint-and-varnish compounds is due to interphase energetic interactions in the coating–support and coating–air systems.

(2) To provide adhesion of thin-film fluorinated composite coatings on various high-surface-energy supports, it is necessary to formulate a composite system consisting of a fluorinated component and an oligomer containing polar groups. A solution of the components in a common solvent before application should be a single-phase system.

(3) New paint-and-varnish compounds for strongly adhering coatings with improved properties on sup-

ports with various surface energies were obtained on the basis of fluorinated oligomers, fluorohydrocarbons, and fluoropolymers.

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