

The influence of polymer textured coating molecular structure on its reflectivity

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It is shown that with increasing temperature of formation of polymer coating (polyester enamel on the surface of rolled metal) the value of the average intermolecular distance, at which the free energy has a minimum, increases, which leads to decreasing the density of the coating and its Young's modulus. It is shown that violation of the temperature regime of formation of the textured polymer coating changes the morphology of the surface, which affects the value of its gloss coefficient.

Keywords: polymer films, textured polymer coatings, wrinkled interfaces, mean-field method, optical properties of polymer films.

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One efficient method for protection against corrosion is the application of a polymer coating to steel sheets. Coatings with a textured surface (Fig. 1, *a*) are currently becoming increasingly popular in certain branches of industry (e.g., in construction). When a coating dries, wrinkling patterns grow due to diffusion and assemble in a certain way that is specified both by the chemical structure of the material and the drying regime [1]. It is important to control the parameters of the technological process that govern the quality of resulting coatings. Such quality indicators as thickness, strength, and hardness may be measured quickly and accurately by modern instruments. However, corrosion resistance testing is performed in a salt spray chamber, which is a costly and time-consuming procedure.

It was noted in [2] that an optical measurement system provides an opportunity to determine quickly and accurately not only the surface parameters, but also the internal properties of the material. Naturally, the pigment plays a key role in light absorption by a paint material, but roughness is also a major factor in light reflection from a textured surface [3]. This is the reason why the influence of surface morphology on light reflection is examined in both theoretical [4] and applied [5] studies. The aim of the present study is to probe the influence of the temperature regime of formation of a coating on its specular reflectivity.

A polymer chain is represented as a sequence of N axially symmetric kinetic units with length l and a continuum distribution of their orientations. The thermodynamic flexural rigidity of chains is characterized by energy constant K [6].

A mean (molecular) field is introduced in order to simplify the description of the effects of intermolecular orientational interactions. The dependence of its magnitude on the average interchain distance was obtained in [7]:

$$V = V_0 \frac{b_c}{b}, \quad (1)$$

where b is the intermolecular distance with critical value b_c (phase transition point). Potential energy of a polymer chain

$$U = -K \sum_n (\mathbf{u}_n, \mathbf{u}_{n+1}) - \sum_n (\mathbf{u}_n, \mu \mathbf{V}_0/b), \quad (2)$$

where $\mathbf{u}_n = (u_{n,1}, u_{n,2}, u_{n,3})$ is a unit vector in the direction of the n th kinetic unit and quantity $\mu = \frac{1}{N} |\sum_n \mathbf{u}_n|$ depends on intermolecular distance b , characterizes the average orientation of chain segments, and serves a long-range orientational order parameter. Vector \mathbf{V}_0 is co-directional with the overall orientation of kinetic units of the chain.

The entropy of the system may be estimated based on the following concepts. Let S_0 be the entropy of the system in a completely amorphous state. In the crystalline state, the chain motion is limited. One can say that the chain is located within a cylindrical cavity with radius b . The entropy of this chain section then decreases by an amount proportional to $1/b^2$ [6]. Thus,

$$S = S_0 - \frac{a^2}{b^2}, \quad (3)$$

where a is the coefficient of proportionality. The free energy is then

$$F = U + \frac{Ta^2}{b^2} - TS_0. \quad (4)$$

Figure 1, *b* shows the dependence of the free energy of one kinetic unit on the interchain distance. Calculations were carried out using the Monte Carlo method.

It can be seen from Fig. 1, *b* that the free energy has a minimum at a certain interchain distance b_0 . This minimum shifts toward greater interchain distances with an increase in the coating formation temperature. This conclusion is verified by the results of production tests performed in order to examine the dependence of the polymer film thickness on temperature in a drying oven (see the table). A sheet of

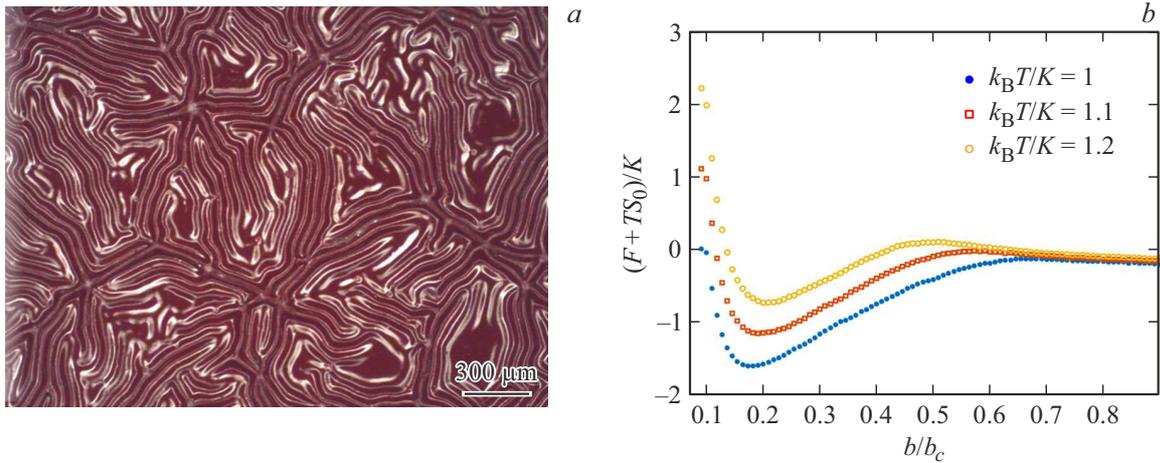


Figure 1. *a* — Image of the surface of a metal sheet with a polyester textured coating. *b* — Dependences of the free energy of the kinetic unit of the polymer system on the intermolecular distance at different coating formation temperatures; $a/b_c = 0.091$, $V_0/K = 1$.

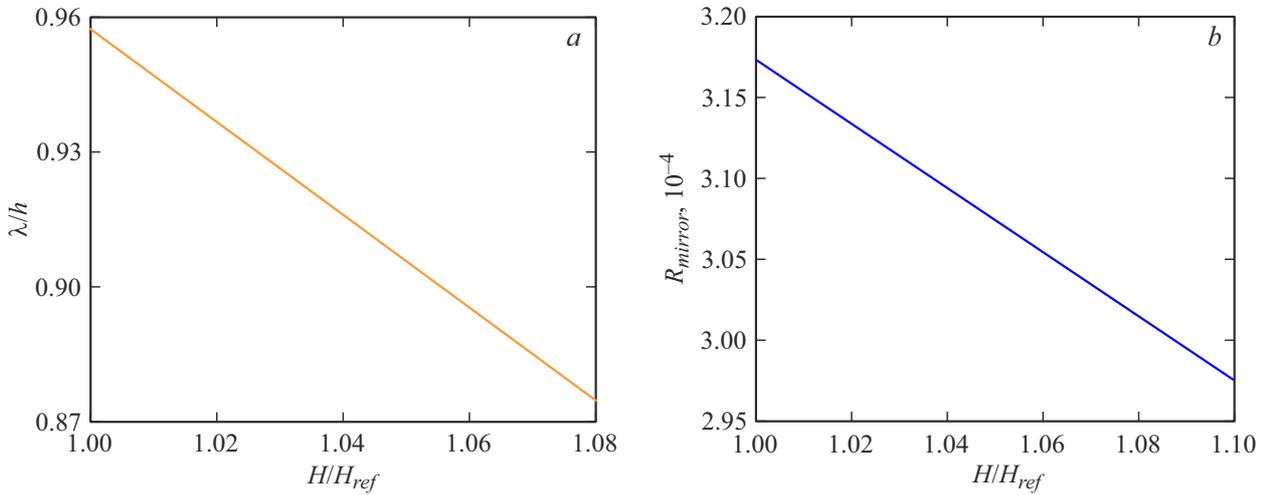


Figure 2. *a* — Dependence of the average ratio of the width of a wrinkle to its height on the coating thickness (polyester enamel); the thickness of the untreated coating layer is constant. *b* — Dependence of the specular reflectivity on the coating thickness.

rolled metal with a polymer coating (polyester enamel) was moved inside the drying oven where the temperature varied from one region to the other. The thickness of the untreated coating layer was constant.

In the second experiment, the temperature in the drying oven was higher; consequently, the temperature at which the polymer molecular structure formed was also higher. Thus, coating thickness H increases due to an increase in intermolecular distance.

A change in density leads to a change in surface morphology (wrinkle size). As was demonstrated in [8], the average ratio of wrinkle width λ to wrinkle height h is specified by the Young's modulus:

$$\frac{\lambda}{h} \sim E^{1/3}. \quad (5)$$

The Young's modulus value is proportional to the second derivative of the free energy with respect to interchain

distance at the point of its minimum. The results of modeling for polyester enamel revealed that the point of minimum free energy shifts toward a greater intermolecular distances with an increase in temperature, while the second derivative of free energy at its minimum decreases in the process (both these effects are illustrated in Fig. 1, *b*). Thus, when the temperature regime of coating formation is violated toward higher temperatures, the Young's modulus value of the coating decreases, while the interchain distance and, accordingly, the coating thickness increase (see the table). As was demonstrated above, the Young's modulus is, in turn, associated with the average ratio of the width of a wrinkle to its height, and an increase in interchain distance leads to an increase in coating thickness, which makes it possible to find the slope of the straight line in Fig. 2, *a*. The average sizes of associates for a reference sample with thickness H_{ref} were determined using a microscope: $\lambda = 34.7 \mu\text{m}$ and $h = 36.2 \mu\text{m}$. A comparison of the results

Technological regimes of drying of a polymer coating and its thickness

Experiment	Position in a drying oven, m							Coating thickness H , μm
	3	9	15	21	27	30	38	
	Temperature, °C							
1	210	292	315	350	360	360	280	25.1
2	260	310	360	400	400	400	330	25.8

of modeling and experimental measurements allowed us to determine the coefficient of proportionality in formula (5) for polyester enamel and the dependence in Fig. 2, *a*.

Additional optical effects associated with strong scattering of light on the surface of such coatings arise due to surface roughness. The study of scattered light and gloss was carried out using the method of geometric optics.

Wave effects were neglected, since the sizes of associates (see above) are much larger than the wavelength of visible radiation. The radial cosine was chosen as a surface for modeling due to its similarity to the actual surface of the polymer coating (Fig. 1, *a*). In computer modeling, a narrow beam of light was directed at a given surface along the normal to it, and the reflection angle was calculated using geometric optics methods. The specular reflectivity of the surface was then calculated using the following formula:

$$R_{mirror} = \frac{\sum_{i=1}^k R_{m_i}}{k}, \quad (6)$$

where k is the total number of incident rays and R is the specular reflectivity for point i on the surface that was calculated using the Fresnel formula with refraction index $n = 1.46$ (polyester enamel). Only the rays reflected at angles close to specular ones (reflection from a smooth surface) are introduced into the sum in expression (6). An angle is considered small if a ray deviates by no more than 2° from specular reflection. Figure 2, *b* shows the dependence of specular reflectivity on the coating thickness. The calculations revealed that when the coating thickness is increased artificially, its gloss coefficient decreases, which was verified visually in the experiment.

An increase in thickness of a polymer coating at the cost of its density is economically advantageous for the manufacturer, but the corrosion resistance decreases. Gloss measurements may serve as an indirect but efficient quality control procedure, since a lower gloss coefficient is indicative of a reduction in density and quality of a paint material.

Conflict of interest

The authors declare that they have no conflict of interest.

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