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Investigation of the influence of artificial defect sizes on the mechanical properties of polymer coatings

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The paper introduces a model of polymer chains near a spherical defect. The reduced free energy dependences of the polymer associate on its width at different values of temperature are obtained. It is shown that the width of surface wrinkles increases with increasing defect size. The value of Young's modulus ratios of the polymer coating and the foundation is reconstructed from the width of the wrinkles. It is shown that with increasing defect size the Young's modulus of the coating increases and its corrosion resistance decreases.

Keywords: polymer films, textured polymer coatings, defects, mechanical properties of polymer films, Young's modulus of polymer films.

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1. Introduction

Corrosion control of metal products has been a priority in many industries throughout time [1]. One of the methods of corrosion control of rolled metal is the application of various polymer coatings on it. The centers of corrosion are cracks in the polymer coating. Coatings with a large Young's modulus crack more strongly due to increased internal stresses and, consequently, provide less corrosion resistance. In industries such as construction, textured polymer coatings, the surface of which is a wrinkled structure, are the most popular and effective. The formation of wrinkles occurs as follows: during the formation of a coating, polymer chains are adsorbed on crystalline granules and lengthen due to polymerization, forming wrinkled domains (associates). Further, the associates increase due to diffusion and, as a result, assemble into a certain structure, the geometry of which mainly depends on the size of artificial defects (crystalline granules) in the paint coating. The purpose of this work is to study the effect of the size of artificial defects on the Young's modulus of a polymer coating.

2. Research object

The model proposed in this paper (Figure 1, *b*) can be used to describe textured polymer coatings of rolled steel sheet, for example polyester (Figure 1, *a*), polyurethane or polyvinyldenafluoride enamels. Such rolled metal sheets have a multilayer structure, the main layers of which are metal, primer (layer thickness 5−7 μm) and polymer enamel itself (layer thickness 20−30 μm). The formation of surface wrinkles is influenced by layers of primer and enamel.

The coating formation process proceeds as follows — a layer of primer is applied to a rolled metal sheet, which is then placed in a drying oven. After drying, polymer paint is applied over the primer, which consists of monomeric units and crystalline granules in a solvent. The system of primer-polymer is mobile during coating formation, which is why, upon subsequent drying at temperatures about 200 °C, surface wrinkles with a width of 30−50 μm are formed due to diffusion.

The key component of the paint, on which the formation of wrinkles and their geometry depend, are defects — crystalline granules with a diameter of 30−100 μm. Granules play two roles in the process of wrinkle formation, firstly, they locally increase the value of the Young's modulus of coating, which causes surface wrinkles to become wider, and secondly, they are the centers of wrinkle formation, as associates originate on their surface.

3. Model

A dynamic model with bending rigidity is used [2], which is a discrete analog of the persistent length model [3]. The polymer chain is represented as a sequence of M axially symmetric kinetic units with a length of l_{unit}. The size of the kinetic element may exceed the size of the chain link l_{link}. A unit vector in the direction of the mth kinetic unit $\mathbf{u}_m^{\text{unit}} = (u_{m,1}, u_{m,2}, u_{m,3})$. The thermodynamic rigidity of the polymer chain contributes to the potential energy of the kinetic unit

$$w_m^{\text{bend}} = -K^{\text{bend}} \cos(\Phi_m), \tag{1}$$

where K^{bend} is the bending rigidity of the chain, Φ_m is the angle between m and $m+1$ kinetic units of one polymer chain.

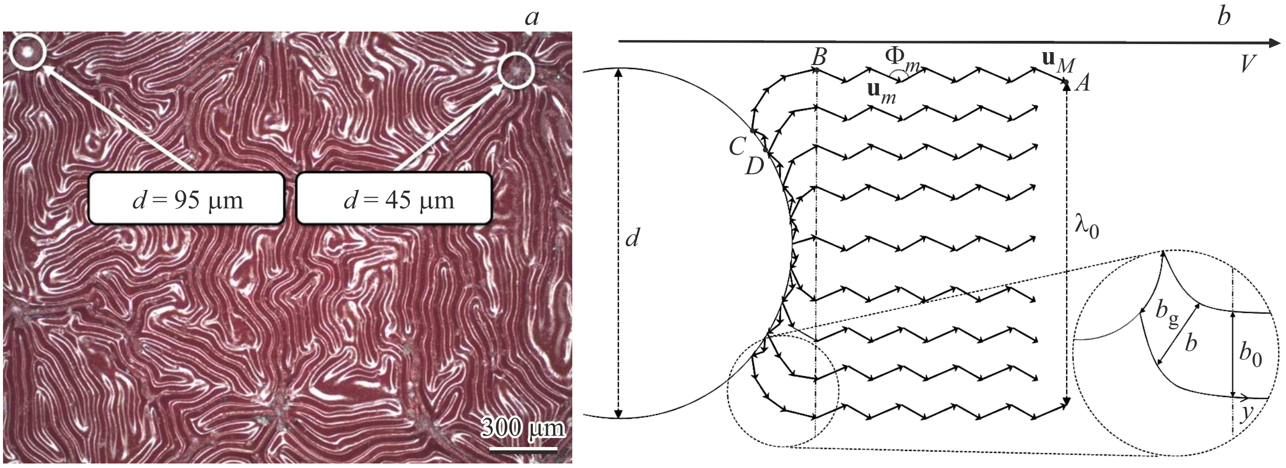

Figure 1. *a* — Photo of polymer coating (polyester enamel), *d* — diameter of crystalline granules, *b* — Schematic representation of the developed model.

The interaction of two kinetic units located in different chains is characterized by energy

$$w_{z,m}^{\text{inter}} = -K_{z,m}^{\text{inter}} \cos(\Psi_{z,m}), \qquad (2)$$

where $\Psi_{z,m}$ is the angle between z and m kinetic units of different polymer chains, the constant $K_{z,m}^{\text{inter}}$ is estimated in Ref. [4] from the Onsager ratio [5]

$$K_{z,m}^{\text{inter}} \sim \left(\frac{l_{\text{unit}}}{r_{z,m}}\right)^3 \frac{D}{r_{z,m} - D} \qquad (3)$$

where D is the diameter of the chain, $r_{z,m}$ is the distance between z and m kinetic units.

The mean molecular field $\mathbf{V}$ is introduced to simplify the description of the effects of intermolecular orientation interactions [6]. Then the interaction energy of the mth kinetic unit with the kinetic units of other chains is determined by the expression

$$w_m^{\text{inter}} = -(\mathbf{u}_m^{\text{unit}}, \mu \mathbf{V}_m), \qquad (4)$$

where

$$\mu = \left| \frac{1}{M} \left(\sum_{m=1}^{M} \mathbf{u}_m^{\text{unit}} \right) \right|$$

is parameter of the long-range orientation order.

The associate adsorbed on a spherical granule with a diameter d consists of N polymer chains. Each chain can be divided into three sections: AB is elongated straight section, BC is elongated curved section, CD is a section adsorbed on a granule. The total energy of the chain consists of the energies of each section.

The AB section is characterized by the energy of orientation interactions

$$w_{\text{AB}} = -\mu_{\text{AB}}^2 V_0 l_{\text{AB}}, \qquad (5)$$

where μ_{AB} and V_0 are the parameter of the long-range orientation order and the modulus of the mean field vector on the section AB of length l_{AB}. The energy in this part is calculated from the minimum of the Lennard–Jones potential energy. The intermolecular distance at the section is b_0.

In the BC section, polymer chains bend, which causes the change of the interchain distance b_m from b_g near the granule to b_0. The energy of orientation interactions in the BC section is calculated using the formula:

$$w_{\text{BC}_1} = -\sum_{m=m_{\text{CD}}+1}^{m_{\text{CD}}+m_{\text{BC}}} \mu_{\text{BC}}^2 V_m \Delta y, \qquad (6)$$

where μ_{BC} is the parameter of the long-range orientation order in the BC section, m_{CD} and m_{BC} is the number of kinetic units in the CD and BC sections, respectively,

$$V_m = V_0 \frac{b_0}{b_m} \text{ [7].}$$

In addition to the energy of orientation interactions in the BC section, the Lennard–Jones potential is taken into account

$$w_{\text{BC}_2} = \frac{4\varepsilon}{l_{\text{link}}} \sum_{m=m_{\text{CD}}+1}^{m_{\text{CD}}+m_{\text{BC}}} \left(\frac{b_0^{12}}{b_m^{12}} - \frac{2b_0^6}{b_m^6} \right) \Delta y - w_0 \frac{l_{\text{BC}}}{l_{\text{unit}}}, \qquad (7)$$

where ε is the depth of the potential pit in the Lennard–Jones potential between segments of adjacent chains,

$$w_0 = -\frac{4\varepsilon l_{\text{unit}}}{l_{\text{link}}}$$

is Lennard–Jones potential at $b_m = b_0$.

At the CD section, the energy was calculated using the formula

$$w_{\text{CD}} = -\psi l_{\text{CD}}, \qquad (8)$$

where the parameter ψ characterizes the adsorption force of a single section of the chain. The ratio between the lengths l_{AB} and l_{DC} is determined from the Boltzmann distribution.

Thus, the potential energy of the nth polymer chain inside the associate can be calculated using the formula

$$w_n = w_{\mathrm{AB}_n} + w_{\mathrm{BC1}_n} + w_{\mathrm{BC2}_n} + w_{\mathrm{CD}_n}. \tag{9}$$

The entropy of the nth chain was calculated using the Clausius formula

$$S_n = \int_0^T \frac{dw_n}{T}. \tag{10}$$

$$(b - \mathrm{const})$$

As it was shown in Ref. [7], the integral (10) is improper and for its calculation, the potential energy (9) can be approximated as a function

$$w_n = \alpha_0 \exp(-\beta_0 T^2) + \alpha_1 T^2 \exp(-\beta_1 T^2)$$
$$+ \alpha_2 T^2 \exp(-\beta_2 T^2), \tag{11}$$

where α_i and β_i are the expansion coefficients.

Then the free energy of the nth chain

$$f_n = w_n - TS_n. \tag{12}$$

The free energy of the associate can be obtained by summing the free energies of all polymer chains located inside it

$$F = \sum_{n=1}^{N} f_n. \tag{13}$$

The dependence of the reduced free energy of the associate on its width λ during the formation of the coating is shown below. The calculations were performed using the Metropolis algorithm. The model is applicable in cases where the size of the defects is commensurate with the thickness of the coating.

4. The effect of the size of artificial defects on the morphology and mechanical properties of the polymer coating

The minimum of the reduced free energy in Figure 2 determines the width of the surface wrinkles λ_0 of the finished coating. Figure 3 shows the dependence of the width of wrinkles λ_0 on the diameter of the defect. The graph also shows experimental points for polyester enamel obtained using images from a digital optical microscope (see Figure 1, a), which correspond well to a solid line at $V_0/K^{\mathrm{bend}} = 7$. It can be noted that for a solid line in the area from 10 to 30 μm, the size of the wrinkle corresponds to the size of the granule, which means that small granules are completely inside the associate and have negligble effect on the formation of wrinkles. It is important to note that the expressions used below and the dependencies obtained with their help give the correct result, provided that the diameter of the granule is comparable to the thickness of the coating.

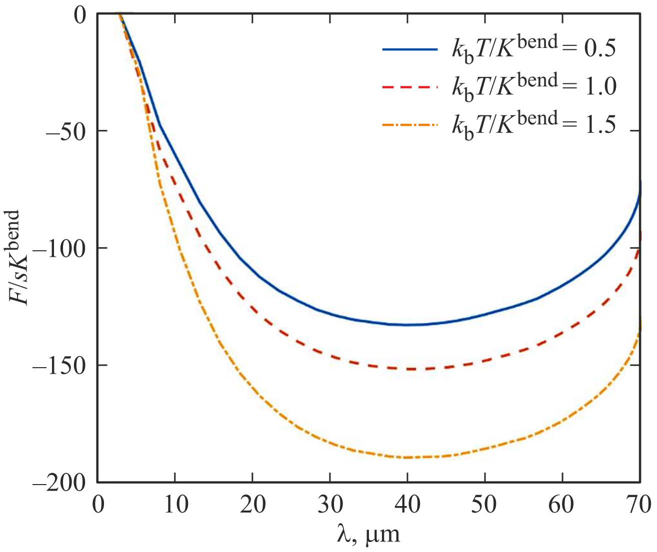

Figure 2. Dependence of the reduced free energy of the associate on its width λ during coating formation, k_b is the Boltzmann constant, s is the area occupied by the associate on the granule, $\frac{v_0}{K^{\mathrm{bend}}} = 7$, $\frac{\psi}{K^{\mathrm{bend}}} = 0.1$, $d = 70\,\mu$m.

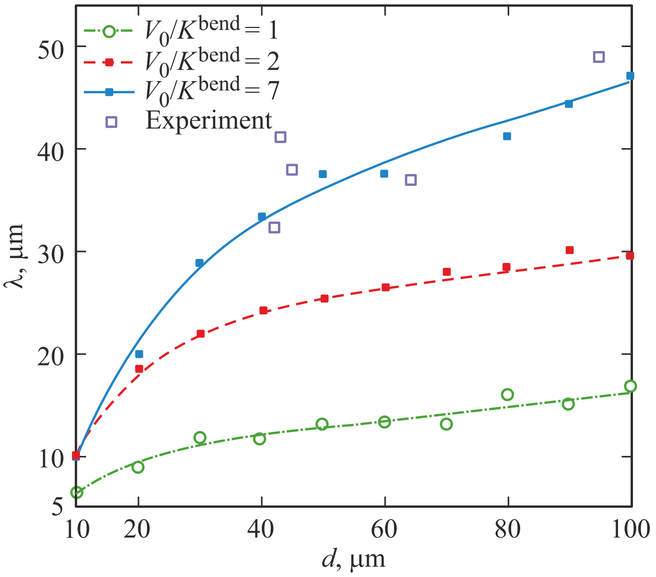

Figure 3. Dependence of the width of the associate λ_0 on the diameter of the granule d on which it is adsorbed, $\frac{\psi}{K^{\mathrm{bend}}} = 0.1$, $\frac{k_bT}{K^{\mathrm{bend}}} = 1$.

The geometry of the surface structures is completely determined by the mechanical properties of the coating, which means that such mechanical characteristics as the Young's modulus can be restored by the size of the wrinkles.

As shown in Ref. [8], the ratio of the Young's modules of the coating E_s and the base (primer) E_f is determined by

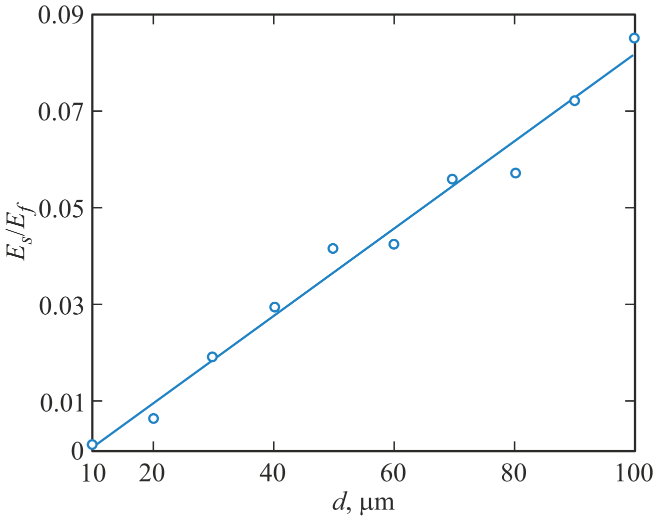

Figure 4. Dependence of the ratio E_s/E_f on the diameter of the granules d, $\frac{\nu_0}{K^{\text{bend}}} = 7$, $\frac{\psi}{K^{\text{bend}}} = 0.1$, $\frac{k_bT}{K^{\text{bend}}} = 1$, $h = 25\,\mu$m, $\nu_s = 0.33$, $\nu_f = 0.38$.

the expression

$$\frac{E_s}{E_f} = \frac{3(1-\nu_s^2)}{(1-\nu_f^2)}\left(\frac{\lambda_0}{2\pi h}\right)^3, \tag{14}$$

where h is the thickness of the polymer coating, ν_s and ν_f is the Poisson coefficients of the polymer coating (≈ 0.33) and the primer (≈ 0.38) accordingly.

During the formation of wrinkles, the degree of polymerization of the coating is less than that of the finished product, so the coating has some mechanical mobility during formation. The degree of polymerization of the finished coating is higher, which is why the value of its Young's modulus will be slightly higher than that obtained using the expression (14). The increase in the Young's modulus of the coating as a result of an increase in the degree of polymerization at the last stages of coating formation can be considered small, since long macromolecules participate in the formation of associates, which means that the degree of polymerization at this point is already quite high. Thus, the expression (14) can also be used in the case of a finished coating.

An increase in the Young's modulus as a result of a decrease in temperature mobility during cooling of the coating can also be neglected, since polymer primers (polyester, epoxy and acrylate) are mainly used in production, the temperature dependences of which differ slightly from those of the coating, which means the ratio of Young's modules of the coating and the base E_s/E_f weakly depends on temperature.

Figure 4 shows the dependence of the ratio E_s/E_f on the diameter of the defects. As can be seen from the dependence, the ratio E_s/E_f increases with increasing defect size. The primer layer does not interact with the granules, from which it can be concluded that the ratio of the Young's modules of the coating and the primer increases due to the growth of the Young's modulus of the coating itself. The nucleation of corrosion centers occurs in the cracks of the coating. As the Young's modulus increases, internal stresses increase and the coating becomes more susceptible to cracking, which means its corrosion resistance decreases. Thus, the optimal size of granules is about $30-40\,\mu$m (with coating thickness of $25\,\mu$m), since granules with size up to $30\,\mu$m practically do not affect the formation of wrinkles, and as the size of the granules increases, the corrosion resistance of the product decreases.

5. Conclusion

The study showed that increasing the size of crystalline granules of polymer paints leads to a linear increase in the Young's modulus of the coating. As the Young's modulus increases, internal stresses also increase, which makes the coating more susceptible to cracking and its corrosion resistance decreases. Thus, the use of crystalline granules of a larger fraction reduces the anticorrosive properties of polymer coatings.

Conflict of interest

The authors declare that they have no conflict of interest.

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