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Spinodal Architecture of Epoxy-Phenolic Compositions

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Using electron microscopy, the phase separation in polymer composite coatings obtained on tinplate by thermal curing of an equimolar mixture of epoxy (EO) and phenol-formaldehyde (PO) oligomers in ethylcellosolve was studied, while varying the amount of orthophosphoric acid that chemically interacts with EO and PO. The conditions for the formation and characteristics of the spinodal architecture of epoxy-phenolic compositions, which are clusters of two interconnected phases enriched with EO and PO curing products, respectively, are discussed. It has been shown that the spinodal decomposition of a mixture containing EO in the form of monophosphates can initiate the formation of an internal percolation cluster of cross-linked EO molecules in the composition. The fractal microstructure provides high adhesion strength and chemical resistance to the coating.

Keywords: epoxy-phenolic protective coatings, electron microscopy, phase separation, fractal clusters, spinodal decomposition.

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1. Introduction

Protective coatings are created on metals by using epoxy-phenolic compositions that are formed by common thermal curing of a mixture of epoxy (EO) and phenol-formaldehyde (PO) oligomers in a solvent [1,2]. They combine properties of EO and PO curing products separately. It is known that solid epoxy resins are good dielectrics and have high adhesion to many materials and resistance to effects of aggressive media. In turn, PO-based products have good chemical resistance and hardness, but are inferior in elasticity [2]. Therefore, it is technologically important to adjust a structure of cross-linked polymer compositions when selecting a component mating method. This task is especially interesting in a theoretical aspect as well due to poor compatibility of the EO and PO oligomers in a solution.

In order to improve compatibility of the components, before production of epoxy-phenolic compositions according to the standard recipe, it is customary to carry out precondensation of the solution of the EO and PO mixture by mixing for 60−120 min at the temperature of $T = 393$ K. The final state of the process includes introduction of an active additive — orthophosphoric acid (PhAc) that facilitates mixture curing [1–4]. This precondensation method rigidly fixes the mixture formulation and is also characterized by long time and high energy consumption.

It is known that precondensation has no chemical interaction between EO and PO, but rather varies a composition and number of oligomer molecule aggregates [1,3,4]. Structure-kinetic aspects of this process were investigated in the studies [3–5]. As a result, a non-monotonic type was detected for kinetic curves of variation of viscosity η in time t in a shear flow of the solutions. It was shown that a progress of the curves $\eta(t)$ depended on a molar ratio of the components $n_1(\mathrm{EO})/n_2(\mathrm{PO})$, a shear rate g and a temperature T [3,5]. With a time increase, a decrease of viscosity is usually observed, which is replaced by a subsequent increase that transits to saturation [3,4]. According to data of the study [3], Figure 1 shows the curve $\eta(t)$ of variation of viscosity of the solution during precondensation of the EO and PO mixture when preparing a lacquer ER-547 [6]. A minimum of the curve $\eta(t)$ when $t \sim 120$ min (Figure 1) corresponds to a minimum particle size and determines an optimal time of precondensation [4] for producing the most uniform chemical network of the cross-linked polymer. According to data of electron microscopy (EM) [3], a density of such a network fluctuates at a scale of about 50 nm. When $t > 120$ min, processes of particle enlargement occur in the solution [4] and effects of phase separation are enhanced, thereby resulting in formation of an inhomogeneous topological structure of compositions.

It is important to note that it is usually not recommended to introduce additives that facilitate particle association into the solution during precondensation as per a classical scheme [4]. For example, PhAc and EO can easily chemically interact with each other to form joining products of a linear and branched structure [7,8] up to cross-linked gels [8]. Therefore, in presence of PhAc a cluster structure of the solution is transformed and its viscosity significantly increases. For this reason, it is proposed to exclude PhAc use during precondensation and storage of solutions of the EO and PO polymer mixture [4]. It should also be said that PhAc and PO also react chemically with each other. However, a possible mass increment of particles being

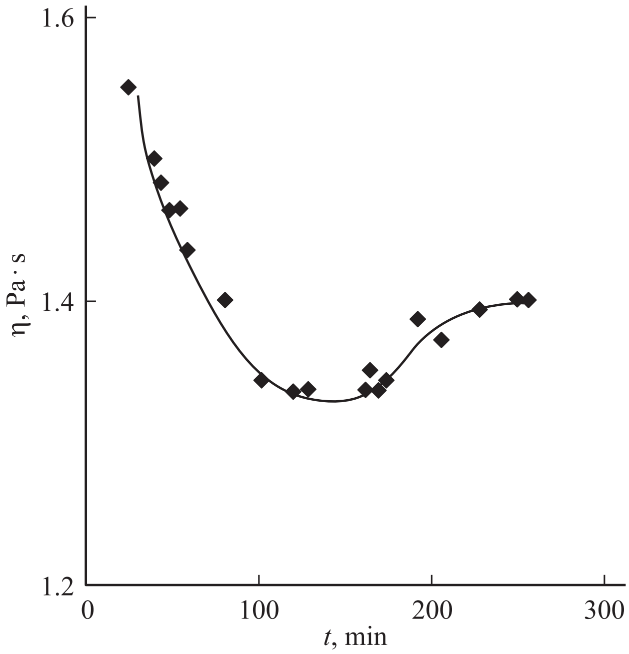


Figure 1. Kinetic curve of variation of viscosity η of the EO and PO mixture in time t of precondensation. The mixture is prepared by the standard formulation of the lacquer ER-547. The oligomer ratio is $n_1(\mathrm{EO})/n_2(\mathrm{PO}) = 0.6$. The shear rate $g = 81\,\mathrm{s}^{-1}$, the temperature $T = 393\,\mathrm{K}$. According to the study [3].

formed when doing so is insignificant as compared to the reaction between PhAc and EO [9].

The study [10] has in detail investigated the dependences $\eta(t)$ when introducing PhAc into a solution of the equimolar oligomer mixture at the initial stage of precondensation. A PhAc concentration c that is to be calculated by the equation $c = n_3/(n_1 + n_2)$ using mole numbers of the components $n_1(\mathrm{EO})$, $n_2(\mathrm{PO})$ and $n_3(\mathrm{PhAc})$ varied within a wide interval of the values $c = 0{-}0.6$ [10]. This interval by more than an order overlaps the value $c = 0.05$ that is usually used for curing the compositions [4].

According to the study [10], Figure 2 shows the curves $\eta(t)$ of variation of viscosity of the solutions during precondensation of the EO and PO mixture with a various content of the PhAc active additive. Without PhAc (Figure 2, the curve *1*) the curve $\eta(t)$ has a minimum around the value $t = 25$ min, which is followed by an increase of viscosity at a decelerating rate. From this point of view, the curve *1* and the curve $\eta(t)$ in Figure 1 are similar to each other, while differences between them are caused by a difference in values of the molar oligomer ratio and the temperature.Introduction of PhAc into the oligomer mixture fundamentally changes the curves $\eta(t)$ (Figure 2, the curves *2–4*). In this case, the curves $\eta(t)$ have a maximum when $t \sim 30$ min, if the PhAc concentration in the oligomer mixture c $(n_1/n_2 = 1)$ satisfies the interval of the values $c = 0.07{-}0.20$. The maximum is followed in a time scale by a drop of viscosity within the limits from 2% $(c = 0.07)$ to 5% $(c = 0.20)$, and after that viscosity either reaches a limit value $(c < 0.17)$ or increases again $(c > 0.17)$. Within the range of the values $0 < c < 0.07$ there is no maximum on the curves $\eta(t)$ [5] and with an increase of t the viscosity increase stage transits into a saturation stage.

Important information about the PhAc role in the precondensation process is provided by kinetic dependences of „excessive" viscosity $\Delta\eta$ of the solutions of the oligomer mixture (Figure 3). The value of $\Delta\eta$ is a difference between values of viscosity of the solutions that contain the PhAc additive and without it (a reference solution).

The curves $\Delta\eta(t)$ obtained when varying the PhAc concentration c in the solution of the oligomer mixture have a non-monotonic type with the maximum when $t_{\max} = 25{-}40$ min. A point of the extremum lies in the upper half-plane of the graphs of the functions $\Delta\eta(t)$. It means that with PhAc, at the initial stage of precondensation viscosity of the solution increases and exceeds viscosity of the reference solution in the point of the maximum. It agrees with an increase of the particle size [4]. However, after reaching the maximum viscosity drops sharply and the value of $\Delta\eta$ becomes negative, which means reduction of viscosity as compared to the reference solution and indicates deep structural changes induced by chemical transformations in the solution [7,8].

The maximum on the kinetic curves $\eta(t)$ and $\Delta\eta(t)$ and a subsequent sharp drop of viscosity when $t > t_{\max}$ are features of a non-equilibrium phase transition of ordering during self-organization of a particle ensemble, which occurs in the solution of the component mixture [11]. A mechanism of this transition predetermines a behavior of viscosity at long times of precondensation (see Figure 2 and 3). Special interest is paid to relaxation of viscosity when it drops to a certain limit value (Figure 2, the curves *2* and *3*; Figure 3, the curves *1* and *2*). Reaching the limit value of viscosity indicates establishment of a quasistationary equilibrium between the molecule aggregates in the solution of the oligomer mixture. At the same time, both limit viscosity itself and its establishment time depend on the PhAc content, reaching the maximum at the dimensionless PhAc concentration $c \sim 0.13$ (Figure 2, the curve *3*). The time of reaching the stable value of viscosity shall be considered as an optimal time of formation of a precondensate solution before its curing. Reaching kinetic stability of the component mixture, reduction of time and energy consumption are main advantages of using P at the initial stage of the precondensation process. However, these advantages are available when strictly controlling the composition and viscosity of a working solution [10].

Explaining the kinetic dependences $\eta(t)$ without and with PhAc in the solution of the oligomer mixture requires different approaches. The minimum on the curve $\eta(t)$ (Figure 2, the curve *1*) can be interpreted as a result of superposition of processes of decomposition and formation

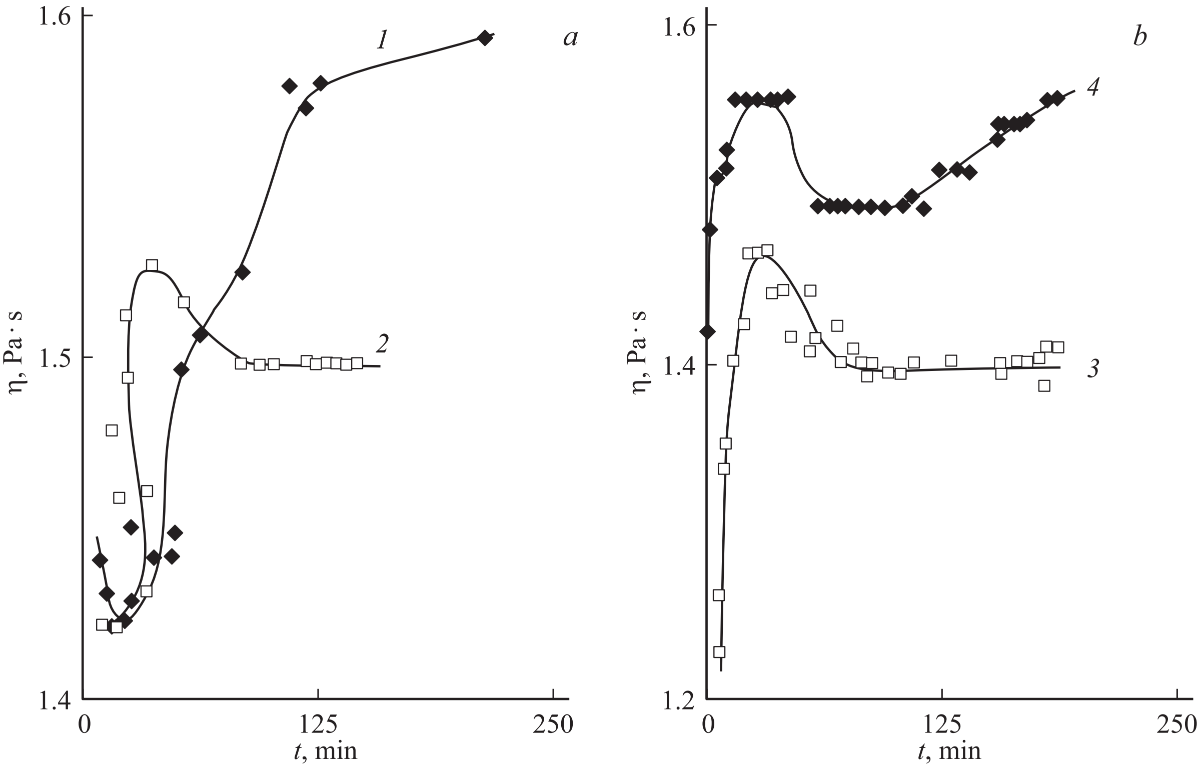


Figure 2. Kinetic curves of variation of viscosity η of the EO and PO mixture in time t of precondensation. The oligomer ratio is $n_1(\mathrm{EO})/n_2(\mathrm{PO}) = 1$. The shear rate $g = 81\,\mathrm{s}^{-1}$, the temperature $T = 333\,\mathrm{K}$. The PhAc content: $c = 0$ (*1*), 0.09 (*2*), 0.13 (*3*) and 0.20 (*4*). According to the study [10].

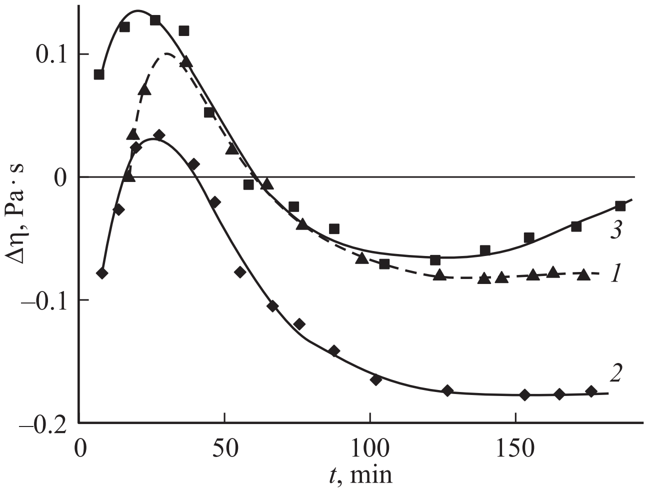


Figure 3. Influence of PhAc on „excessive“ viscosity $\Delta\eta$ of the EO and PO during precondensation. $n_1(\mathrm{EO})/n_2(\mathrm{PO}) = 1$. The PhAc content: $c = 0.09$ (*1*), 0.13 (*2*) and 0.20 (*3*). According to the study [10].

of molecule aggregates of the various type [3], while explanation of the maximum (Figure 2, the curves *2–4*) shall concern processes of self-organization of the particle during phase separation that is observed [10] after thermal curing of polymer coatings.

Phase separation in the solution of the EO and PO mixture can be induced [12] by competitive chemical interactions of PhAc with the oligomers during origination of areas that are highly different in particle mobility. In this case, the mechanisms of separation shall be predetermined according to the study [12] by a depth of a chemical transformation and depend on the time of precondensation t and the PhAc concentration c.

The study [10] used the EM method to detect various types of phase separation in a space chemical network of the polymer coatings produced on tinplate during thermal curing of the precondensate of the EO and PO mixture with the different PhAc concentration c. The time of precondensation was 120 min, i. e. it was optimal according to rheokinetics data for the recommended value $c \sim 0.13$ (Figure 2 and 3). With a decrease of the parameter c, gradual enhancement of the effects of phase separation in the coatings is traced according to the study [10]. Relative excess of PhAc ($c > 0.2$) in the solution of the oligomer mixture results in formation of separate inclusions in the polymer matrix — nanoclusters of the cross-linked PO molecules. The interval $0.04 < c < 0.2$ corresponds to a microphase structure of the coatings, while without PhAc the polymer composition extended, mutually independent portions of the phases enriched with the EO and PO curing products, respectively [10]. It is important to note that in the study [10] the samples of the polymer compositions were structurally analyzed by digitally processing surface images at the scale $R < 1.5\,\mu$m. Since the real scale of nonuniformities in some samples is several micrometers, the previously obtained results can not fully represent evolution of the microstructure of the polymer compositions when the PhAc content is changed in the oligomer mixture.

We also note that the later study [13] detected a non-monotonic dependence of full surface energy γ of the polymer coatings on the parameter c, which is to be explained, wherein the minimum of γ corresponds to the value $c \sim 0.13$ and agrees with maximum values of adhesion strength and chemical resistance of the coatings [14].

The present study has in detail investigated structural aspects of phase separation in the samples of the epoxy-phenolic compositions produced in the study [10]. The present study is aimed at explaining non-monotonic variation of the properties of the samples as the effects of phase separation are enhanced in them, which is caused by chemical reactions in the precondensate solutions of the oligomer mixture. For this purpose, we have obtained correlation functions of the density-density type for phase clusters in the scale range $0.5-4\mu$m, studied indicatrices of distribution of a microphase density and calculated parameters of the microstructure of the polymer compositions.

2. Experimental procedure

The study used resin samples: epoxidian E-05 (EO) with an epoxy number of 1.8 and phenol-formaldehyde (PO) based on diphenylpropane and formaldehyde (produced by „Pigment“ Russia) with the number average molecular weight of 2850 and 1030, respectively. Based on the equimolar oligomer mixture, we prepared an ethyl cellosolve solution of the 20 % concentration that corresponds to formation of a fluctuation network of particle entanglements [5]. The solution was precondensed, i. e. the solution was stirred vigorously at $T = 333$ K in presence of PhAc. The time of precondensation was 120 min. PhAc was introduced into the solution at the initial moment of precondensation. The dimensionless PhAc concentration varied within the range $c = 0-0.6$.

The polymer composite coatings on tinplate, which had the thickness of $4-6\,\mu$m, were formed by spraying the precondensate solutions onto a substrate with their subsequent curing in air for 10 min at $T = 483$ K.

The microstructure of the polymer coatings was studied by means of an electron-microscopic method of decorating the sample surface with silver chloride nanoparticles created during vacuum thermal sputtering [15]. Two-dimensional images of carbon replicas were digitally statistically analyzed for interparticle distances in ensembles with at least 8000 nanoparticles per an area of $\sim 80\,\mu\mathrm{m}^2$. Space correlations of the density-density type were studied using radial functions $g(R)$ and the indicatrices of the relative density of distribution of the nanoparticles according to procedures of the studies [16,17].

3. Results and their discussion

The silver chloride-decorated surface of the polymer coatings has areas of localization of fractions of fine (of the size 20–30 nm) and large (of the size 150–500 nm) AgCl particles (Figure 4). A heterogeneous surface microstructure causes various strength of binding of the nanoparticles with functional groups of the cross-linked polymer [16]. Quinone methide groups that are formed when the compositions are cured in presence of PO contribute to reduction of silver chloride to metal silver nuclei — centers of growth of quite large AgCl particles. Clusters or ensembles of the finer AgCl particles represent a phase enriched with the cross-linked EO molecules.

Without PhAc, during precondensation of the solution of the oligomer mixture the composition curing process results information of extended areas of localization of the two phases which are separately cross-linked EO and PO (Figure 4, *d*). Relative excess of PhAc ($c \geq 0.2$) in the solution results in formation of the chemical network of the epoxy-phenolic composition with clearly limited inclusions of nanoclusters of the PO-oligomer curing products. The nanoclusters have an almost spherical form and the size 400–600 nm (Figure 4, *a*). Since continuity of the polymer matrix is undisturbed, then it can be concluded that nanoclusters are formed as per a mechanism of nucleation and growth in the precondensate solution of the oligomer mixture [18].

With a decrease of the PhAc content to the critical value $c^* \sim 1/6$ the polymer composition gets a labyrinth structure due to phase separation in the solution (Figure 4, *c*). This structure is formed by interrelated clusters of the two phases, whose correlation length ξ is several micrometers. The magnitude ξ by more than order exceeds a hydrodynamic radius of the molecule aggregates in the solution of each of the two oligomers [3]. This architecture of the composition is typical for spinodal decomposition in a binary system [19] and formed during precondensation of the solution of the oligomer mixture when the solution reaches limit viscosity (Figure 2, the curves *2* and *3*).

Transition to the mode of spinodal decomposition of the component mixture at the critical value $c^* \sim 1/6$ is explained by variation of a structure of the PhAc and EO adducts. In the equimolar oligomer mixture, the value $c^* \sim 1/6$ corresponds to the condition $n_3/n_1 \sim 1/3$, at which three EO molecules are per one PhAc molecule. Since all the three PhAc hydroxyl groups can react with the EO epoxy groups, then a reaction of formation of EO trisubstituted monophosphate occurs in the solution as per

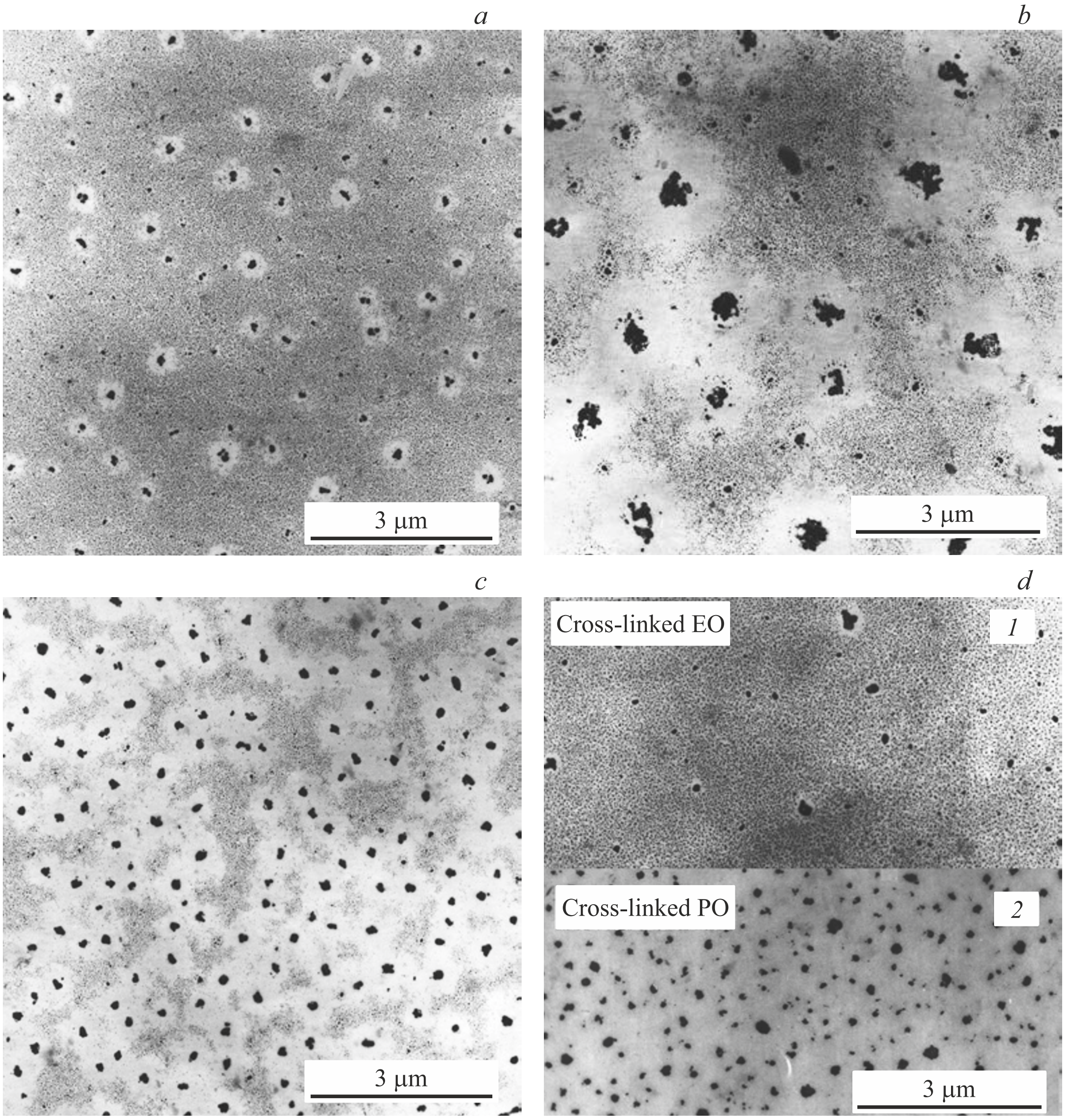
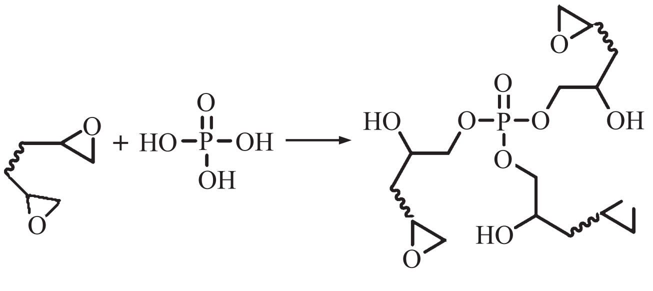


Figure 4. Electron microphotographs of the silver chloride-decorate surface of the samples of the polymer coatings on tinplate. The PhAc content: $c = 0.20$ (*a*), 0.13 (*b*), 0.09 (*c*) and 0 (*d*). The panel *d*: (*1*) and (*2*), includes surface fragments that belong to the EO and PO curing products, respectively.

the scheme [8]:



Triether can be subjected to hydrolysis with formation of di- and mono-ethers [8]. When $c > c^*$, the solution contains EO highly branched oligophosphates with a high molecular weight [4].

It complicates microphase separation in the oligomer mixture and curing of the mixture results in formation of the dense chemical network of the polymer. This space network has lower adhesion to the substrate and higher internal stresses that result in reduction of protective characteristics of the polymer coating [20].

Spinodal decomposition of the component mixture provided that $c < c^*$ makes a process of structure formation of the cross-linked polymer very sensitive to variation of the composition, concentration of the solution and the thickness of the polymer layer [16] as well as a nature of the substrate [13].

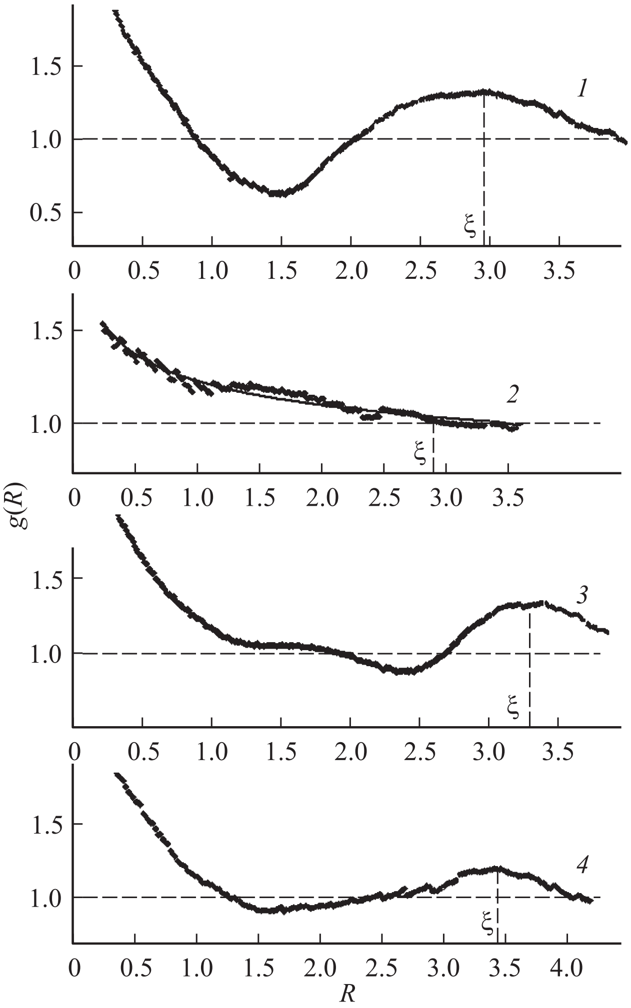


Figure 5. The radial distribution functions $g(R)$ of the density–density type for the clusters of the phase enriched with the EO curing products. The polymer coatings are produced from the precondensate solutions of the oligomer mixture in the mode of spinodal decomposition. A step of surface image scanning is $0.1\,\mu$m. The PhAc content: $c = 0.17$ (*1*), 0.13 (*2*), 0.09 (*3*) and 0.04 (*4*).

Figure 5 shows „coarse-grained" radial functions [17] $g(R)$ of distribution of the density of ensembles of the decorating nanoparticles ρ on the surface of the samples of the polymer coatings produced in the mode of spinodal decomposition of the component mixture within the parameter value range $c = 0.04-0.17$. The functions $g(R)$ belong to the clusters of the phase enriched with the epoxy component curing products.

The density ρ fluctuates and generally its fluctuations result in non-monotonic variation of the functions $g(R)$ as the scale R grows. At the same time, the correlation functions $g(R)$ have a maximum (Figure 5, the curves *1, 3* and *4*), which is typical for the materials with a so-called „spinodal" architecture [21]. A position of the maximum corresponds to a period ξ of space modulation of the density of the phase clusters. The value of ξ is within the interval $3-3.5\,\mu$m, while a ratio of areas of the phase clusters is $2:3$ in favor of the phase with predominance of the cross-linked PO molecules.

A series of the samples of the polymer coatings has a prominent sample that has a topological structure different from the others. This sample corresponds to the PhAc content in the mixture $c = 0.13$ (Figure 4,*b*). In this case, the correlations of the density–density type are described by the function $g(R)$ that decreases as per a power law $g(R) \infty R^{D-2}$ for fractal objects with fractal dimensionality D [22] (Figure 5, the curve *2*). The value of D is 1.86 ± 0.03 and close to dimensionality of an internal percolation particle cluster in the two-dimensional space ($D = 91/48$) [22]. A body of this cluster is formed by the cross-linked EO molecules, while cavities are filled with the PO curing products. At the same time, the ratio of the phase areas is $3:2$ and reverse in relation to the reference samples. This phase inversion in favor of the composite's epoxy component is energetically favorable, since a degree of self-association of the EO molecules in ethylcellosolve by two orders higher as compared to PO [3]. The energetically favorable phase configuration explains a minimum value of full surface energy γ of this polymer coating in a number of the studied ones [13].

The fractal structure of the epoxy-phenolic composition at the scale ξ is characterized by isotropic distribution of the density of the phase clusters. It is indicated by indicatrices of relative variation of the density of distribution of the decorating particles $\Delta\rho/\rho$ (Figure 6). Axial surface texture that usually accompanies microphase separation in the coating samples (Figure 6, the curves *1, 3, 4*) is fully absent in this case (Figure 6, the curve *2*).

Formation of the fractal structures during spinodal decomposition is not mandatory. However, in an area of transition through the spinodal dynamic fractal structures [24] can occur due to self-organization of the phase clusters [23]. Stability of such structures can significantly increase in a dependence on the composition of the phases and a ration of the volumes as it is in the case in question.Due to their unique mechanical properties, „spinodal" structured materials are intensely studied recently [21,25].

An important circumstance is interrelation of the PhAc content in the precondensate solution of the oligomer mixture and the density of the epoxy component phase in the polymer composition. It is indicated by the influence of a control parameter c on the density of a quasi-lattice of decorating particles correlated to areas of localization of the cross-linked EO molecules. A type of the quasi-lattice is determined by a coordination number m and the most probable distance r between the particles. The values of m and r to be specified by an area and position of the peak of the function $2\pi\rho R g(R)$ of radial particle distribution (Figure 7) make it possible to calculate the density of the quasi-lattice [26].

It is calculated to show that within the interval $0.04 < c < 0.2$ of the values of the parameter c (in the mode of spinodal decomposition of the component

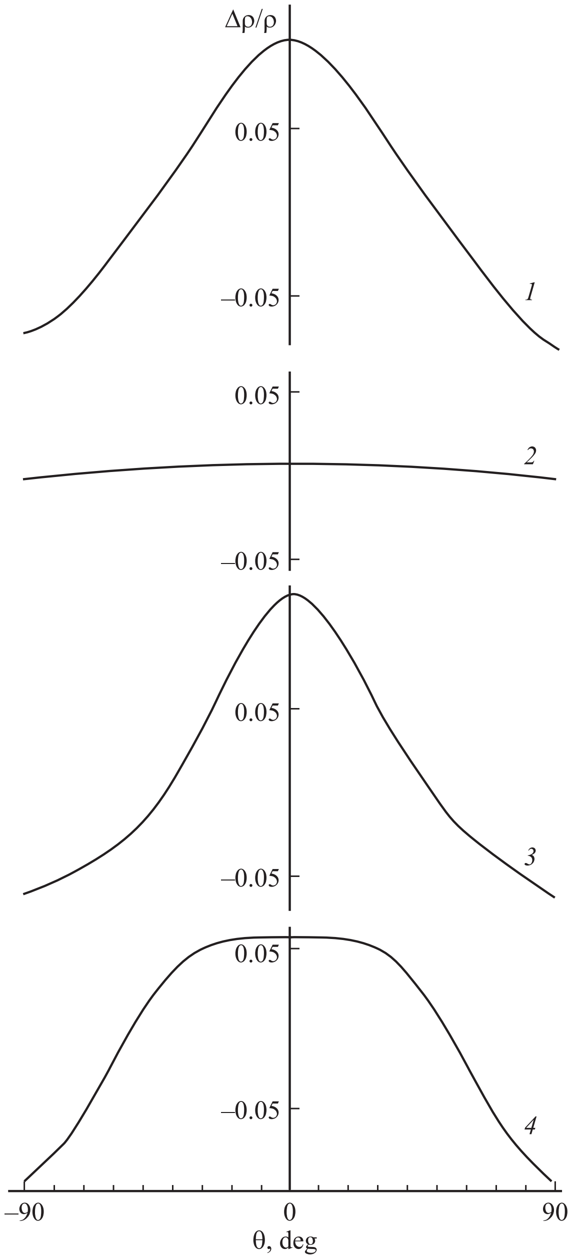


Figure 6. Indicatrices of relative variation of the (in relation to the surface-average) density of the AgCl nanoparticles $\Delta\rho/\rho$ on the surface of the samples of the polymer coatings. The polymer coatings are produced from the precondensate solutions of the oligomer mixture in the mode of spinodal decomposition. The PhAc content: $c = 0.17$ (*1*), 0.13 (*2*), 0.09 (*3*) and 0.04 (*4*). The axis of ordinates ($\theta = 0$ deg) corresponds to a film texture axis — the direction with a maximum value of ρ.

mixture) the phase of the cross-linked EO is matched in the compositions with isomorphic square quasi-lattices of the decorating particles with the same coordination number $m \sim 4$ at the different translation step r (Figure 7,*b, c*). When $c < 0.04$ and $c > 0.17$, there are quasi-lattices of the hexagonal type ($m \sim 6$) with the various local density of the particles (Figure 7,*a, d*). The density of the quasi-lattices of the decorating particles in the samples of the coatings was compared so as to allow estimating the values of the relative density ρ_r of the clusters of the phase of the cross-linked EO in a dependence on the PhAc content c in the composition. In relation to the reference sample of the coating ($c = 0$) the magnitude ρ_r oscillates along the scale of the parameter c and within the interval $0.04 < c < 0.2$ it varies in strict compliance with limit viscosity η of the precondensate solution of the oligomer mixture (Figure 8). It is a sign of stability of the molecule clusters when the compositions are formed. As expected, a global minimum of the function $\rho_r(c)$ corresponds to a fractal microstructure

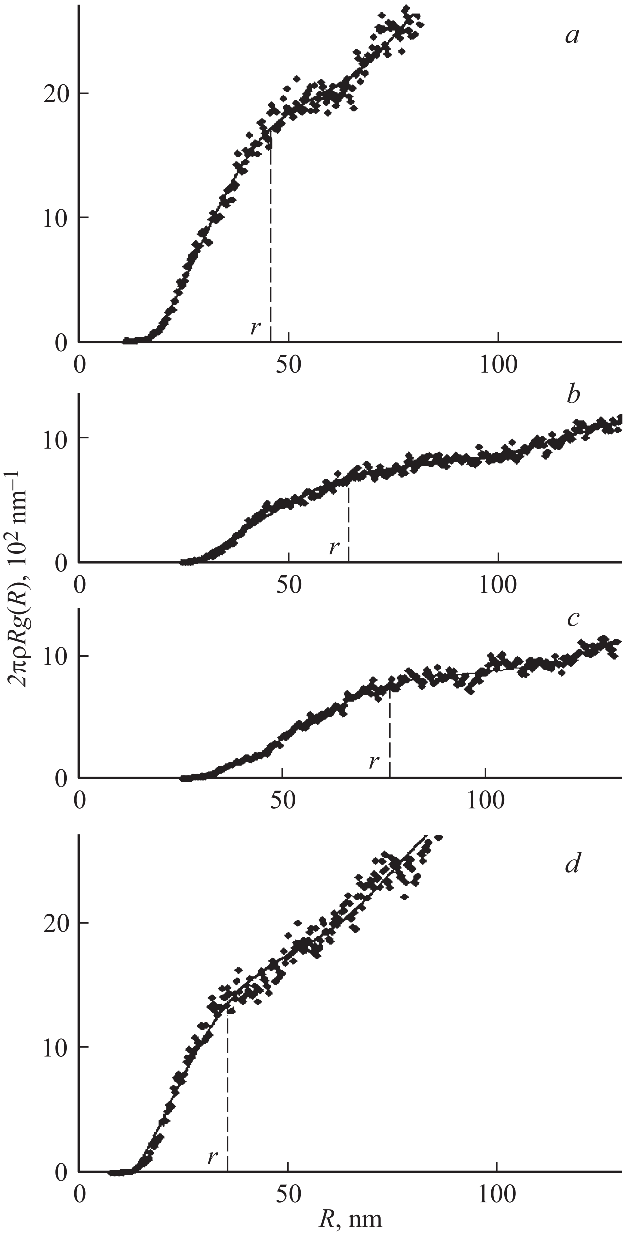


Figure 7. Functions of radial distribution of the decorating particles for the clusters of the phase enriched withe the EO curing products. An step of surface image scanning is 6 nm. The PhAc content: $c = 0$ (*a*), 0.04 (*b*), 0.13 (*c*) and 0.2 (*d*).

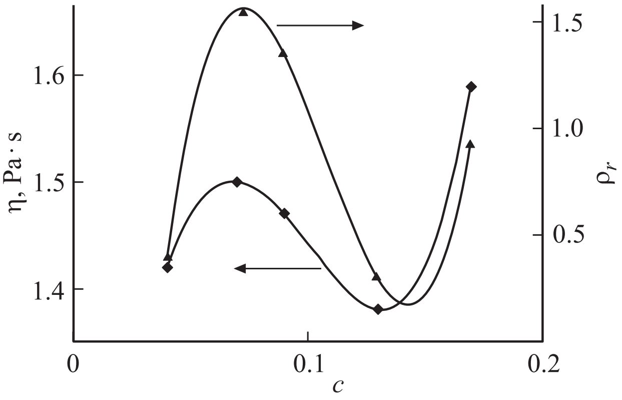


Figure 8. Dependences of the relative density ρ_r (in relation to the reference sample of the coating produced without PhAc) of the phase of the cross-linked EO in the composition and limit viscosity η of the precondensate of the oligomer mixture on the parameter c.

and a minimum of full surface energy of the polymer coating.

4. Conclusion

The present study changes traditional representations [4] about a rigid connection between the homogeneous topological structure and the improved operating properties of the epoxy-phenolic protective coatings. The obtained results show that high values of adhesion strength and chemical resistance are attributed to microheterogeneous compositions of the type of interrelated clusters of the two phases enriched with the EO and PO curing products, respectively. In this case, the length ξ of the space correlations of the „density–density" for the phase clusters is several micrometers and by more than an order exceeds the value of ξ of fluctuations of the density in the single chemical network of the cross-linked epoxy-phenolic polymer [3,4]. Periodicity of distribution and anisotropy of the density of the phase clusters allow us to speak about the so-called „spinodal" architecture of the compositions. This method of mating the composition components is achieved when adding PhAc into the solution of the oligomer mixture at the initial stage of the precondensation process under control of the molar ratio of the components and variation of viscosity of the solution in time.

When interacting with the oligomer molecules in the solution, the active additive PhAc selectively reduces mobility of the particles being formed when doing so and thereby it can structure the component system by the type of spinodal decomposition of the binary liquid. During precondensation the non-equilibrium phase transition (spinodal decomposition) results in reduction of viscosity of the solution to a time-stable limit value. Possibility and duration of this transition of ordering significantly depend on the amount c of the PhAc additive.

When varying the control parameter c, various mechanisms of phase separation in the precondensate solution of the oligomer mixture are realized, thereby causing nonmonotonic variation of the properties in a number of the samples of the formed epoxy-phenolic compositions.

The critical value $c^* \sim 1/6$ of the dimensionless PhAc concentration c corresponds to predominant formation of the EO monophosphates in the solution of the equimolar component mixture, thereby enabling formation of the internal percolation cluster of the EO cross-linked molecules in the epoxy-phenolic composition. The cavities of this cluster are filled with the PO curing products. The fractal topological structure of the chemical network of the cross-linked polymer provides the extremum of the coating properties, in particular, the minimum of full surface energy [13] as well as the maximums of adhesion strength and chemical resistance [14].

Conflict of interest

The author declares that he has no conflict of interest.

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