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ВПЛИВ ПОЛІВІНІЛХЛОРИДУ НА ХІМІЧНУ СТІЙКІСТЬ ПОЛІЕСТЕРНИХ КОМПОЗИТІВ

Досліджено вплив полімерного модифікатора – полівінілхлориду на хімічну стійкість поліестерних композитів. Встановлено вплив компонентного складу та природи неорганічного дрібнодисперсного наповнювача на стійкість поліестер-полівінілхлоридних матеріалів до дії агресивних середовищ. Виявлено, що введення дрібнодисперсних наповнювачів у поліестерну матрицю призводить до зростання коефіцієнта дифузії середовища у досліджувані матеріали. На підставі електрохімічних досліджень виявлено, що введення наповнювачів, зокрема $CaCO_3$ та Al_2O_3 у модифіковану поліестерну матрицю, призводить до підвищення антикорозійних властивостей матеріалу.

Ключові слова: поліестер, полівінілхлорид, модифікування, водопоглинання, хімічна стійкість, покриття.

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THE INFLUENCE OF THE POLY(VINYL CHLORIDE) ON THE CHEMICAL STABILITY OF POLYESTER COMPOSITES

The influence of the polymeric modifier – poly(vinyl chloride) on the chemical stability of polyester composites was investigated. The influence of component composition and nature of inorganic finely dispersed filler on the stability of polyester-poly(vinyl chloride) materials to the action of aggressive media was established. It was found that the introduction of finely dispersed fillers into a polyester matrix leads to an increase of the medium diffusion coefficient into the investigated materials. On the basis of electro-chemical studies it was found that the introduction of fillers in particular $CaCO_3$ and Al_2O_3, into a modified polyester matrix leads to an increase of the anticorrosive properties of the material.

Key words: polyester, poly(vinyl chloride), modification, water absorption, chemical resistance, coating.

Problem statement. The effectiveness of the use of polymer composite materials on the basis of unsaturated polyester for polymeric concrete, bulk floor, artificial stone, adhesives, sealants and protective coatings is largely determined by their resistance to aggressive media and high temperatures [1, 2].

Polyester materials are characterized by high resistance to high temperatures and chemically aggressive media. However, in tough conditions of exploitation under the effect of dynamic loads in the presence of chemical reagents such materials lose up to 70 % of physical and mechanical characteristics [3]. To eliminate this effect the polyester materials are subjected to physical methods of modification, in particular, the combination with high-molecular compounds of different nature.

Analysis of recent research and publications. Modification of polyester composites by applications of different nature, in particular organic and mineral, promotes the increase of physical-mechanical and techno-operational parameters, primarily the chemical resistance and anticorrosion properties, which allows the use of sush coverage in difficult operating conditions, where mechanical and thermal loads are combined with the action of aggressive environments [4]. The introduction of inorganic fine fillers, in particular $CaCO_3$ and Al_2O_3 into a polyester composition, will be aimed at regulating the technological and operational properties of modified composites due to their effect on their morphology as a result of interphase and intermolecular interactions with the participation of systems components [5]. The introduction of polymeric modifier – polyvinyl chloride into a polyester matrix which containing a disesterphalate plasticizer and a finely dispersed filler provides an increase in the technological compatibility of the components, the formation during the hardening the structure of the type of "semi-permeable grid", which affects the characteristics of the material, especially their physical and mechanical properties [6]. The introduction of poly(vinyl chloride) in polyester compositions leads to an increase in the values of surface hardness, the strength of adhesive compounds and changes of deformation characteristics due to the morphological changes in materials with the formation of a fluctuation grid between a structured polyester resin and poly(vinyl chloride) macromolecules.

In this regard, the study of the stability of modified polyester composites to the action of aggressive media of various types as well the study of changes of the properties of materials after the prolonged action of aggressive media are relevant.

The purpose of the work. The establishing of the influence of aggressive environment on the chemical stability of composites based on modified polyester resins.

Materials and methods of research. To the research used an unsaturated polyester resin of the brand Estromal A023 ("LERG", Poland). As a polymer modifier poly(vinyl chloride) (PVC) of the brand Lacovyl PB1156 (TU U 24.1-33129683-004:2011) was used. As finely dispersed inorganic fillers, calcium carbonate (ISO 11931:2012) with a density of 2710 kg/m^3 (maximum filling degree of polyester in the conditions of research – 235 parts by weight on 100 parts by weight of an oligomer) and aluminum oxide (TU 6-09-425-75) with a density of 3700 kg/m^3 (maximum filling rate – 150 parts by weight per 100 parts by weight of oligomer). Additionally, the diestherphalate plasticizer dibutyl phthalate (GOST 8728-88) was introduced into the composition, which is well-combined with poly(vinyl chloride) (the interaction parameter is χ = -223 J/mol), which simultaneously is a solvent and plasticizer for polyester resin and poly(vinyl chloride).

Water absorption of polyester composites was determined according to ISO 62:2008. The chemical resistance of composites based on unsaturated polyester resins of the brand Estromal A023 was evaluated according to ISO 2812-1:2007.

Surface hardness was determined on a Hepler consistometer for 293 K by squeezing a steel cone polymer with an angle of exacerbation of 58^0 08' under a load of 50 N for 60 seconds.

Forecasting durability of products based on polyester resins was carried out in accordance with GOST 25881-83, which is based on determination of the coefficient of chemical stability of the investigated material. To predict the value of the coefficient of chemical stability during the accepted lifetime (τ > 30 days), the dependence was used:

$$\lg K_{ch.\,st.} = a + b \cdot \lg \tau, \qquad (1)$$

where $\lg K_{ch.\,st.}$ i $\lg \tau$ – logarithms of the coefficient of chemical stability and the accepted lifetime; a i b – steel for this type of material and the given environment coefficients.

Anticorrosion properties of polyester coatings on steel plates were investigated on the bridge of an alternating current P-5083 with automatic fixing of capacitance and resistance in a specially made electrochemical cell. As a corrosive medium 3 % NaCl solution and synthetic acid rain of the following composition were chosen: 3.18 mg/l H_2SO_4 + 4.62 mg/l $(NH_4)_2SO_4$ + 3.20 mg/l Na_2SO_4 + 1.58 mg/l HNO_3 + + 2.13 mg/l $NaNO_3$ +8.48 mg/l NaCl, pH = 4,5.

Research results and their discussion. During to the use of the polymeric composite materials they are exposed to water, aqueous solutions of acids or alkalis, which are chemically active media, consisting of various types of kinetic units: water molecules and electrolytes, hydrated molecules and ions, and the like. The transfer of such a multicomponent medium through a polymeric material has a complex physical-chemical character and depends on the nature, concentration and temperature of the medium and the component composition of the composite.

It is known [7] that the polyester materials are resistant to the action of mineral and organic acids, alkalis, gasoline, oils and many organic solvents. However, it should be noted that aggressive media whose molecules are well penetrated into the polymer matrix (for example, chloride acid), filling the free volume of the system, lead to swelling of the polymer, in particular to increase the mass and volume of the sample, as well as significantly change the conditions molecular motion and characteristics of relaxation processes.

Due to the fact that during the development of polymeric composite materials the interaction of an aggressive medium with a polymer matrix and a filler should be considered, it is expedient to study the influence of the modifier and finely dispersed filler on the chemical stability of the obtained composites.

The influence of the component composition and nature of the inorganic fine dispersible filler on water absorbing (W) and the swelling coefficient (K) of the polyester composites are given in Table.

Influence of PVC and filler on water absorption (W), diffusion coefficient (D) and swelling coefficient (K) of polyester composite

№	Composition content, pts. wt.				W, %	$D \cdot 10^{-8}$, cm^2/sec	K_{NaOH}, %	K_{H2SO4}, %
	PVC	$CaCO_3$	Al_2O_3	DBF				
1	–	–	–	–	1.81	1.83	0.69	0.36
2	20	–	–	–	3.23	1.84	1.67	1.29
3	–	235	–	–	2.42	4.31	0.44	-0.14
4	20	235	–	–	3.12	5.58	1.34	0.22
5	–	235	–	3	2.01	1.31	3.92	-0.08
6	20	235	–	3	1.11	7.26	1.66	0.03
7	–	–	150	–	0.71	3.11	1.51	0.87
8	20	–	150	–	1.51	10.0	1.30	2.44
9	–	–	150	3	1.34	–	2.89	0.39
10	20	–	150	3	1.01	6.37	1.39	0.93

It is found that equilibrium water absorption for polyester composites is established within 7–14 days. Water absorption of unmodified polyester material is about 1.5 %. The introduction of PVC into a polyester matrix leads to a significant increase of water absorption (3.5 %), which is obviously due to the additional heterophasicity of the system [8]. The water absorption of composites containing $CaCO_3$ in its composition is quite high and is ≈ 1–3 %, while the composites with Al_2O_3 are 0.5–1.3 %. Obviously, the dynamics of swelling of polyester composites in water is significantly influenced not only by the topological structure of the polyester (the parameter of which is the density of the mesh of chemical bonds), but also by its supramolecular structure. Modified polyester materials containing DBF have the highest resistance to water because they have more equilibrium supramolecular structure, the formation of which is due to the presence of DBF, which acts as a solvent and a plasticizer for polyester resin and poly(vinyl chloride).

For modified polyester composites with $CaCO_3$ the swelling (K) of samples after 14 days of exposure in 3 % NaOH and H_2SO_4 solutions is 1.3-1.6 % in alkaline medium and 1.0 % in acid, and for Al_2O_3 composites – does not exceed 1.3–1.5 % in alkaline environment. The introduction of DBF in non-

PVC composites leads to a decrease in chemical resistance in alkaline media (K = 2.3–3.9 %). However, in acidic media, a slightly different pattern is observed: the introduction of DBF into modified and unmodified polyesters composites containing $CaCO_3$ leads to an increase in chemical resistance.

It is established that in a solution of H_2SO_4 filled with Al_2O_3 polyester composites increase faster in volume. Along with this, for polyester composites with $CaCO_3$ on the processes of swelling, obviously, the interaction of the filler with the components of the aggressive medium is superimposed. In this case, the excipient is washed away from the material, resulting in loss of mass and irreversible changes in the morphology of the composite.

It should be noted that, in addition to the physico-chemical interactions occurring between the components of a polymeric composite and an aggressive medium, the processes of diffusion of the medium into the polymer matrix, which occur predominantly along the regions with a "loose" chemical network, are determined by the influence of materials stability, in particular in the regions of the boundary layer around the particles of the filler. It was found that the introduction of inorganic finely dispersed fillers into a polyester matrix leads to an increase of the diffusion coefficient of the medium of the investigated materials (Table 1). This indicates the penetration of aggressive media molecules into the structure of the material and the creation of obstacles for molecular movement, which obviously affects changes in the physico-mechanical characteristics of composites (Fig. 1), in particular the value of the surface hardness (F) of all samples after exposure in water are less than the values of surface hardness prior to testing.

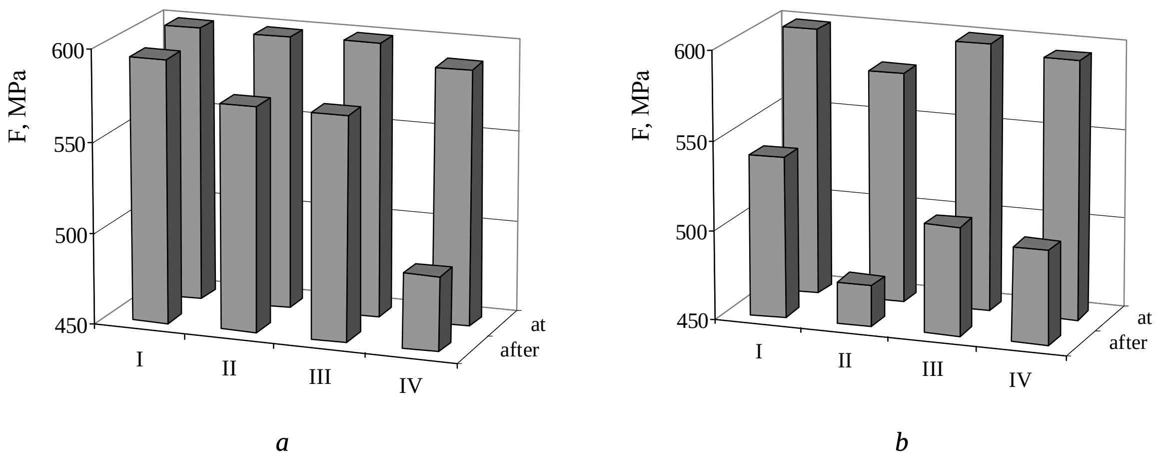

Fig. 1. Change of surface hardness of polyester composites with $CaCO_3$ (a) and Al_2O_3 (b) after exposure in wate: PVC content, wt. p.: I, III–0; II, IV – 20. DBF content, wt. p.: I, II–0; III, IV – 3

Experience in the use of materials on the basis of unsaturated polyester resins indicates that the overwhelming majority of their failure is due to a complex of external effects – load, temperature, aggressive environment, etc., which can lead to a decrease in operational properties or even destruction of the material. It is noted that the change in the properties of polymer material in products have a physical and chemical factors of influence. Physical factors change the supramolecular structure and relaxation properties of the polymer, and chemical – change the molecular weight, molecular mass distribution and the chemical composition of the polymer [9].

Therefore, from the practical point of view an important issue during the design of constructions with the use of polyester composites and the determination of their permissible field of application is the ability to predict the performance (durability) of composites in building products, polymer coatings and structures.

The results of studies on the durability of composites based on modified by poly(vinyl chloride) unsaturated polyester resins with inorganic fine particles of $CaCO_3$ and Al_2O_3 in a medium of 3 % NaOH are shown in Fig. 2.

It has been established that polyester composites with inorganic fine particulate filler $CaCO_3$, in comparison with based Al_2O_3 composites, are characterized by higher indicators of durability of materials, indicating the expediency of using this material for coatings, building products and structures.

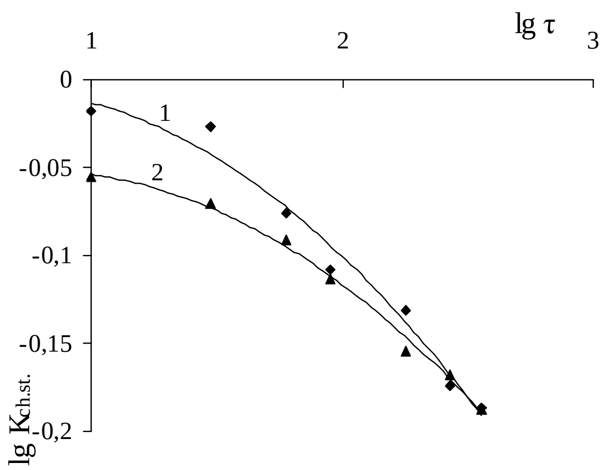

Fig. 2. Dependence of lg $K_{ch.\ st}$. from lg τ of polyester composites depending on the nature of the filler: PVC content – 20 wt. p. $CaCO_3$ content, wt. p.: 1 – 235, 2 – 0; Al_2O_3 content, wt. p.: 1 – 0; 2 – 150

It is possible to estimate the protective properties of the coatings in the environment by studying the components of the impedance of the metal coating system. The kinetic dependence of the coating resistance on time makes it possible to estimate the change in the dielectric properties of the polymer layer in the medium and to set the time when the defining factor is not the insulation properties of the coating, but the resistance of the polarization of the electrode processes on the surface of the metal section – the polymer coating [10]. In this regard, electro-chemistry studies were conducted to determine the influence of the content of the polymer modifier and the nature of the fillers on the anticorrosion properties of polyester materials. The results are shown in Fig. 3.

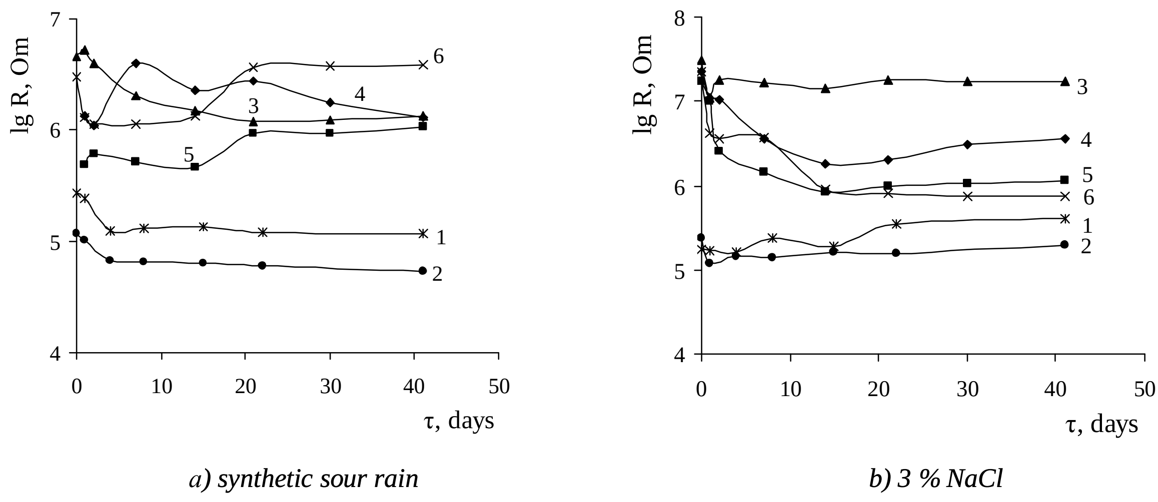

Fig. 3 Change of logarithm of electrical resistance of polyester coatings over time. PVC content, wt. p.: 1- 0; 2, 4-6 – 10; 3 – 20. $CaCO_3$ content, wt. p.: 1-4, 6 – 0; 5 – 25. Al_2O_3 content, wt. p.: 1-5 – 0; 6 – 25; DBF content, wt. p.: 1-3, 5, 6 – 0; 4 – 3

Definition of impedance parameters (electrical resistance and capacitance at a frequency of 10 kHz) of metal-coating systems showed that for polyester compositions deposited on a metal substrate, during 40 days exposure in an aggressive medium, the resistance of some polyester compositions was considerably high in the first The days of research, then somewhat reduced and stabilized at a certain level, indicating the swelling of the coating in a corrosive environment. In this case, the coatings retain their protective effect and function, preferably as a barrier to water molecules and corrosive ions.

It has been found that the introduction of inorganic finely dispersed fillers, in particular $CaCO_3$ and Al_2O_3, into a modified polyester matrix leads to an increase in the corrosion properties of the material. Along with this, modified polyester materials from Al_2O_3 in the synthetic acid rain medium have the highest protective effect, as evidenced by the highest resistance values ($3.6 \cdot 10^6 – 3.9 \cdot 10^6$ Om).

The longest protection of the metal in a 3 % solution of NaCl provides a coating, which includes polyvinyl chloride in an amount of 20 wt. p.. and DBF (the resistance value is $16,6 \cdot 10^6$ – $17,4 \cdot 10^6$ Om and $3,1 \cdot 10^6$ – $3,6 \cdot 10^6$ Om respectively). This is most likely due to the peculiarities of the formation of coatings from heterophase systems in a thin layer. Polyester compositions containing 10 weight part of PVC have the slightest corrosion resistance of up to 3 % NaCl solution and synthetic acid rain indicating the penetration of the aggressive medium to the steel substrate and the loss of protective properties of the coating.

Conclusions. It was established that the stability of polyester composites to the action of chemical media depends on the nature and concentration of the medium, the component composition of the composite, in particular on the content of the polymeric modifier – polyvinyl chloride and inorganic finely dispersed filler. It is found that the equilibrium water absorption of polyester composites is established within 7-14 days. Founded that the modified polyester materials containing DBF are characterized by the highest resistance to action of water. The introduction of DBF into modified and unmodified polyester composites containing $CaCO_3$ leads to an increase of chemical resistance in H_2SO_4 medium. The introduction of inorganic finely dispersed fillers into a modified polyester matrix leads to an increase of the anticorrosion properties of the material.

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