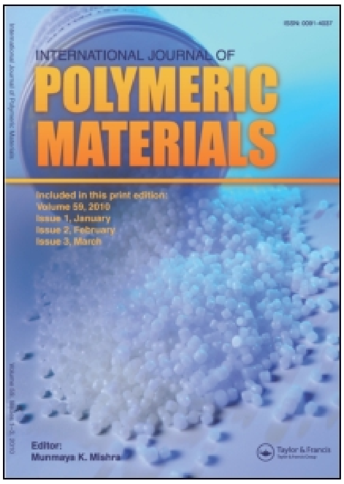

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Effect of Basalt Surface on the Properties of Boundary Layers of Network Polymers

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The activation of basalt as filler results in change of structure and properties of composite based on these fillers.

KEY WORDS Basalt-based plastic, boundary layer of thermosetting plastic, degree of hardening, adhesion strength, surface activity

INTRODUCTION

The basalt fibres or flakes as fillers have been recently widely used in reinforced plastics and coatings. These fillers possess the higher modulus of elasticity than the traditional ones. These materials are more chemically resistant. The sources for basalt fillers are practically unlimited. At the same time the mechanical properties of plastics with these fillers fail to correspond to their potential opportunities. So it seemed necessary to study the processes in the developing of these materials.

As it was shown[1,2] one of the main causes of the strength decrease of polymeric composites is the existence of "weak" boundary layers on the interface. The formation of such layers[3] is associated with the conditions of application of the adhesive, presence of the admixtures both in the binder and on the surface of solid bodies. It leads to the formation of defects in the adhesive joint and to the distortion of the test results of adhesion strength. Besides that the formation of poor boundary layers are associated with the adsorptive interaction of the polymeric binder—solid body boundary, change of conformations of the adsorbed polymeric chains and decrease of their molecular mobility.[2]

The selective sorption of polymeric matrix components and the blocking of the functional groups by the solid body surface can result in disturbance of the stoichiometry of a reaction mixture. The decrease of molecular mobility can reduce the rate of reaction, interaction and properties of a boundary layer, cohesion strength of the composite.

The purpose of this paper was the investigation of the effect of the basalt fillers surface on the adhesion strength composites, based on epoxy and nonsaturated polyester resins.

EXPERIMENTAL

We used epoxy resins ED-20 and MP-400 and hardeners polyethylene polyamine (PEPA), dicyanethyl ethylenetriamine (DDETA), monocyanethyl diethylenetriamine (MDETA).

For investigation of the basalt effects we used samples made from polyester resin ПН609-21М which is 60% solution of oligodiethyleneglycol maleinnaphthalate (DEGMF) in triethylene glycol dimethacrylate (TGM-3). The resin was hardened by the oxidation-reduction system in the form of methylethylcetone peroxide—cobalt naphthenate. Octyltrimethylammonium bromide (OAB), cetyltrimethylammonium bromide (CAB), product of interaction of allyl alcohol, 2, 4-toluyleneliisocyanate (AT1) have been used as surface-active substances (SAS).

The process of hardening of the boundary layer of epoxy and polyester compositions has been studied by the IR-spectroscopy method (of repeatedly disturbed total internal reflection—RDTIR) on the spectrometer UR-20. The prism KRS-5 ($N = 18$, $C = 45°$) and the germanium prism ($N = 14$, $C = 45°$) were used for simulation of the substrate surface. The thickness of a polymer layer was 0.5–1 nm for the element made of germanium and 2–3 nm for KRS-5. The inhibition of polyester resin polymerization by oxygen of the air was excluded by applying a polyethylene film to the surface of a system to be hardened. The thickness of applied epoxy and polyester composition was up 20–30 nm. To evaluate the glass transition temperature and the parameter of polymer-solvent interaction, we used the method of inversed-phase gas chromatography. Basalt-1 and basalt-2 served as fillers and a model of substrate. Glass transition temperature T_g has been determined from the experimenral curve of retention volume logarithm dependence on inversion temperature log V_{g-1}/T. The polymer-high surface interfacial tension has been determined by the methods, described in Reference 7. The mercury has been used as a high energy surface. The basalt disks and flakes were obtained from melt by the method of inflation. Two types of basalt flakes were basalt-1—flakes from ordinary basalt and basalt-2—flakes from activated basalt. Activation has been carried out by the adding of surface active elements to the melt composition. The surface was equal to 430 mN/m and 405 mN/m respectively. The surface of basalt flakes has been treated by bianchor urethane-containing surface-active substances (SAS).

To determine the adhesion strength the basalt disks have been cemented to each other, then the obtained packet has been cemented with the aid of a stronger cement between steel mushrooms and this specimen has been destructed at a normal tension.

The investigation of the properties of both types of basalt flakes has been performed with the use of the methods of electron paramagnetic resonance (EPR) and electron spectroscopy. The spectra of EPR have been measured at 300 K on the spectrometer YES-ME-3X, the first derivative of an absorption line have been recorded. The study of the elementary composition of basalt flakes and of the variation of the content of elements through the thickness of a specimen during its activation has been performed on the scanning electron microscope "Came-Bacs," equipped with an energy dispersion system "Link-860" intended for an X-ray microanalysis.

The investigations have included: a qualitative analysis of distribution of the elements from the predetermined area of a specimen; a qualitative analysis of distribution of the elements through the cross-section of a specimen; a qualitative analysis in several local points of a specimen with respect to the scanning line.

RESULTS AND DISCUSSION

The results of the electron microscope examinations enable to affirm that the distribution chart of elements of ordinary basalt flake differs in the uniform distribution of elements the field and through the cross-section of a flake (Figure 1). The uniformity of distribution of Si, Fe and Ca is confirmed by the investigations of the characteristic Sikα, FeKα and CaKα—radiations as well as by the qualitative analysis in scanning by a probe across the plate and by the quantitative analysis in the local areas of a specimen at different distance from the flake edge (Figure 1).

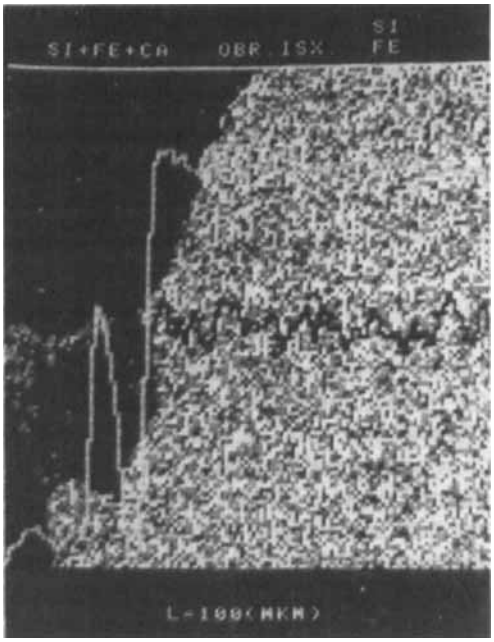

FIGURE 1 Image of ordinary basalt flake in the characteristic SiKα, FeKα, and CaKα—radiations with imposed-on-it intensities of scanning on the line in SiKα and FeKα-radiations.

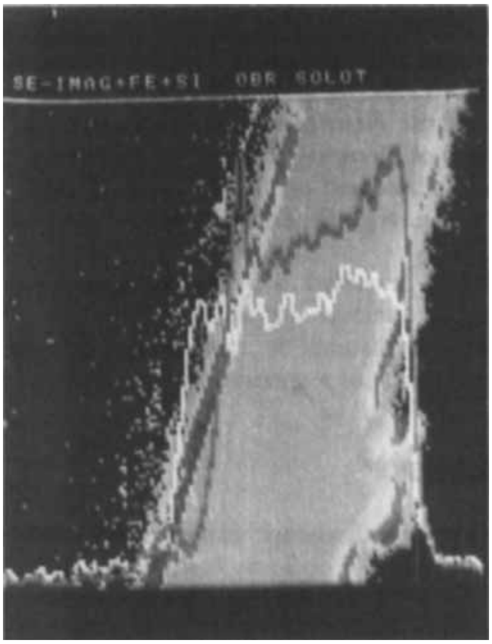

FIGURE 2 Scanning electron mіscroscope image of activated flake cross-section with the curves of intensity of iron and silicon radiation inposed on it.

TABLE I

Specimen	Analysis number	Content of elements, mass percent		Relation of elements C_{Si}/C_{Fe}
		Si	Fe	
Initial	Average	17	6,6	2,5
Activated	1	15	6,5	1,8
	2	16,7	8,6	1,9
	3	21	8,7	1,5

Figure 2 presents the scanning electron microscope image of an activated flake in the reflected electrons after digital processing. It is seen that unlike the initial specimen (Figure 1) the flake structure is heterogeneous. Near the surface of the flake we can observe the thin (1.5 nm) layers of a phase which differs in composition from its central part. The increase of the content of Si and the decrease of such elements as Fe and Ca is typical for these sections.

It is seen that the content of Si is the greatest near the surface of the flake. In this case we observe the slow vanishing of silicon from its right-hand surface to the centre and the rapid increase in the narrow (1.5 nm) zone at the left-hand surface of the specimen. The increase content of Fe and Ca is observed on one of the flake surface.

The data of the quantitative analysis in the local areas of the initial and activated specimens are specified in Table I.

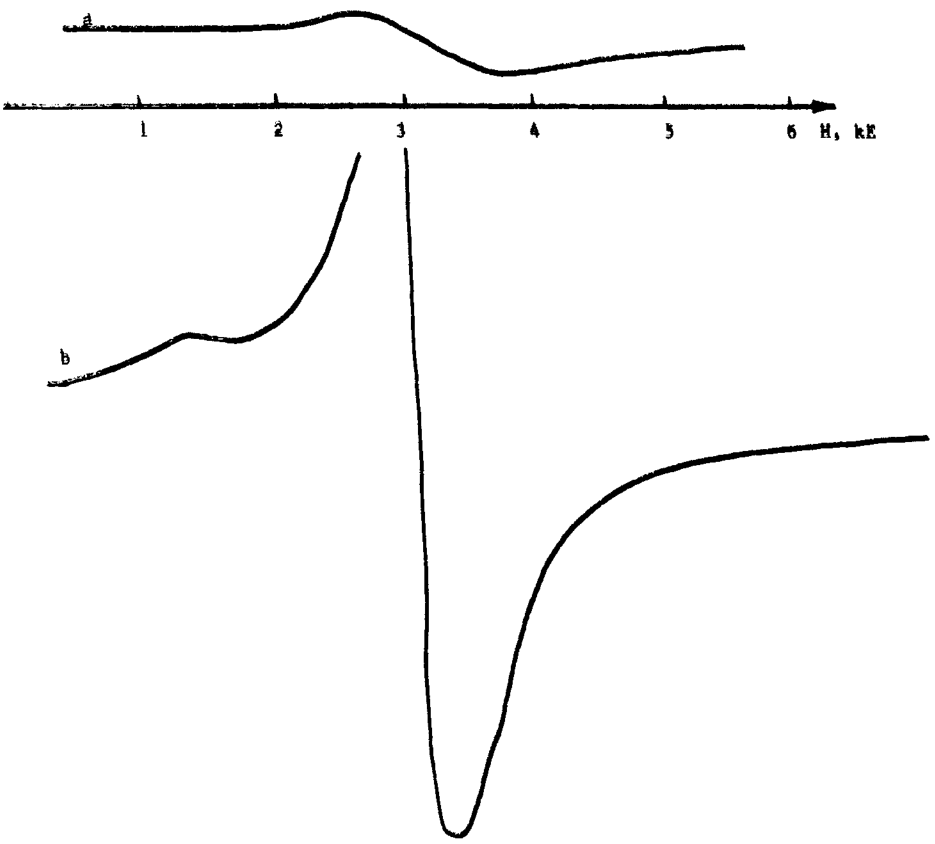

FIGURE 3 Spectrum of EPR of ordinary basalt flake (a) and activated one (b).

It is seen that the content of Si at the side surfaces of the activated specimen is the greatest and reaches the value of 21% which is higher than the content of Si in the centre of the flake and by 2% lower than in the initial specimen. The content of Fe through the cross-section of the activated specimen is higher than in the initial one. The relation of the content of Si to the content of Fe is also not retained through the specimen thickness.

The obtained data are indicative of the change of the stoichiometric composition of the specimens through the cross-section during their activation. The redistribution of the elements in the boundary layer of the basalt flake (basalt-2) results in the considerable change of its surface tension and other properties. The basalt flake matrix includes about 52% of silicon oxide (quartz and cristobalite), 16%-Al_2O_3, 15%-Fe_2O_3, 3%-MgO, 8.37-CaO. In accordance with References 4 and 5 the coordinated-nonsaturated atoms of metals can be the active centres of polymerization on the metal oxides. In the process of polymerization the coordinated-nonsaturated atom of metal concurrently retains the growing chain of polymer and the monomer molecule. The activation of the basalt flake results in redistribution of the elements in the volume and on the surface. On the flake surface we observe the increased content of Si and Fe which can be the active centres of polymerization.

The investigation of the spectra of EPR of the specimens (Figure 3) are indicative of the activity of the obtained basalt flakes.

For the ordinary basalt flakes we have observed the slightly anisotropic spectrum of EPR which consists of two intensive absorption lines in region $H_1 = 1.4K_e$ and $H_2 = 3K_e$ and a series of weaker lines. The character of the spectrum shows the presence in the specimen structure of a short-range order. The analysis of the specimen composition and characteristics of EPR of the spectrum (factor value, line width) enables to assume that the spectrum of EPR is determined by ions of Fe^{+3} in two different positions with concentrations $N_1 = 3 \times 10^{18}$ spin and $N_2 = 1 \times 10^{19}$ spin. These can be the positions with different local symmetry—rhombic and axial.[6] Absorption in small fields ($H = 1.4\ K_e$) can be conditioned by the crystalline fields of axial symmetry, absorption in field $H = 3K_e$.[7] After activation the intensity of EPR lines in region $H_2 = 3K_e$ sharply increases. This is conditioned by essential increase of the portion of a rhombohedral phase in the flake structure. In this case the total concentration of the paramagnetic centres (PMC) reaches the value of 6×10^{19} spin. The presence of unpaired electrons with concentration of 6×10^{19} spin in the activated basalts flakes enables to assume that the surface of the activated basalt flakes possesses the initiating centres responsible for the processes of polymerization in the absorption layer.[4]

Earlier it has been shown that the layer of epoxy polymer on the metal surface does not change the polymer condition.[9,10] The treatment of basalt surface by SAS

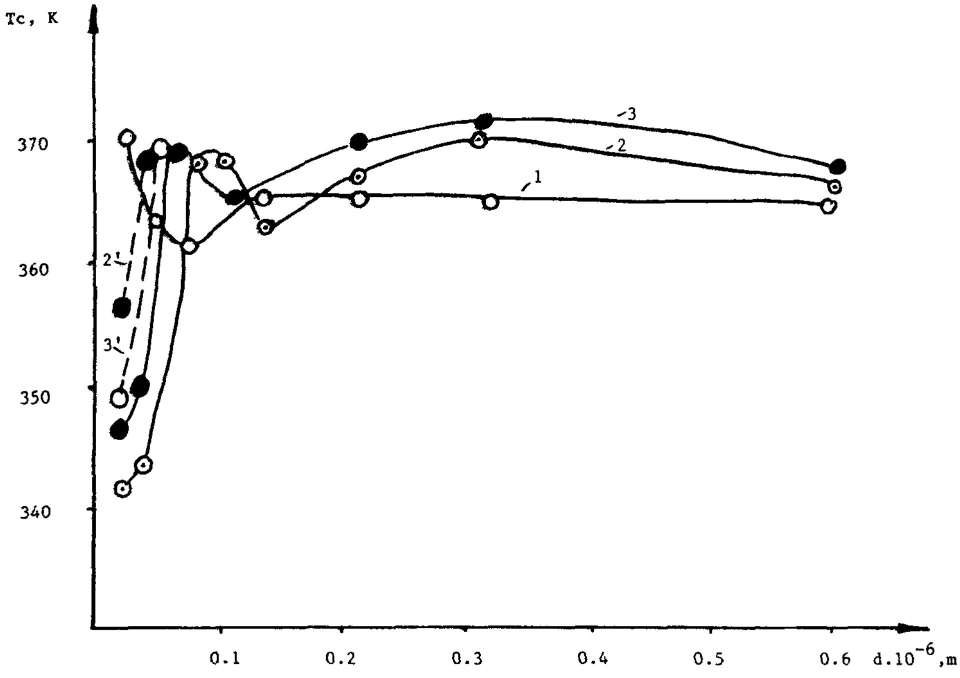

FIGURE 4 Dependence of glass transition temperature T_c on film thickness for ED-20-PEPA on basalt-2 with applied layer of SAS (1), basalt-2 (2.2'), basalt-1 (3.3'), 2,3-warming-up for 5 h, 2', 3'-warming-up for 10 h at 423 K.

renders an effect on the glass transition temperature of polymer. As it is seen from Figure 4, in case of a low-energy surface (basalt, treated by SAS) the polymer glass transition temperature does not depend on the variation of the thickness of a polymer layer. The increase of glass transition temperature T_g of a film 0.01×10^{-6} m thick is associated with the limitation of mobility of the polymer chains near the solid surface. The character of change of T_g for the surface of basalt-1 and basalt-2 is indicative of a complex structure of the boundary layer. For the film $(0.01-0.03) \times 10^{-6}$ m thick on the curve log V_g − $1/T$ no fracture is observed in the investigated temperature range. We assume that the boundary layer 0.03×10^{-6} m thick of the epoxy composition does not change to the polymer condition. As it was shown in Reference 11, the high-energy surface can selectively sorb the epoxy resin as a result of which the adhesive layer is impoverished by hardener, the stoichiometry of the composition becomes disturbed. The polymer layer enriched by epoxy resin has a considerable expanse. In addition, the incomplete hardening of the boundary layer of the adhesive can be caused by the decrease of mobility of polymer chains due to the interaction energy limitation of the conformation collection, blocking of the active groups of components of the composition by the solid surface.

The warming-up of the specimens at 423K for 5 h results in the appearance on curves log V_g − $1/T$ of a fracture, corresponding to the glass transition temperature of the polymer in the films $(0.01-0.03) \times 10^{-6}$ m thick. In this case the surface of basalt-1 effects the glass transition temperature more than that of basalt-2. The warming-up at the same temperature for 10 h results in the increase of T_g. The further warming-up of the specimens for 15 h does not cause the increase of T_g. Insufficient hardening of the adhesive on the boundary with the high-energy surface is the impoverishment of the boundary layer of the composition by the hardener. The increase of the glass transition temperature of the polymer in the film 0.5×10^{-6} m thick can be explained by a fact that this layer contains the excessive quantity of hardener which reacts with resin during long-time thermal treatment.

Starting from the thickness of 0.3×10^{-6} m the properties of the boundary layer of the polymer approach to the volumetric ones.

The considered data enable to determine the specific changes of the value of the retention volume V_g depending on the film thickness.

For the polymer located on the basalt surface treated by SAS we observe the negligible change of V_g in case of variation of the film thickness. When the untreated basalt flakes have been used with the film thickness of 0.03×10^{-6} m we observe the sharp increase of V_g that can be explained by the decrease of structure density. Figure 5 presents the dependence of thermodynamic interaction of polymer-solvent $X_{1,2}$ on the film thickness. As it is seen, the values of the parameter for epoxy film 0.03×10^{-6} m without and with hardener are approximately the same. It is indication of incompleteness of the process of gelformation. The warming-up of the film 0.03×10^{-6} m thick on the basalt surface results in the increase of parameter $X_{1,2}$ which is associated with the reaction of the polymer additional hardening during warming-up. With the increase of the film thickness the effect of the polymer support on the value of $X_{1,2}$ becomes much less though it is still traced at the thickness of up to 0.3×10^{-6} m.

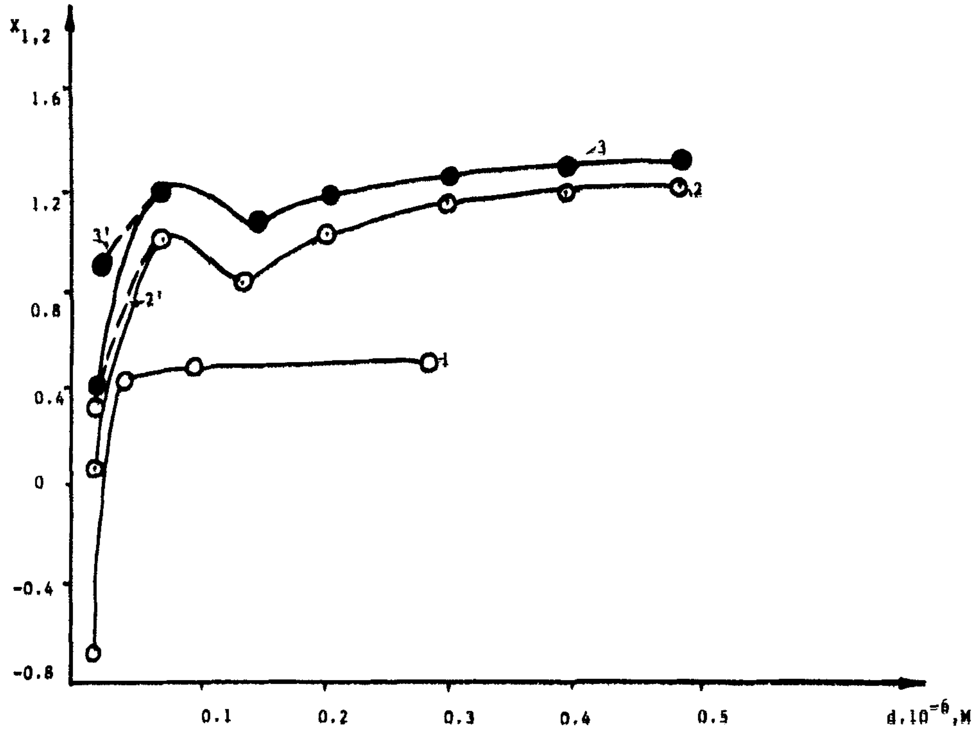

FIGURE 5 Dependence of parameter of polymer-solvent interaction $X_{1,2}$ on film thickness for ED-20 (1) and ED-20-PEPA (2.2', 3.3'). Supports: 1—basalt-2 with a layer of SAS applied to it; 2—basalt-2; 3—basalt-1; 2-3—warming-up for 5 h; 2', 3'—for 10 h at 423 K.

The increase of polarity of the hardeners, i.e. their surface activity on the polymer—high energy surface boundary upon replacement of MDETA by DDETA results in the attainment of the approximately equal surface activity of resin and amine, so the interfacial tension of the mercury—ED-20 boundary makes up 342 mN/m, MDETA-372 mNm, DDETA-354 mNm. The increase of the surface activity of the hardener results in the growth of the degree of conversion of the epoxy groups in the boundary layer (Figure 6). It is known that the considerable increase of the polymer adhesion strength can be attained by adding of surface-active substances.[12] With this aim the halogen salts of quarternary ammonium bases have been added to the epoxy compounds. The adsorption of molecules of SAS on the interface partly eliminates the preferential sorption of epoxy resin and formation of an insufficiently hardened boundary layer. Increasing the degree of hardening of the epoxy compound in a thin layer (Figure 6), the used surface-active substances (SAS) practically do not exert an influence on the degree of hardening of the polymer in the block, the adhesive strength of cemented basalt disks varies symbatically to the degree of conversion of the epoxy groups in the thin layer (Table II). The adhesive strength increases especially sharply upon treatment of the basalt surface by SAS. The treatment of the surface of the disks made of basalt-2 by bianchor urethane-containing SAS has enabled to obtain the adhesive strength equal to 56 MPa in application of the polyester base.

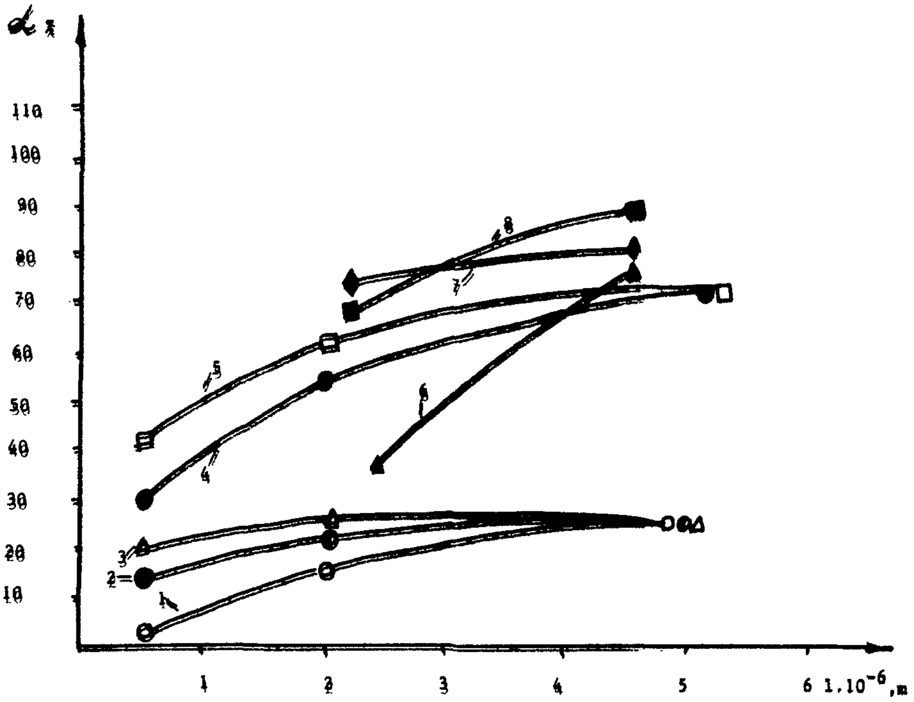

FIGURE 6 Dependence of the degree of conversion of epoxide (1–5) and polyseter one (6–8) compositions on the film thickness in 1 day after mixing: 1—ED-20 + PEPA, 293 K; 2—ED-20 + PEPA with adding of 2% of CAB; 3—ED-20 + PEPA with adding of 3 CAB; 4—ED-20 + MDETA, 423 K; 5—ED-20 + MDETA, 423 K; 6—PN-609-29M + 2% PMEK + 1% NK, 293 K; 7—composition 6 with adding of 10% of ATJ, 293 K; 8—composition 7 with adding of 10% of ATJ, 357 K.

TABLE II

Strength of adhesion joint of basalt disks

Resin	Hardener	Additive	Hardening temperature	Adhesive strength, (MPa)	
				Basalt-1	Basalt-2
ED-20	PEPA	–	293	11.2	16.8
ED-20	PEPA	CAB	293	22.8	24.7
ED-20	PEPA	CAB	293	23.3	24.9
ED-20	MO ETA	–	423	59.6	67.4
ED-20	DD ETA	–	423	69.1	69.6
PN-609-21M	PMEK+IK	–	293	28.0	30.6
PN-609-21M	PMEK+IK	ATJ	293	40.0	44.6
PN-609-21M	PMEK+IK	ATJ	353	38.6	38.7

As it is seen in Figure 6, the degree of conversion of polyester composition in the boundary layer is also considerably lower than in the volume. To clarify the causes of this phenomenon, the composition of the ingredients of polyester resin—TGM-3 and DEGMF has been investigated by the method of RDTIR. It has been established that DEGMF is practically not polymerised both in the volume and on the boundary with elements KRS-5. Upon polymerization of TGM-3 the degree of transformation of double links in the layer 2–3 nm thick and rate of hardening in the thin layer differs from the values in the volume.

While investigating the dependence of the rate of polymerization of the composition in the relation of copolymerizing components,[13] we have established that the insufficient hardening of the boundary layer of polyester resin has been conditioned by concentration in it of STGM-3 (which has not entered into the copolymerization reaction) of the low-reaction oligomerous molecules of DEGMF. The increase of the content of DEGMF in the boundary layer is confirmed by the rise in the intensity of the absorption bend of a benzene ring in the region of 1580 cm^{-1} for hardened resin IIH-609-21M in the layer 2–3 nm thick by 4.5 times as compared with the value in the volume. We came to conclusion that the insufficient hardening of polymer near the highly effective solid surface is associated with the preferential sorption of DEGMF on the phase boundary. The warming-up of the polymeric film results in the increase of its degree of hardening. However, even after this the degree of transformation of double links near the solid surface is lower than in the volume of the composition. The warming-up for 6 h at 353 K increased the degree of transformation of polyester resin in the layer 2–3 nm thick up to 65% and in the volume of up to 87% respectively.

The adding to polyester resin of product ATJ which displays the surface activity on the polymer—high energy surface boundary[14] results in the rise of the degree of polymer hardening in boundary layer up to 15–20% (Figure 6). We suppose the dual character of action of ATJ on the phase boundary. Firstly, the formation of an adsorption layer of ATJ must change the conditions of adsorption interaction of the composition components on the interface which has been observed upon adding of SAS to the epoxy resin. Secondly, the allyl groups of ATJ can be copolymerized the double links of DEGMF,[15] increasing the degree of hardening of the system in the boundary layer. So the degree of hardening of the system in the ratio of 40:60 has made up 97%.

The increase of the degree of transformation of the reaction system in the boundary layer causes the increase of strength in cementing the basalt. In this case the strength of cementing of basalt-2 in all cases is higher than that of basalt-1. The adhesion strength of polyester polymer upon warming up at 352 K also has increased by more than 30%, the adding of SAS (ATJ) has resulted in the still greater rise of strength.

CONCLUSION

The mechanical characteristics of basalt-based plastics upon application of the epoxy and polyester binders are determined by the degree of transformation of the system in the boundary layer and the selective sorption of the system components which, in its turn, is dependent on the surface tension of the substrate.

The activation of basalt resulting in redistribution of elements in its surface layer change in the crystalline structure and surface tension, causes the appreciable increase of adhesion strength.

The same effect is attained by treatment of basalt surface with SAS or adding of SAS to the binder composition.

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