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Research paper



The Influence of Inorganic Fillers on the Protective Properties of Epoxy Polymer Composite Materials

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Abstract

The influence of regularities of the chemical-mineralogical nature, the dispersity, and the surface properties of inorganic fillers on the protective properties of epoxy polymer composite materials have been investigated. Polymeric compositions based on epoxy resin of ED-20 brand and aliphatic amine curing agent of diethylenetriamine of DETA brand have been chosen as the research materials. The fillers were the air-dry dispersed materials of different nature: oxide, clay and quartz. The resistance of the composites to water and aqueous solutions (absorbency) was investigated by dipping the samples into an aggressive aqueous medium. For the received samples of the filled composites, thermogravimetric (TG) and differential scanning calorimetry (DSC) method were used using the SDT Q600 device manufactured by TA Instruments (USA). It has been found that the thermal stability and the absorbing capacity of the filled composites in water and aqueous acidic and alkaline mediums correlate with each other. It has been shown that to obtain materials with improved protective characteristics, it is necessary to use oxide or clay fillers with the basic (alkaline) surface function.

Keywords: *acid-base interaction; composite material; epoxy polymer; inorganic filler; protective properties.*

1. Introduction

Composite materials based on epoxy resins are commonly used as gluing agents for element connection with various surfaces (concrete, stone, wood, metal, glass), protective coatings that increase the service life of traditional materials, constructive elements for building structures and infrastructure object reconstruction and renovation as well as independent building elements and architectural construction creation (poured floor, fiber-glass products, etc.) [1-5]. High strength, resistance to aggressive media and non-toxicity make it possible to use epoxy materials to restore water pipelines [6] and drainage [7]. Sufficient endurance under the influence of γ-radiation causes the use of epoxy polymer coatings for infrastructure objects in nuclear power [8]. The technologies are developed and the efficiency of restoration of bearing portable wooden beams and elements with the use of polymeric compositions based on epoxy resins is shown [9-11].

The urgent direction is the use of epoxy polymers in preservation and restoration of architectural monuments, as well as for the design of products [12, 13]. Epoxy-silicate hybrid materials were found to be most effective for the restoration of stone, glass and ceramic elements of architectural heritage [12-16].

2. The Analysis of the Recent Researches and Publications

Protective properties, such as resistance to water effect, aggressive aqueous mediums, high temperatures, of epoxy composite materials that are used in building, transport and architecture, play the critical role. The resistance to liquid mediums is characterized by the sample ability of absorbing the liquid at a definite time. This results in some structure changes and the service properties of epoxy composite materials deprivations [17, 18]. The resistance to open fire effect and high temperatures is determined by the structure endurance of the polymeric material net at all levels [19-21].

Inexpensive dispersed inorganic fillers are added to epoxy compositions with the aim to increase the economical and the eco-friendly value of the materials [22-25]. The dispersed inorganic fillers addition allows to regulate the technological properties of the compositions [17, 26] and improve the physical and mechanical characteristics [18, 27]. The influence regularity researches of the dispersed inorganic fillers on the protective properties solve the problem of a new multifunctional epoxy filled material development that is able to be used in aggressive exploitation conditions.

3. The Purpose and the Tasks of the Research

The purpose of the research is investigating the influence of the dispersed inorganic materials of different chemical-mineralogical nature (oxide, clay and quartz) on the structure and the protective properties of epoxy polymer composite materials. This will help making the reasoned choice of fillers for epoxy materials with special protective characteristic formations.

To fulfill the purpose of the research, the following tasks are assigned: 1. The properties and nature investigation of the most common inorganic fillers used in epoxy composites. 2. Determination of correlation between chemical-mineralogical nature of the fillers and the protective properties of epoxy composites.

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4. The Main Part of the Study

As the research materials, filled polymeric compositions based on ED-20 epoxy resin and stoichiometric quantities of aliphatic amine curing agent of diethylenetriamine (DETA) have been chosen. The compositions (EP) were solidified in the air (293-298 K) for at least 72 hours, the solidification continued at 373 K for 4 hours. Filler, in amount of 10% of the volume, was added to the epoxyamine system and stirred to a homogeneous mixture. The fillers were the air-dry dispersed materials of different chemical and mineralogical nature: oxide, clay and quartz.

4.1. Investigation of the Properties of Disperse Fillers

The surface area of the fillers was defined by BET method (Brunauer, Emmett, Teller). X-ray diffraction analysis was performed using DRON-2 X-ray diffraction meter. Mineral composition and surface properties of fillers are given in Table. 1

Table 1: The filler properties

Filler	Mineralogical Composition	Surface area, m^2/g
Quartz fillers		
Quartz sand (SN)	β-quartz $SiO_2^{\bullet}$ Montmorillonites $(Al,Mg)_2(OH)_2[Si_4O_{10}]\cdot nH_2O^{*}$	2.91
Quartzite (KQ)	β-quartz $SiO_2^{\bullet}$ Montmorillonite $(Al,Mg)_2(OH)_2[Si_4O_{10}]\cdot nH_2O^{*}$ Kaolinite $Al_2Si_2O_5(OH)_4^{*}$ Orthoclase $K_2O\cdot Al_2O_3\cdot 6SiO_2^{+}$ Albite $Na_2O\cdot Al_2O_3\cdot 6SiO_2)^{+}$	3.03
Clay fillers		
Bentonite clay (BC)	Montmorillonite $(Al,Mg)_2(OH)_2[Si_4O_{10}]\cdot nH_2O^{\bullet}$ β-quartz SiO_2^{+} Kaolinite $Al_2Si_2O_5(OH)_4^{+}$	15.62
Kaolin (KH)	Kaolinite $Al_2Si_2O_5(OH)_4^{\bullet}$ β-qurtz SiO_2^{+} Biotite $(Fe,Mg)_3[OH]_2(Al,Fe)Si_3O_{10}^{+}$ Hydrous micas $(K,Na)Al_2(Si,Al)_4O_{10}(OH)_2\cdot nH_2O^{+}$	8.78
Oxide fillers		
Red mud wastes (WU)	Hematite α-$Fe_2O_3^{\bullet}$ Goethite $FeOOH^{\bullet}$ Limonite $Fe_2O_3\cdot H_2O^{+}$ Tetracalcium aluminate $4CaO\cdot Al_2O_3\cdot Fe_2O_3^{+}$ Ettringit $3CaO\cdot Al_2O_3\cdot 3CaSO_4\cdot 32H_2O^{+}$	11.35
Rutile (RT)	Rutile $TiO_2^{\bullet}$ Anatase $TiO_2^{\bullet}$	1.30

*Designations: ● – basic mineral phase; + - side mineral phase; * - traces.*

In the absence of a phase separation between the surface of the fillers and the polymer of any interactions, it can be assumed that the properties of the filled composites are due to the parameters of the disperse structure (structural factor). Indicators that may affect the dispersed structure of the composites include: the size of the filler particles, the specific surface area, the volumetric content of the fillers in the composite. To consider the dispersive structure parameter influence of the fillers, the distance between the fragments in the dispersively filled polymer composites were calculated according to the formula:

$$a = d \times [\sqrt[3]{\frac{K}{\omega}} - 1] \quad (1)$$

where a – the distance between the fragments of the filler, μm; d – size (diameter) of the fragments, μm; K – coefficient that characterizes the density packaging of the filler fragments; ω – the volume fraction of the filler in the composite material (0.1). For the chosen fillers, surface morphology and fragment size researches were held with the help of electron micrographs taken by scanning electronic microscope of JSM-6390LV brand. The results of the dispersive inorganic filler research are given in Table 2.

Table 2: The dispersive structure parameters of the fillers in filled composites

Filler	Fragments average diameter d, μm	Packaging coefficient K	Fragments distance a, μm
Oxide fillers			
RT	10	0.63	8.5
WU	3	0.58	2.4
Clay fillers			
KH	5	0.47	3.4
BC	15	0.53	11.2
Quartz fillers			
KQ	15	0.66	13.1
SN	13	0.57	10.2

The structural factor is important, but not the only one that should be taken into account. In order to take into account the possible physical and chemical interactions on the surface of the phase separation in the filled composites, the nature of the surface of the fillers must be considered. Acid-basic properties of surface active centers are directly related to the chemical and mineral composition of inorganic solids [28-31]. Thus, in order to evaluate the influence of the surface factor, it is necessary to study the acid-base properties of the surface of disperse fillers and to establish relationships with the chemical and mineral composition.

The function of pK_a^{pot} active center acidity, that is prevalent on the filler surface, was determined by pH_{susp} potentiometrical measurement in water [32]. Quantitative evaluation of the acid-based surface active filler centers was determined by the pK_a-metric method. The method is based on the adsorption of Gamete color indicators from aqueous solutions and photos by colorimetric measurements. In fig. 1-3 shows pK_a-specters of acid-base active centers on the surface of disperse fillers.

In Table 3, the results of the calculation of the specific number of acidic $\sum q_A$ (pK_a<7), the basic $\sum q_B$ (pK_a>7) and the total amount $\sum q$ of the surface active centers are given.

Table 3: Quantitative characterization of acid-base surface active inorganic fillers

Filler	$\sum q_A \cdot 10^{-12}$, $1/sm^2$	$\sum q_B \cdot 10^{-12}$, $1/sm^2$	$\sum q \cdot 10^{-12}$, $1/sm^2$	pK_a^{pot}
Oxide fillers				
RT	73.18	95.84	169.02	8.2-8.5
WU	25.89	67.05	92.98	9.7-11.4
Clay fillers				
KH	78.18	120.93	199.11	9.1
BC	148.55	185.23	333.78	7.4-7.5
Quartz fillers				
KQ	48.51	80.14	128.65	7.1-7.2
SN	152.23	189.52	341.75	8.5-8.9

Comparing the results of the study of quartz fillers SN and KQ (Fig. 1, Table 4), in which the content of SiO_2 (quartz) is approximately the same (97-99%), it is evident that the acid-base nature of the surface is significantly influenced by the quantity and chemical nature mineral impurities. So, in addition to quartz, in the SN there is montmorillonite, and in the composition of KQ montmorillonite, kaolinite, albite and orthoclase. The surface of SN in general is characterized by an alkaline nature (pK_a^{pot} = 8.5-8.9), in which, besides the neutral Brensted centers, there are strongly acid centers with $pK_a \approx$ -0.5-1.5 (possibly partly of Lyus's nature) and alkaline centers with $pK_a \approx$ 9-10. The surface KQ has a neutral character (pK_a^{pot} = 7.1-7.2) with a small amount of acid, neutral and alkaline centers. In general, the SN surface is characterized by almost 3 times the larger specific number of active centers than KQ.

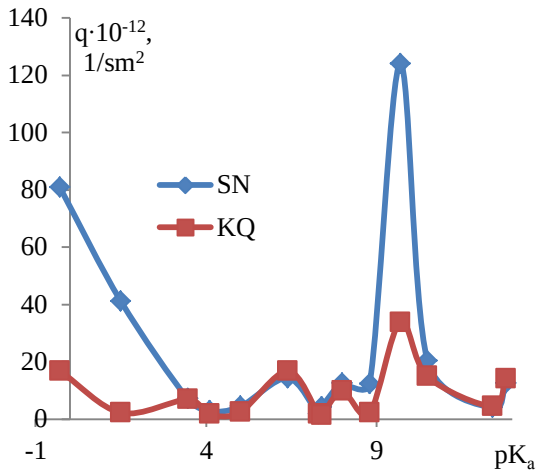


Fig. 1: pK_a-specters of acid-base active centers on the surface of Quartz sand (SN) and Quartzite (KQ): q – a specific number of surface active centers, pK_a – negative logarithm of the acid dissociation constant of the surface active centers.

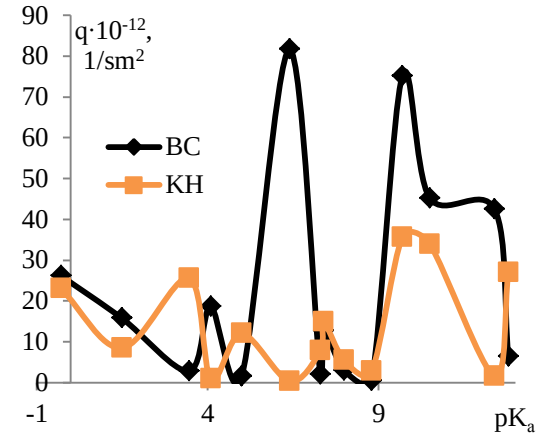


Fig. 2: pK_a-specters of acid-base active centers on the surface of Bentonite clay (BC) and Kaoline (KH): q – a specific number of surface active centers, pK_a – negative logarithm of the acid dissociation constant of the surface active centers.

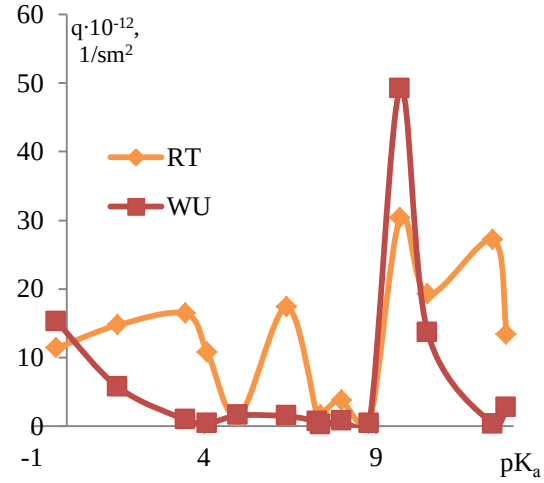


Fig. 3: pK_a-specters of acid-base active centers on the surface of Rutile (RT) and Red mud wastes (WU): q – a specific number of surface active centers, pK_a – negative logarithm of the acid dissociation constant of the surface active centers.

In fig. 2 shows the pK spectra of the active centers of clay fillers BC and KH. Obviously, that the acidity of the surface of this type of fillers, also significantly depends on the mineral composition. BC consists of montmorillonite with impurities of quartz and kaolinite. The surface BC is almost neutral (pK_a^{pot} = 7.1-7.2) with a predominant number of neutral $pK_a \approx 7$ and very basic $pK_a \approx$ 9-12 active centers. The main mineral phase of KH is kaolinite, and by the side – quartz, biotite and hydrous micas. The surface of KH has 2.5 times less specific number of active centers and alkaline (pK_a^{pot} = 9.1).

The comparative estimation of oxide fillers shows that the surface acidity and total specific surface area active surface area RT (TiO_2) exceeds WU (Fe_2O_3) (Fig. 3, Table 4). Obviously, in this case, the nature of the surface of the filler is directly proportional to the acid-base properties of the oxide. The obtained data of the pK-metric research are confirmed by the results of the quantum-chemical modeling of the acid-base properties of the active centers. So, as a result of the simulation, it was found that the Bronsted center's acidity of the TiO_2 surface is higher than that of Fe_2O_3 [33].

4.2. Investigation of Properties of Epoxy Polymer Composites

The composite resistance to water and aqueous solutions was researched by the method of the sample dipping into an aggressive aqueous medium at a temperature of 20 ± 5°C. As aggressive mediums, distilled water, 0.1 N NaOH and H_2SO_4 solutions were used. The absorbing capacity of the samples of the filled epoxy materials in aggressive mediums according to the mass relative gain $\Delta m = (m_0 - m) \cdot 100 / m_0$ over a definite period of time was calculated.

For the influence analysis of the structural factor on the absorbing capacity of the filled composites, it is necessary to compare the distant value between the fragments and the sample mass relative gain in water mediums. Thus, the distance between the fragments (a) in the composites with fillers increases in the series:

$$WU(2.4) < KH(3.4) < RT(8.5) < SN(10.2) < BC(11.2) < KQ(13.1). \quad (2)$$

The sample mass gain of the composites (Δm) increases in the series:
for distilled water:

$$KH(0.43) < WU(0.5) < RT(0.56) < BC(0.64) < KQ(3.1) < SN(3.53); \quad (3)$$

for H_2SO_4 solution:

$$WU(0.49) < KH(0.53) < RT(0.7) < BC(0.71) < KQ(4.33) < SN(5.19); \quad (4)$$

for NaOH solution:

$$KH(0.38) < WU(0.47) < RT(0.58) < BC(0.6) < KQ(3.01) < SN(3.82). \quad (5)$$

Comparing the received series (2-5), it is possible to conclude that, for molecules and ions of the aggressive medium immission into the composites, the structural factor is not crucial. It shows that, between the surface groups of the fillers and the functional groups of an epoxy net, there are physical-chemical interactions with bond formations. These bonds form so called "physical" net of a composite. It is evident, that solid interaction formations at the interface of the phases "polymer-filler" results in the forming of a denser composite structure. On the other hand, intensive inter-phase interactions can cause the appearance of internal stress and are able to lead to the deprivation of a composite durability in liquid mediums. Hence, to receive a full picture, it is essential to consider the chemical-mineralogical characteristics and the surface features of the fillers. Generalizing the results of the research of the filler chemical-mineralogical influence on the absorbing capability, it is possible to conclude, that the sample mass gain of epoxy composites in all aqueous mediums increases in the series:

oxide fillers < clay fillers < quartz fillers.
The surface acidity of the fillers decreases, and pK_a^{pot} of the surface groups increases in the series:

$$KQ(7.15) < BC(7.45) < RT(8.35) < SN(8.7) < KH(9.1) < < WU(10.5). \quad (6)$$

Comparing the received series (3-5) and (6), it is essential to state, that the durability of the filled composites to aqueous medium effects enlarges with the increase of pK_a^{pot} of the surface group filler; in other words, the decrease of the acidity and the increase of the surface basicity. It is connected with the increase of the inter phase interaction intensity according to the acid-base mechanism, where, in the role of the base, the filler surface is presented, and the role of the acid is presented by an epoxy polymer. Such kind of conclusion is brought into accordance with the research results [23,34], which demonstrate that an epoxy resin molecules are characterized by week acid properties. Thus, generalizing the determined regularities of the inorganic filler influence on the durability of the filled epoxy composites in aqueous mediums, it can be stated that, during the analysis, it is necessary to consider the following factors: structural (considering the size of the fragments and the volume fraction), chemical-mineralogical (considering the chemical and mineralogical composition) and surface (considering the chemical nature of the surface centers). The results of the research show, that in order to receive epoxy composites with the increased durability to aqueous mediums, it is essential to use the fillers of oxide or clay nature with the basic alkaline function of the surface.
To evaluate the thermal stability of the received samples of the filled epoxy composites, thermogravimetric analysis (TG) and differential scanning calorimetry (DSC) method were used involving the SDT Q600 device manufactured by TA Instruments (USA). The researches were held under an argon atmosphere at a temperature interval of 20−900°C and at a speed of 5ºC/min temperature increase. The mass of the samples was 1,5−4 mg. The Stage temperature intervals of the destruction were estimated according to the temperature of mass loss curve. The glass transition (T_g) was calculated according to DSK curve. The temperature at the maximum heat release (T_{max}) was calculated according to the diagrams. The received results are demonstrated in table 4.
As the result of the thermal testing, it has been found out that, the glass transition of the epoxy composites decreases in 9-18ºC while a filler adding. The results obtained are satisfactorily consistent with the studies of other authors [35-38]. The authors [37, 38] associate this fact with the violation of the topological structure or the formation of topological defects of the netting, and the general plasticisation of the polymer. The authors [35] believe that the decrease in the T_g of the polymer netting is due to the intense interaction between the amino groups of the filler and the oxygen atoms of the metal oxides due to hydrogen bonds and possibly donor-acceptor interactions. It is evident, that the inter phase interactions exist in a filled polymer. They have an acid-base character and have an ability to affect the segmental mobility of the interstitial molecular links as well as the density of a formed network polymer [23]. Acid-basic character of interphase interactions is confirmed by the fact that the largest values of T_g have composites with alkaline nature of the surfactants WU (pK_a^{pot} = 10.5) and KH (pK_a^{pot} = 9.1). For example, in composites with fillers with weak-grained or neutral nature of the surface KQ (pK_a^{pot} = 7.15), BC (pK_a^{pot} = 7.45), RT (pK_a^{pot} = 8.35), the glass transition temperature decreases by 17-18ºC. In this case almost neutral with pKa≈7 and strongly alkaline active centers with $pK_a \approx$ 9-12 predominate on the BC surface. On surfaces SN and RT simultaneously with alkaline centers with $pK_a \approx$ 9-10 and $pK_a \approx$ 9.5 there are active acidic centers with pK_a = -0.5-3.5. In composites with alkaline and strongly alkaline fillers SN (pK_a^{pot} = 8.7), KH (pK_a^{pot} = 9.1), WU (pK_a^{pot} = 10.5), the glass transition temperature decreases by 11, 9 and 10 °C, respectively. Thus, it is evident that in the formation of the structure of epoxy composites on phase boundary between the acid-basic interactions, in most cases involved surface strongly alkaline active centers of fillers. At the same time, with increasing acidity of the surface of fillers, the segmental mobility of interstitial molecular units increases and the T_g of the polymer netting decreases.

Table 4: Thermal test results of epoxy composites

Composite	T_g,ºC	T_{max},ºC	Mass loss at T_{max}, %	T,ºC at mass loss,%			
				5	10	50	90
EP (filler free)	90	330	98	295	325	330	330
Oxide fillers							
RT	-	-	-	>900	>900	>900	>900
EP+RT	73	360	30	250	308	400	400
WU	-	-	-	275	625	>900	>900
EP+WU	80	454	67	274	320	435	517
Clay fillers							
KH	-	-	-	475	526	>900	>900
EP+KH	81	361	99	295	335	335	335
BC	-	-	-	471	867	>900	>900
EP+BC	72	482	70	265	309	417	509
Quartz fillers							
KQ	-	-	-	>900	>900	>900	>900
EP+KQ	72	265	6	252	287	470	517
SN	-	-	-	>900	>900	>900	>900
EP+SN	79	270	8	239	276	424	546

It is known [39, 40] that the thermodestruction of the epoxy polymer netting takes place in three stages:
- the first stage at temperatures below 200 ºC, on which there is additional hardening [39];
- the second stage at temperatures from 200 °C to 330 °C, in which the ligaments or "weak points" of the polymeric mesh −C−O− and −C−N− [39, 40] are destroyed;
- the third stage at temperatures above 330ºC, where the destruction of the hydrocarbon skeleton of the net occurs.

As is known, the patterns of thermal destruction of filled epoxy polymers do not differ from the mechanisms of destruction of the non-filled and occur in three stages [41-43].
The analysis of the given thermal testing shows, that the composites can be formed adding the inorganic oxide, clay and quartz fillers. The composite temperature at the starting of the destruction (at 200−330ºC temperature interval and at 5−10% mass loss) decreases in 8−56ºC. The presence of the fillers makes the thermal destruction process of a polymer net with −C−O− i −C−N− bond breaking easier. Over further destruction process, the increase of a temperature (up to 70−187ºC for oxide, 5−179ºC for clay and 94−216ºC for quartz fillers) at the starting of the decomposition (at 50−90% mass loss) is observed [24]. Perhaps, the thermal stability increase of the carbohydrate skeleton of an epoxyamine net, if any inorganic filler is, connected with the increase of a unit total number and a lacing density. The obtained results are evidently the consequence of the surface acid-base active center catalytic effect of the fillers.

5. Conclusion

Thus, as the result of the scientific researches, it has been found out that the thermal stability and the absorbing capacity of the filled composites in water and any aqueous acid and alkaline measures considerably depend on the surface properties, chemical and mineralogical nature of the inorganic fillers. It has been investigated that in order to receive epoxy polymer composite materials with an increased thermal stability and, at the same time, with a decreased absorbing capacity, it is essential to use oxide or clay fillers with a basic (alkaline) surface function.

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