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POLYMER COMPOSITES ON THE BASIS OF EPOXY RESIN WITH MINERAL FILLERS MODIFIED BY TETRAETOXYSILANE

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Abstract. Ultimate strength, softening temperature, and water absorption of the polymer composites based on epoxy resin (type ED-20) with unmodified and/or modified by tetraethoxysilane (TEOS) minerals diatomite and andesite are described. Comparison of experimental results obtained for investigated composites shows that the ones containing modified filler have better technical parameters mentioned above than composites with unmodified filler at corresponding loading. It was experimentally shown that the composites containing binary fillers diatomite and andesite at a definite ratio possess optimal characteristics – so called synergistic effect. Experimental results are explained in terms of structural peculiarities of polymer composites.

Keywords*:* polymer composite, epoxy resin, modified filler, ultimate strength, softening temperature, water absorption, synergistic effect of fillers.

1. Introduction

In recent times mineral fillers attract attention as active filling agents in polymer composites [1, 2]. Thanks to these fillers many properties of the composites are improved – durability and rigidity increase, shrinkage during hardening process and water absorption decrease, thermal stability, fire proof and dielectric properties are improved and finally the price of such composites becomes cheaper [3-5]. At the same time it must be noted that the mineral fillers at high content lead to some impairment of different physical properties of composites. Therefore the attention of the scientists is attracted to substances which would eliminate the mentioned leaks. It is known that silicon organic substances (both low and high molecular) display hydrophobic properties, high elasticity and durability in a wide range of fillings and temperatures [6, 7].

The purpose of this work is investigation of the effect of some minerals (diatomite and andesite) modified by TEOS on physical properties of composites based on epoxy resin.

2. Experimental

Mineral diatomite as a filler was used. The organic solvents were purified by drying and distillation. The purity of starting compounds was controlled by an LKhM-8-MD gas liquid chromatography; phase SKTF-100 (10 %, the NAW chromosorb, carrier gas He, 2m colon). FTIR spectra were recorded on a Jasco FTIR-4200 device.

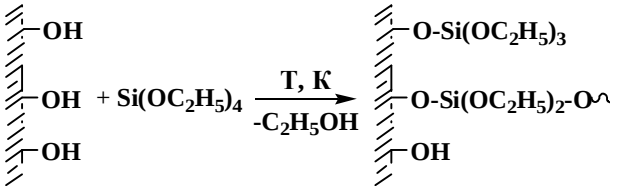
The silanization reaction of diatomite surface with TEOS was carried out by means of three-necked flask supplied with mechanical mixer, thermometer and dropping funnel. For obtaining of modified by 3 mas % diatomite to a solution of 50 g grind finely diatomite in 80 ml anhydrous toluene the toluene solution of 1.5 g (0.0072 mol) TEOS in 5 ml toluene was added. The reaction mixture was heated at the boiling temperature of used solvent toluene. Than the solid reaction product was

filtrated, the solvents (toluene and ethyl alcohol) were eliminated and the reaction product was dried up to constant mass in vacuum. Other product modified by 5 % tetraethoxysilane was produced *via* the same method.

The following parameters were defined for obtained composites: ultimate strength (on the stretching apparatus of type "Instron"), softening temperature (Vica method), density and water absorption (at saving of the corresponding standards).

3. Results and Discussion

High temperature condensation reaction between diatomite and TEOS on one side and between andesite and the same modifier on the other side was carried out in toluene solution (~ 38 %). The masses of TEOS were 3 and 5 % from the mass of filler. The reaction systems were heated at the solvent boiling temperature (~ 383 K) during 5–6 h under stirring. The reaction proceeds according to the following scheme:



The direction of reaction defined by FTIR spectra analysis has shown that after reaction between mineral surface hydroxyl, $–OSi(OEt)_3$ and the $–OSi(OEt)_2O–$ groups are formed on the mineral particles surface.

In the FTIR spectra of modified diatomite one can observe absorption bands characteristic of asymmetric valence oscillation for linear ≡Si–O–Si≡ bonds at 1030 cm^{-1}. In the spectra one can see absorption bands characteristic of valence oscillation of ≡Si–O–C≡ bonds at 1150 cm^{-1} and for ≡C–H bonds at 2950–3000 cm^{-1}. One can see also broadened absorption bands characteristic of unassociated hydroxyl groups.

On the basis of modified diatomite and epoxy resin (of type ED-20) the polymer composites with different content of filler were obtained after careful wet mixing of components in mixer. After that the blends with hardening agent (polyethylene-polyamine) were placed to the cylindrical forms (in accordance with ISO standards) for hardening, at room temperature during 24 h. The hardened samples were exposed to temperature treatment at 393 K during 4 h.

The concentration of powder diatomite (average diameter up to 50 micron) was changed in the range 10–60 mas %.

The curves in Fig. 1 show that at increasing of filler (diatomite) concentration in the composites the density of materials essentially depends on both diatomite and modifying agent (TEOS) concentration. Naturally the decreasing of density of composites at increasing of filler concentration is due to increasing of micro empty areas, which form in composition materials at high filling (Fig. 1, *curve* 1). The composites with diatomite modified by TEOS contain smaller amount of empty areas as they are filled with modifying agent (Fig. 1, *curves* 2 and 3).

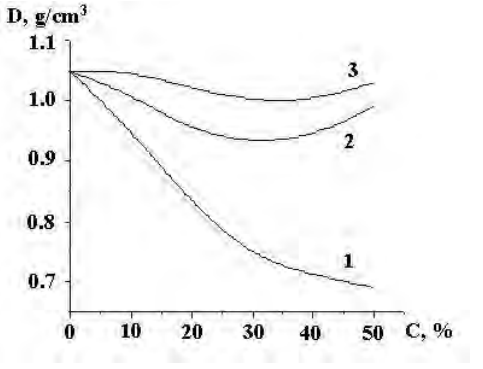


Fig. 1. Dependence of the density of the composites based on epoxy resin on the concentration of unmodified (1), modified by 3 mas % (2) and 5 mas % (3) tetraethoxysilane diatomite

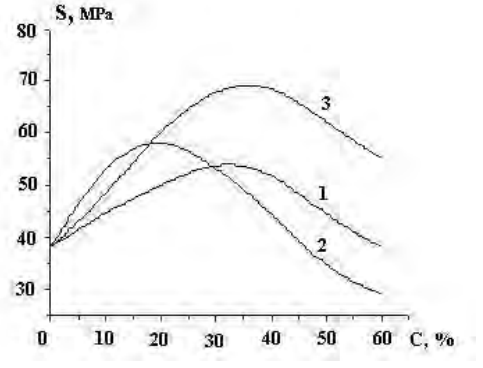


Fig. 2. Dependence of ultimate strength of the composites based on ED-20 with unmodified (1) and modified by 3 mas % (2) and 5 mass % (3) TEOS diatomite

Investigation of composites softening temperature was carried out by apparatus of Vica method. Fig. 3 shows the temperature dependence of the indentor deepening on the mass of the sample for composites with fixed concentration (20 mas %) of the fillers unmodified and modified by TEOS.

The dependence of ultimate strength on the content of diatomite (modified and unmodified) presented in Fig. 2 shows that it has an extreme character. However, the positions of corresponding curves maximums essentially depend on the amount of modifying agent TEOS. The general view of these dependences is in full conformity with well known dependence of $\sigma - C$ [8]. The sharing of the maximum of

curve for composites containing 5 % of modified diatomite from the maximum for the analogous composites containing 3 % modifier to some extent is due to increasing of the amount of the bonds between filler particles and macromolecules at increasing of the concentration of the filler.

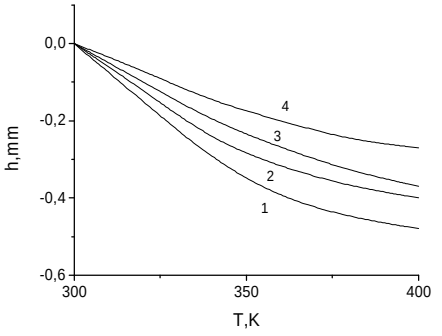


Fig. 3. Temperature dependence of the indentor deepening in the sample for composites containing 0 (1), 20 mas % (2), 20 mas % modified by 3 % TEOS (3), 20 mas % modified by 5 % TEOS (4) diatomite

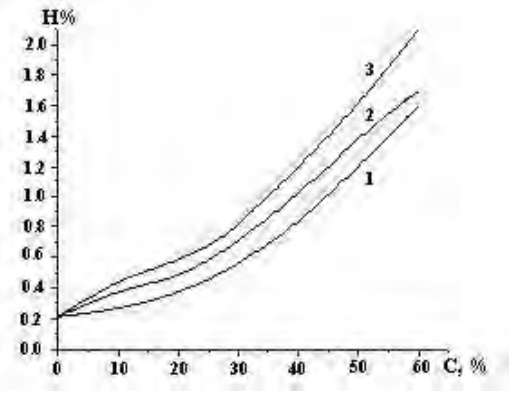


Fig. 4. Dependence of the water-absorption on the concentration of filler in the composites based on epoxy resin containing diatomite modified by 5 % (1) and 3 % (2) tetraethoxysilane and unmodified one (3)

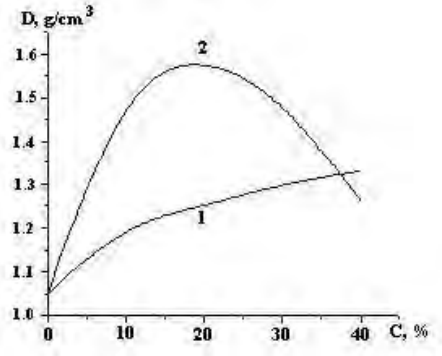


Fig. 5. Dependence of the density on the concentration of diatomite in binary fillers with andesite: unmodified (1) and modified by 5 % tetraethoxysilane (2) fillers for composites based on epoxy resin. Full concentration of binary filler in composites 50 mas %

The investigation of binary fillers effect on the properties of the composites with same polymer basis (ED-20) was conducted. Two types of minerals – diatomite and andesite – with different ratios were used as fillers. It was interesting to establish the effect of both of the ratio of the fillers and the effect of modifier TEOS on the same properties of the polymer composites investigated above.

The curves presented in Fig. 5 show the effect of modifying agent TEOS on the dependence of the density of composites containing the binary filler diatomite and andesite on the ratio of the latest when the total content of fillers is 50 mas %, which the maximal ultimate strength corresponds to. The maximum of the noted effect corresponds to composite filler ratio diatomite/ andesite in which is about 20/30. Probably microstructure of such composite corresponds to optimal distribution of filler particles in the polymer matrix at minimal inner energy of statistical equilibration, at which the concentration of empty areas is minimal because of dense disposition of the composite components. It is known that such structures contain minimal amount both of micro and macro structural defects [8].

Such approach to microstructure of composites with optimal ratio of the composite ingredients allows supposing that these composites would possess high mechanical properties and thermo-stability and low water absorption. Moreover the composites with same concentrations of the fillers modified by TEOS possess all the noted above properties better than the composites with unmodified binary fillers (Figs. 6-8). Indeed the curves in Figs. 6-8 show that the maximal ultimate strength, thermo-stability and simultaneously hydrophobicity correspond to composites with the same ratio of fillers to which the maximal density corresponds.

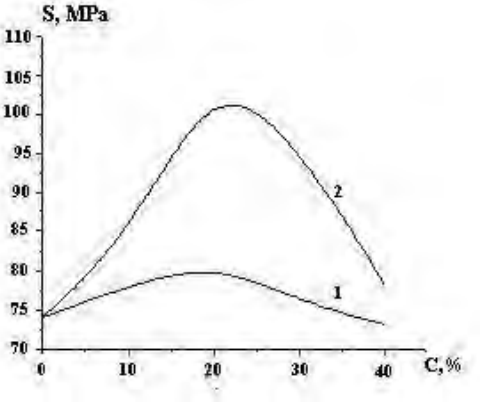


Fig. 6. Dependence of the ultimate strength on the concentration of diatomite in binary fillers with andesite: unmodified (1) and modified by 5 % tetraethoxysilane (2) fillers for composites based on epoxy resin. Full concentration of binary filler in composites 50 mas %

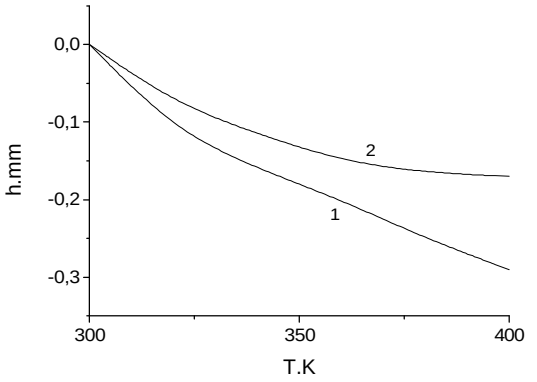


Fig. 7. Thermo-stability of composites with binary fillers at diatomite/andesite ratio =20/30

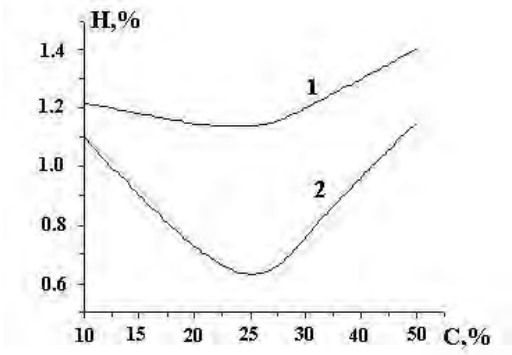


Fig. 8. Dependence of water-absorption of composites based on epoxy resin on the concentration of diatomite in binary fillers with andesite: unmodified (1) and modified by 5 % tetraethoxysilane (2) fillers. Total concentration of binary fillers in composites 50 mas %

The obtained experimental results may be explained in terms of composite structure peculiarities. Silane molecules displaced on the surface of diatomite and andesite particles lead to their activation and participate in chemical reactions between active groups of TEOS (hydroxyl) and homopolymer (epoxy group). Silane molecules create the "buffer" zones between filler and the homopolymer. This phenomenon may be one of the reasons of increasing of strengthening of composites in comparison with the composites containing unmodified fillers. The composites with modified diatomite display higher compatibility of the components than in case of the same composites with unmodified filler. The modified filler has stronger contact with polymer matrix (thanks to silane modifier) than unmodified diatomite. Therefore mechanical stresses formed in composites by stretching or compressing forces is absorbed effectively by relatively soft silane phases, *i.e.* the development of micro defects in carbon chain polymer matrix of composite districts, and finishes in silane part of material, the rigidity of which decreases.

The structural peculiarities of composites are also displayed in thermo-mechanical properties of the materials. It is clear that softening of composites with modified by TEOS composites begins at relatively high temperatures. This phenomenon is in good correlation with corresponding composite mechanical strength. Of course the modified filler has more strong interactions (thanks to modifier) with epoxy polymer molecules than the unmodified filler.

The amplified competition of the filler particles with macromolecules by TEOS is also well displayed on the characteristics of water absorption. In general loosening of micro-structure because of micro empty areas is due to increasing of filler content. Formation of such defects in the microstructure of composite promotes water absorption processes. Water absorption of the composites with modified diatomite is lower than of the composites with unmodified filler to some extent. Decreasing of water absorption of composites containing silane compound is the result of their hydrophobic properties.

Composites with binary fillers possess so called synergistic effect – non-additive increasing of technical characteristics of composites containing the fillers at a definite ratio, which is due to creation of the dense distribution of ingredients in composites.

4. Conclusions

Comparison of the density, ultimate strength, softening temperature, and water absorption for polymer composites based on epoxy resin and unmodified and modified by tetraethoxysilane mineral fillers diatomite and andesite leads to conclusion that modifying agent stipulates the formation of heterogeneous structures with higher compatibility of ingredients and consequently to enhancing of the noted above technical characteristics.

References

[1] Katz H. and Milevski J.: Handbook of Fillers for Plastics, RAPRA, New York 1987.
[2] Mareri P., Bastrole S., Broda N. and Crespi A.: Comp. Sci. Techn., 1998, **58**, 747.
[3] Tolonen H. and Sjolind S.: Mechanics of Comp. Mat., 1996, **31**, 317.
[4] Rothon S.: Particulate Filled Polymer Composites, RAPRA, New York 2003.
[5] Lou J. and Harinath V.: J. Mat. Proc. Techn., 2004, **152**, 185.
[6] Khananashvili L., Mukbaniani O. and Zaikov G.: New Concepts in Polymer Science. Elementorganic Monomers: Technology, Properties, Applications. VSP, Utrecht 2006.

[7] Aneli J., Khananashvili L. and Zaikov G.: Structuring and Conductivity of Polymer Composites. Nova Sci. Publ., New York 1998.
[8] ZelenevY. and Bartenev G.: Fizika Polymerov. Vysshaya Shkola, Moskwa 1978.

ПОЛІМЕРНІ КОМПОЗИТИ НА ОСНОВІ ЕПОКСИДНОЇ СМОЛИ З МІНЕРАЛЬНИМИ НАПОВНЮВАЧАМИ МОДИФІКОВАНИМИ ТЕТРАЕТОКСИСИЛАНОМ

Анотація. *Наведені результати дослідження межі міцності, температури розм'якшення і водопоглинання полімерних композитів на основі епоксидної смоли (ЕД-20), що містить немодифіковані і модифіковані тетраетоксисиланом (ТЕОС) мінерали діатоміт і андезит. Порівнянням експериментальних результатів встановлено, що композити з модифікованим наповнювачем характеризуються кращими технічними параметрами у порівнянні з аналогами з немодифікованим наповнювачем. Експериментально показано, що композити з бінарним наповнювачем (діатоміт і андезит) при певному співвідношенні компонентів виявлять синергетичний ефект. Одержані результати пояснюються з точки зору структурних особливостей полімерних композитів.*

Ключові слова: *полімерний композит, епоксидна смола, модифікований наповнювач, межа міцності, температура розм'якшення, водопоглинання, синергетичний ефект.*