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MACROMOLECULAR COMPOUNDS AND POLYMERIC MATERIALS

Synthesis of a Composite Polymeric Material in the System Consisting of Epoxy–Anhydride Matrix and Analcime- and Montmorillonite-Containing Rock

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Abstract—The conditions of synthesis of a composite material in the system consisting of an epoxy–anhydride polymeric matrix and an analcime-containing rock were studied. Addition of the filler allows the service characteristics to be improved by 20–25%. Samples with a low content of analcime-containing rock (up to 1 wt %) exhibit the best service characteristics.

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One of promising routes of modification of an epoxy polymer matrix is the use of natural layered and porous silicates, in particular, montmorillonite and zeolites [1–4]. The crystal structure of montmorillonite allows the size of interlayer voids to be increased by using various surfactants, in particular, quaternary ammonium bases, with possible accommodation of guest molecules in these voids [5]. Depending on the amount of foreign molecules, either "swelling" of intracrystalline voids or exfoliation of a filler particle along interlayer fragments of the structure, with formation of a hybrid nanocomposite [6], can be observed.

Zeolites (alkali and alkaline-earth metal aluminosilicates) are porous bodies characterized by a definite framework structure and regular pore geometry (intracrystalline voids and channels) into which various molecules can penetrate upon dehydration. Exchangeable cations and aluminosilicate framework can be modified by chemical treatment, which allows control over chemical forces acting on sorbed molecules [7].

In this connection, it is of certain interest to combine two types of fillers, e.g., mineral rocks, containing both montmorillonite and zeolite. In addition, the development of mineral-filled polymeric composite materials with new service properties and functional possibilities is an important factor for efficient utilization of natural raw materials and for development of new resource-saving technologies.

In this study we examined the physicochemical features of the synthesis of a polymeric composite material in the system consisting of an epoxy polymer matrix and of a zeolite- and montmorillonite-containing rock.

EXPERIMENTAL

As a polymeric matrix we used a well-known system of ED-20 epoxy–4,4'-isopropylidenediphenol oligomer and isomethyltetrahydrophthalic anhydride (*iso*-MTHPA).

The mineral composition of the analcime- and montmorillonite-containing rock is given in Table 1.

Chemical transformations occurring in the course of heat treatment of an analcime-containing rock were studied with an MOM Q-1500D derivatograph at a heating rate of 5 deg min^{-1}.

The phase composition was refined by X-ray phase analysis. The diffraction patterns were taken with a DRON-4M diffractometer using CuK_α radiation (λ = 1.5418 Å).

The powder patterns were interpreted using the International Center of Diffraction Data (JPCD–ICDD) database. The relative content of crystalline phases in the material was determined with a Powder Cell program for X-ray phase analysis. The error in determining the amount of crystalline phases was ± 5% at a confidence level of 0.95.

Processes occurring in the course of synthesis of the composite material were examined by differential scanning calorimetry (DSC, Shimadzu DSC-60 device) and by chemical analysis for functional groups. Epoxy groups were determined by the method based on reaction of an epoxy compound with hydrochloric acid, followed by titration of excess acid in acetone with an alkali solution. The equivalence point in acid–base titration was determined with Methyl Red indicator. For iso-MTHPA, the content of free carboxy groups was determined from the difference between the total acidity of the curing agent and the acidity corresponding to the content of anhydride groups. The total acidity was determined by titration with an alkali solution in pyridine. The acidity corresponding to the content of anhydride groups was determined after the reaction with aniline, yielding 1 equiv of carboxylic acid and 1 equiv of amide.

The strength properties were determined with an IR 5057-60 tensile-testing machine ensuring sample extension with a constant rate of motion of the active clamp and measurement of the load with a relative error of ≤1%.

As seen from Table 1 [8], the analcime-containing rock consists of the clay component (about 50%), quartz (20%), and analcime (25%). The major components of clay are montmorillonite, analcime, and quartz.

Table 1. Mineral composition of analcime-containing rock

Mineral	Content, wt %
Quartz	20
Montmorillonites	35
Feldspars	10
Kaolinite	5
Calcite	5
Analcime	25

Analcime is an alkali metal aluminosilicate mineral belonging to the class of zeolites. Their crystal structure is characterized by the presence of voids (up to 0.2 nm) [7]. Therefore, they have large surface accessible to adsorption of foreign molecules. However, the size of the entrance window in analcime is as small as 0.26 nm, allowing sorption of only small molecules such as acetylene or water. Shushkov and Noskov [8] showed that thermal or acid treatment of analcime increases the pore volume and the mean pore diameter (by 10–20%).

Figure 1 shows the thermogram of an analcime-containing rock sample. It can be seen that the adsorbed water is removed at temperatures of about 140°C. The second endothermic peak at 520°C corresponds to removal of water of crystallization. The third peak is exothermic and is associated with oxidative processes occurring in the sample after removal of hydroxy groups and with structural changes.

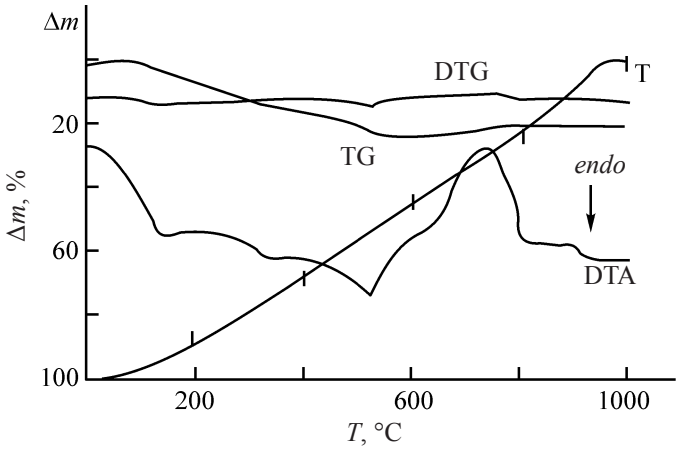

Fig. 1. Thermogram of a sample of analcime-containing rock: (Δ*m*) weight loss and (*T*) temperature.

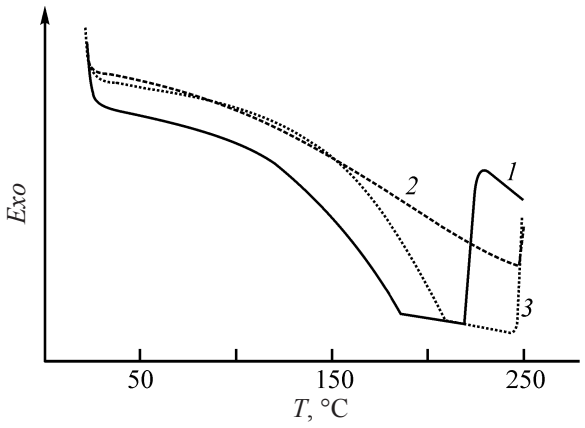

Fig. 2. DSC curves for the systems (*1*) phenyl glycidyl ether–analcime-containing rock, (*2*) ED-20–analcime-containing rock, and (*3*) *iso*-MTHPA–analcime-containing rock. (*T*) Temperature; the same for Fig. 3.

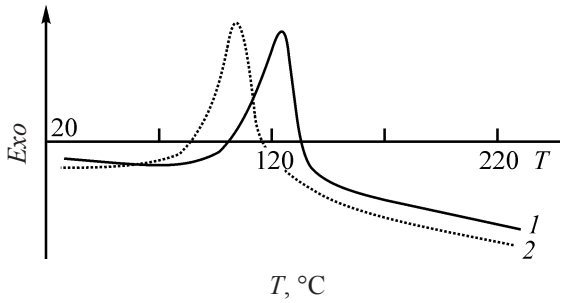

Fig. 3. DSC curves of polymerization in the systems (*1*) ED-20–*iso*-MTHPA and (*2*) ED-20–*iso*-MTHPA–0.5 wt % analcime-containing rock.

In this step of the study, the analcime-containing rock was not subjected to any additional treatment apart from heating to 200°C. After sieve analysis (ELSA-M screen) we took the fraction with the particle size smaller than 40 μm.

The systems ED-20–analcime-containing rock, *iso*-MTHPA–analcime-containing rock, and phenyl glycidyl ether–analcime-containing rock were studied by DSC (Fig. 2).

The results of DSC and chemical analysis show that components of the polymeric matrix do not react with filler particles, i.e., improvement of the service properties of the material is due to physical adsorption caused by hydrogen bonds forming an additional strong network which compensates increased nonuniformity and defectiveness in boundary layers.

Figure 3 shows typical DSC curves characterizing polycondensation in the course of synthesis of the composite materials. The temperatures of the onset, maximum, and end of the exothermic peak and the magnitude of the exothermic effect of the reaction are given in Table 2.

Table 2. DSC data for polycondensation in the course of synthesis of a composite in the system consisting of ED-20, *iso*-MTHPA, and analcime-containing rock

Content of analcime-containing rock, wt %	T_{on}	T_{max}	T_{end}	Energy effect, J g^{-1}
	°C			
–	81	123	149	222
0.5	60	105	126	246
1	81	124	140	229
5	83	127	163	218
10	85	128	161	236
15	90	130	160	211

Table 2 shows that, as the analcime content is increased from 1 to 15 wt %, the temperature of the reaction onset in the synthesis of the composite material slightly increases. For the system consisting of ED-20, *iso*-MTHPA, and 0.5 wt % analcime-containing rock the temperature of the polycondensation onset decreases by 20°C. Apparently, at low filler concentrations, oligomer molecules in the adsorption layer undergo ordering due to specific orientation of polar groups (glycidyl, hydroxy) relative to particles of the analcime-containing rocks, creating "kinetically favorable" order and thus catalyzing the three-dimensional polymerization.

Evaluation of the service characteristics (Martens softening point T_M, bending strength σ_b, tensile strength σ_t) (Table 3) of the composite material shows that the samples containing up to 1 wt % filler exhibit the best properties, i.e., the effect of small additions is observed. In this case, improvement of the service characteristics is attributed to formation of a reinforcing framework by filler particles, orientation of macromolecules, and their transition into thin ordered films. The major factor, however, is the adhesion of the polymer to solid surfaces. As a rule, adhesion in polymers is due to physical (including hydrogen) bonds forming an additional strong network and compensating increased nonuniformity and defectiveness in boundary layers. However, as the interaction of the polymer with the surface becomes stronger, internal stresses weakening the composite also increase. The same interaction affects the structure and properties of the polymer in boundary layers whose

Table 3. Physicochemical characteristics of the composite material consisting of an epoxy–anhydride matrix and an analcime-containing rock

Content of analcime-containing rock, wt %	T_M, °C	σ_t	σ_b
		MPa	
0	110 ± 2	44 ± 4	110 ± 5
0.5	132 ± 2	63 ± 4	145 ± 5
1	123 ± 2	55 ± 4	125 ± 5
5	123 ± 2	53 ± 4	125 ± 5
10	118 ± 2	50 ± 4	120 ± 5
15	115 ± 2	45 ± 4	110 ± 5
25	105 ± 2	35 ± 4	100 ± 5

contribution increases with an increase in the surface area of the phase boundary.

CONCLUSION

Composite materials with improved service properties (softening point, bending strength) compared to the unfilled polymers were prepared from an epoxy polymer and an analcime-containing rock. The improved properties are due to physical adsorption interactions between the polymer and filler.

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REFERENCES

1. Kulichikhin, V.G., Antonov, S.V., Makarova, V.V., et al., *Ross. Nanotekhnol*., 2006, vol. 1, nos. 1–2, pp. 170–182.
2. Lomakin, S.M. and Zaikov, G.E., *Vysokomol. Soedin*., 2005, vol. 47, no. 1, pp. 104–120.
3. Akimbaeva, A.M. and Ergozhin, E.E., *Izv. Vyssh. Uchebn. Zaved., Khim. Khim. Tekhnol.*, 2006, vol. 49, no. 6, pp. 127–128.
4. Schaak, R.E. and Mallouk, T.E., *Chem. Mater*., 2002, vol. 14, no. 4, pp. 1455–1471.
5. Pomogailo, A.D., *Vysokomol. Soedin., Ser. C*, 2006, vol. 48, no. 7, pp. 1318–1351.
6. Gerasin, V.A., Zubova, T.A., Bakhov, F.N., et al., *Ross. Nanotekhnol.*, 2007, vol. 2, nos. 1–2, pp. 90–105.
7. Treacy, M.M.J., Foster, M.D., and Randall, K.H., *Micropor. Mesopor. Mater.*, 2006, vol. 87, pp. 255–260.
8. Shushkov, D.A. and Noskov, A.V., *Litol. Polezn. Iskop*., 2007, no. 5, pp. 530–535.