Influence of modified natural zeolite on the thermal stability of epoxy based composites

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***Abstract*—The effect of modified natural zeolite of the Shivyrtuysky deposits on the thermal behavior of epoxy composites at the heating was studied. The modification of the zeolite particles with aluminum oxyhydroxide (AlOOH) nanofibers was made. AlOOH nanofibers were obtained at the heating and oxidation of aluminum powder by water. The parameters of thermal-oxidative and thermal destruction of the samples with a filler concentration of 1, 2, 5 and 10 wt. % were determined. The limiting oxygen index was determined by the calculation method.**

Keywords—epoxy resin, thermal stability, filler, zeolite

I. Introduction

Epoxy polymers have a range of unique properties, such as ease of curing, low shrinkage during curing, high mechanical and electrical insulating properties, adhesive ability, chemical resistance [1, 2]. Therefore, epoxy resins are widely used in construction, mechanical engineering, electrical engineering and other areas of production. However, there is a disadvantage that complicates the use of epoxy resins: their high flammability and increased fire hazard [3, 4].

The flammability of epoxy resins can be reduced by introduction of fillers with flame retardant properties into the epoxy matrix. The use of traditional halogen-containing flame retardants based on bromine and chlorine leads to the formation of highly dangerous and persistent toxic substances, such as phosgene, cyanide compounds, dioxins. Therefore, modern research is aimed at finding and developing environmentally friendly fire retardants. Among inorganic fillers, researchers are attracted by fillers based on natural minerals that are not highly toxic, they are relatively cheap and widely distributed in nature materials [5–7].

Natural zeolites belong to the group of crystalline aluminosilicate minerals. The structure of zeolites has channels and cavities occupied by cations and water molecules that can be freely removed and absorbed by the structure, due to which ion exchange occurs [8]. The structural features of the crystal lattice, the mineral composition, the presence of adsorbed water in the structure of natural zeolites, allow the use of zeolites to reduce the flammability of polymers.

The use of natural zeolites as flame retardant materials for protecting polymeric building structures from fire was shown by Beyer H.K. et al. [9]. Lee J.-Y. et al. studied “the effect of natural zeolite on the mechanical characteristics of epoxy resin” [10]. They demostrated that “the mechanical properties of the composites were improved with decreasing particle size of the zeolite, and the Young's modulus increased with the zeolite content raise in the epoxy polymer” [10]. Bourbigot S. et al. studied the intumescent system based on combination of ammonium polyphosphate and zeolite. They showed that “the presence of zeolite in the studied intumescent system under investigation led to an enhancement in the flame retardant properties of polymeric materials due to the formation of phosphorus-containing carbon compounds at high temperatures” [11].

The aim of this work is to determine the effect of modified zeolite of the Shivyrtuysky deposit on the thermal properties of epoxy polymers.

II. Experimental

A. Objects of investigation

To obtain epoxy composites, epoxy resin of grade ED-20 was used. The curing of the epoxy resin was performed using an amine hardener of polyethylene polyamine (PEPA). Fine powder (<50 μm) of zeolite rock from the Shivyrtuysky deposit of Russia was taken as a filler.

The zeolite particles were modified by precipitation of AlOOH nanofibers on their surface, which are formed “by heating and oxidizing of the submicron aluminum powder in the chemical reaction with water under certain conditions in accordance with the method of hydrothermal synthesis” [12, 13]. The containing zeolite particles suspension with a fraction size less than 0.1 mm and aluminum powder in distilled water was heated to 80 ºC. In order to accelerate the aluminum-water reaction rate alkaline catalyst was used: 10 % aqueous solution of sodium hydroxide NaOH. The addition of NaOH in water contributes in removing the aluminum oxide layer, and water can contact with the aluminum metal. Thus, the AlOOH nanofibers are deposited on the zeolite particles. The stirring of the reaction mixture was carried out using a magnetic stirrer. Then, the modified zeolite was washed to neutral pH, filtered and dried at room temperature.

According to the chemical composition, the zeolitic rock of the Shivyrtuysky deposit belongs to high-silica, and characterized by a high Si/Al ratio (> 4) [14]. The total content of SiO_2 and Al_2O_3 in the Shivyrtuysky zeolitic rock is 79.1 %. The molar ratio of $SiO_2/A1_2O_3$ is 9.25. The content of zeolite in the rock of the Shivyrtuysky deposit can reach 95 %. We used the samples which contain up to 60 % of clinoptilolite.

B. Preparation

The procedure for the manufacture of epoxy-based composites consisted of the following steps.

The zeolite powder surface was treated with PEPA. Then, the required quantity of the zeolite filler was introduced into epoxy resin, and this composition was mixed by hand during 5 min without additional heating. The zeolite content in the epoxy compositions ranged from 1 to 10 mass %. After that, the hardener was added to the mixture in a ratio of epoxy resin to the hardener 10:1 by mass. Then, the composition

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was mixed for another 3 min. The resulting mixtures were cured in the molds made of silicone at room temperature during 24 h. The composition of the specimens is presented in Table I.

TABLE I. FORMULATIONS OF EPOXY COMPOSITES

Sample	ED-20 (wt. %)	PEPA (wt. %)	Zeolite (wt. %)
E0	100	10	0
S1	100	10	1
S2	100	10	2
S5	100	10	5
S10	100	10	10

C. *Characterizations*

The size and morphology of the studied zeolite samples were investigated using scanning electron microscope (SEM) TM-3000 and transmission electron microscope (TEM) JEOL JEM 100 CX II. The Fourier transform infrared spectrum (FTIR) for the studied zeolite rock was recorded using spectrometer Nicolet 5700 in the spectral range 4000-400 cm^{-1}. The values of specific pore volume and specific surface area of modified zeolite were determined by the BET method using a Sorbtometr M instrument. The thermal analysis (thermogravimetric analysis) was made using SDT Q600 thermal analyzer. TG- curves were measured from 25 °C to 850 °C at a rate of heating 10 °C/min under argon atmosphere and air.

III. RESULTS AND DISCUSSION

A. *Characterizations of Zeolite*

Fig. 1 shows SEM image of the modified Shivirtuysky zeolite. Fig. 2 shows the TEM image of the zeolite particles modified with AlOOH nanofibers. On the surface of the zeolite particles, several AlOOH nanofibers are observed; they have a width from 2 to 5 nm and a length from 50 to 150 nm.

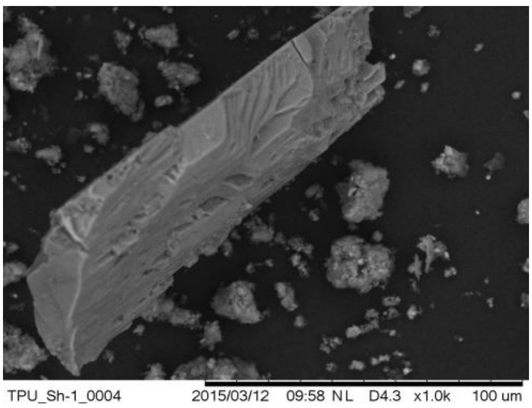

Fig. 1. SEM image of zeolite.

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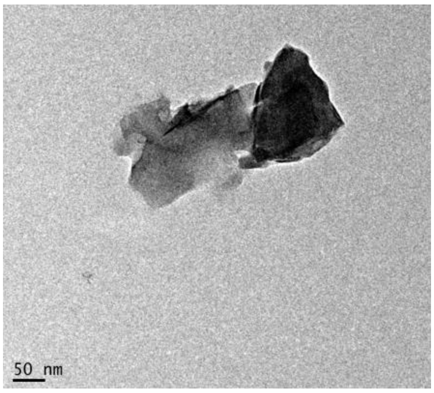

Fig. 2. SEM image of Fe NP.

The specific surface area of the modified Shivyrtuysky zeolite determined by the BET method is 69.6 m^2/g, and specific pore volume is 0.030 cm^2/g. This corresponds to a AlOOH content of about 17 % in zeolite.

The chemical functional groups on the zeolite particles surface were identified using the method of FTIR spectroscopy. The FTIR spectrum of the modified zeolite sample are given in Fig. 3. The most intensive absorption band in the FTIR spectrum of the modified by AlOOH nanofibers zeolite is observed at 1058 cm^{-1}. This "band corresponds to asymmetric stretching vibrations of Si-O-Al and Si-O-Si. The absorption band at 740 cm^{-1} corresponds to symmetric stretching vibrations of these bonds" [8]. The absorption bands at 442 and 482 cm^{-1} correspond to the bending vibration O-Si(Al)-O. The band at 1626 cm^{-1} corresponds to bending vibration of zeolitic and adsorbed water H-O-H. In the range from 3000 to 3750 cm^{-1} there are strong absorption bands which are "associated with the existence of zeolite water" [15]. The peaks at approximately 3383, 3095, 1162, 1058, 740, and 482 cm^{-1} are typical absorption bands for AlOOH [15].

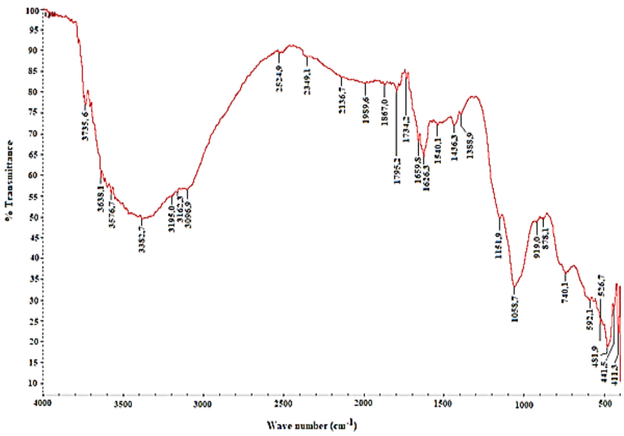

Fig. 3. FTIR spectrum of zeolite.

B. *Characterizations of Epoxy Composites*

The results of thermogravimetric analysis obtained at the heating of the zeolite filled epoxy composites in air atmosphere are given in Fig. 4. From TG results the following data were obtained: T_5 – the value of temperature at which the mass loss was 5%; T_{50} – the value of temperature at which the mass loss was 50%; T_{90} – the value of temperature at which the mass loss was 90%; and residual at 600 °C. The results obtained are given in Table II.

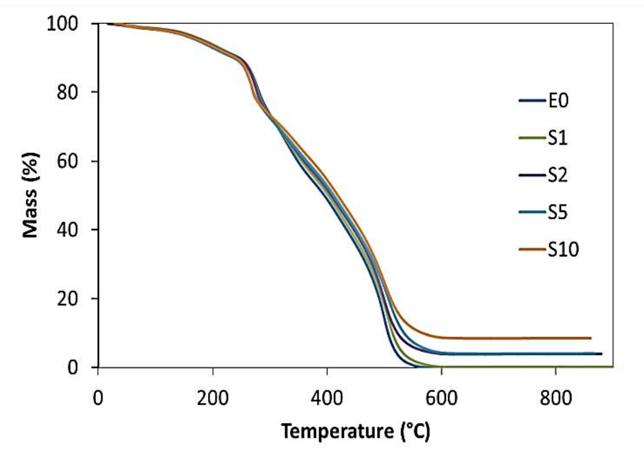

Fig. 4. TG curves of epoxy composites filled with zeolite at heating under air.

According to the data obtained, the initial temperature of decomposition of the epoxy samples upon heating T_5 is depended on the concentration of filler. Thus, the temperature T_5 obtained for the unfilled epoxy resin E0 is 183 °C, and for other samples, T_5 is lower than for E0, except for the sample S1. The mid-point temperature at 50 % mass loss T_{50} increased for the samples S1, S2, S5, S10 compared to that of the unfilled epoxy resin E0. In addition to this, increasing the content of filler in epoxy composites leads to an increase in the residue at 600 °C.

TABLE II. THERMAL PROPERTIES OF ZEOLITE BASED EPOXY COMPOSITES AT HEATING UNDER AIR

Sample	T_5 (°C)	T_{50} (°C)	T_{90} (°C)	Residue (at 600 °C) (%)
E0	183	395	507	0
S1	186	402	514	0.1
S2	181	407	523	4.0
S5	174	412	535	4.3
S10	179	419	567	8.7

The results of thermal analysis of the epoxy composites received from TG data at the heating in argon are presented in Table III. Table III shows the values of temperature at which the mass loss of the epoxy composites was 5, 50 and 90 % – T_5, T_{50}, T_{90}, respectively, and limiting oxygen index (LOI).

TABLE III. THERMAL PROPERTIES OF ZEOLITE BASED EPOXY COMPOSITES AT HEATING IN ARGON

Sample	T_5 (°C)	T_{50} (°C)	T_{90} (°C)	LOI
E0	192	376	554	20.8
S1	211	374	742	22.2
S2	186	373	588	20.9
S5	195	368	-	22.5
S10	184	368	-	23.3

The limiting oxygen index is the parameter which is used to characterize flammability of polymeric materials. It can be determined as the minimum concentration of oxygen (in percent) in the mixture of oxygen and nitrogen that is needed to support combustion of polymers. In our work we calculated LOI from TG results made at the heating in argon according to the Van Krevelen and Hoftyzer equation [16]:

$$LOI = 17.5 + 0.4Ch,$$

here Ch is char yield at 850 °C

According to the data obtained at the heating of studied samples in argon, the decomposition temperature T_5 for the unfilled epoxy resin is 192 °C. The value T_5 is higher by 19 °C for the sample S1 and by 3 °C for the sample S5 in comparison with that of the sample E0. For the sample S2 the value T_5 is lower by 6 °C and for the sample S10 is lower by 8 °C in comparison with that of the unfilled epoxy E0. The temperature corresponding to 50 % mass loss for all the studied samples is lower than that of the unfilled epoxy polymer. It can be seen from data presented in Table III that the unfilled epoxy resin has LOI value of 20.8. It means that the sample E0 is referred to flammable material according to classification [17] (the materials with LOI less than 20.95%). The incorporation of the zeolite into epoxy matrix resulted in an increase in LOI, except the sample S2. The zeolite based epoxy composites can be ascribed as slow-burning materials (the materials having LOI in the range of 20.95–28).

The results obtained can be explained by the influence of the release of water adsorbed by zeolite particles, as well as by the physical-mechanical approach. The particles of zeolite restrain the motion of macromolecular chains in the epoxy polymer and lead to the formation of the carbon residue upon heating. The carbonaceous residue acts as a heat barrier in the epoxy composites and prevents the heat flux into the polymer matrix and the destruction of the epoxy resin.

IV. CONCLUSION

In our study, the zeolite based epoxy composites were fabricated with a content of the filler 1; 2; 5 and 10 wt. %. The zeolite particles were modified with nanofibers of aluminum oxyhydroxide. The parameters of thermal degradation and thermo-oxidative degradation of the produced epoxy samples were determined by the method of thermal analysis. The data obtained indicate the effectiveness of the use of zeolite particles as filler for epoxy resin in order to enhance the thermal stability and reduce the flammability of the epoxy composites. It is shown in the work that the effect of the improving the thermal stability depends on the content of the filler and can be explained by the formation of the carbonaceous material at the heating.

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