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Thermal and Mechanical Characteristics of Polymer Composites Based on Epoxy Resin, Aluminium Nanopowders and Boric Acid

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Abstract. The epoxy polymers are characterized by low thermal stability and high flammability. Nanoparticles are considered to be effective fillers of polymer composites for improving their thermal and functional properties. In this work, the epoxy composites were prepared using epoxy resin ED-20, polyethylene polyamine as a hardener, aluminum nanopowder and boric acid fine powder as flame-retardant filler. The thermal characteristics of the obtained samples were studied using thermogravimetric analysis and differential scanning calorimetry. The mechanical characteristics of epoxy composites were also studied. It was found that an addition of all fillers enhances the thermal stability and mechanical characteristics of the epoxy composites. The best thermal stability showed the epoxy composite filled with boric acid. The highest flexural properties showed the epoxy composite based on the combination of boric acid and aluminum nanopowder.

1. Introduction

Epoxy resins are thermosetting polymers which are widely used in industry as adhesives, surface coatings, construction materials due to such properties as high adhesion, chemical resistance, low shrinkage at curing, good mechanical properties [1, 2]. In the case of bonding the structural elements of the heating apparatus and electronic devices it is necessary to provide heat removal which requires the improving the thermal conductivity of adhesives. It has been shown in many works that the metal powders addition in the adhesives such as aluminum, copper, silver, etc. can improve mechanical, thermal and electrical properties of polymeric composites [3–7]. At the same time, the epoxy polymers are characterized by low thermal stability and high flammability.

To enhance both the functional and flammability properties of the epoxy polymers, nanoparticle fillers are considered to be promising [8–11]. The mechanism of thermal stability enhancement in polymer nanocomposites is associated with barrier effect, restriction of molecular motions, radical trapping, formation of protective char layer, sorption and catalytic effects [12]. Due to high specific

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surface area of nanofillers and high surface-volume ratio, the interfacial area between the polymer and the nanofillers is greatly increased, and improvement of thermal, mechanical properties and flame retardancy of polymer nanocomposites can be achieved at very low fillers concentration compared to microfillers. However, nanoparticles alone cannot provide sufficient flame retardant effect, and it is recommended to use nanoparticles in combination with other flame retardants [12–14].

Boron compounds, including boric acid, are known as effective flame retardant additives [15, 16]. As a rule, boric acid is used in cellulosic products and coatings: wood, plywood, particle board, wood fibre, paper, cotton. At the heating, boric acid releases water in the endothermic process that reduces polymer temperature and degradation. It was found in our previous work [17] that the introduction of boric acid as a filler into epoxy resin by 1; 5; 10 % of its weight has a positive effect on the thermal stability of the composites. An increase of the temperature on 40.8 °C at 50 % weight loss and a decrease of 20.4 % weight loss at 600 °C were observed for the sample with a filler content of 10 wt. % in comparison with the pure epoxy polymer.

The aim of this work was to study the effect of aluminum nanopowder alone and in combination with boric acid on the thermal stability and mechanical strength of the epoxy composites.

2. Experimental

The materials used in this study were epoxy-diane resin ED-20 as polymer matrix, polyethylene polyamine (PEPA) as hardener (ZAO Contact, Dzerzhinsk, Russia), nanosized powder of aluminum (Al NP) and microsized powder of boric acid (BA) (Tulafarm, Tula, Russia) as fillers.

Al NP was produced by electrical explosion of wires [18, 19] in Tomsk Polytechnic University (Tomsk, Russia). The hydrogen was used as working ambient in the discharge chamber. Air-passivation was carried out by Ar+0.1 vol. % air directly after production with a view to protect nanoparticles against oxidation [19]. The properties of Al NP were studied in detail in [20]. The metal content in Al NP was 77 %. The crystalline aluminum oxide phase was not detected by X-ray diffraction analysis, but the presence of the oxide-hydroxide functional groups on the particles surface was confirmed by Fourier transform infrared spectrometry [20]. Besides, on the particles surface of Al NP water and atmospheric gases are adsorbed.

Boric acid was milled in a mortar before the sample preparation. According to the electronic microscopy study about 45 % of particles of BA had the size less than 40 μm [17].

The preparation of epoxy composites was performed as follows. The surface of fillers was modified by a hardener to improve the adhesion of the particles with the epoxy resin. Then, the required amount of fillers was added into epoxy resin. The epoxy resin with the filler was mixed by hand for 5 min at room temperature. After that PEPA was added into mixture and mixed again for 3 min. The ratio of epoxy resin and hardener was 10:1 by weight. The obtained mixtures were cured in the silicone molds at room temperature for 24 h. The formulations of the prepared epoxy composites are given in table 1. The images of the prepared samples are shown in figure 1.

Table 1. The formulations of the epoxy composites.

No.	Sample	ED-20 (wt. %)	Al NP (wt. %)	BA (wt. %)
1	E0	100	0	0
2	EA	100	5	0
3	EAB	100	5	10
4	EB	100	0	10

The obtained epoxy composites were studied by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) using a thermogravimetric analyzer SDT Q600 (TA Instruments, USA). The thermal behavior of the epoxy composites was studied under non-isothermal linear heating (10 ºC/min) in air atmosphere from room temperature to 900 °C.

To determine the mechanical properties of the composites a GOTECH AI-7000m universal testing machine (GOTECH Testing Machines Inc., Taiwan) was used. The mechanical test was carried out according to ISO 178:2010. The samples had the form of a rectangular beam with the size 40×16×2.5 mm. At least three samples of every composition were tested by three-point bending method. The cross-head rate was 2 mm/min.

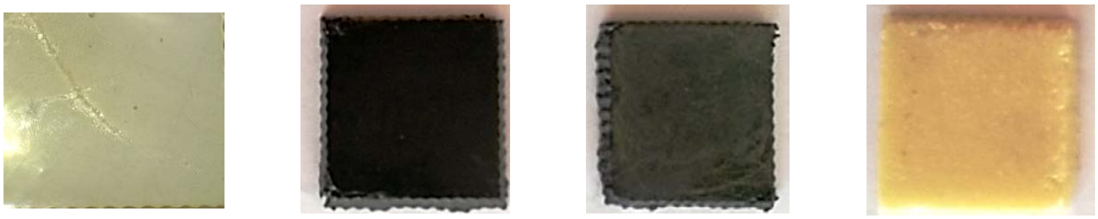
a) b) c) d)

Figure 1. Images of the prepared samples: neat epoxy polymer E0 (a); Al NP filled sample EA (b); Al NP and boron acid filled sample EAB (c); boron acid filled sample EB (d).

3. Results and discussion

The results of thermal analysis for the neat epoxy polymer and epoxy composites are shown in figures 2 and 3. It can be seen that the degradation of the samples occurred in three stages. The first two stages are considered to lead to production of a stable at lower temperatures carbonaceous residue [21, 22]. The third stage is related to oxidation of remaining carbonaceous char.

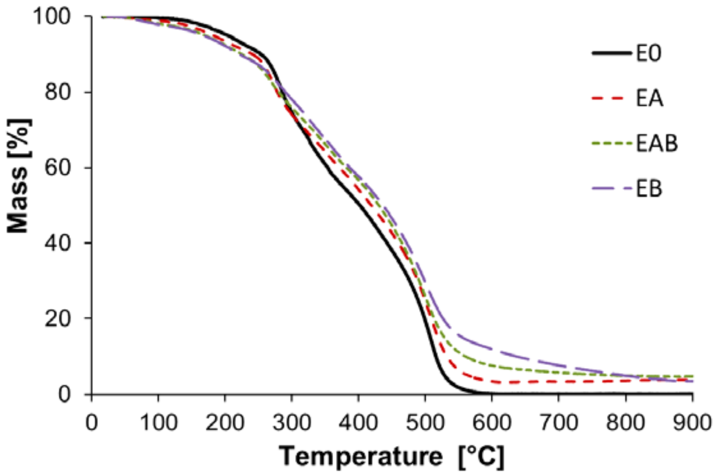

Figure 2. TGA curves of the epoxy composites.

It can be seen from figure 2 that addition of the fillers to the epoxy resin leads to increased mass loss at the heating to 280 °C because the fillers release water in this temperature range. The temperature at 5 % mass loss ($T_{5\%}$) decreases for the filled samples compared to that of the neat epoxy polymer. Evaporated water reduces the polymer temperature that leads to increasing the thermal stability of the composites at temperature above 280 °C.

The data of thermal analysis show that the introduction of Al NP has a positive effect on the thermal stability of the epoxy composites. The temperature at 50 % mass loss ($T_{50\%}$) is 419 °C and it is higher by 18 °C for the sample filled with Al NP than that of the neat epoxy polymer. The residue of the sample EA at 600 °C is 3.4 %, while the neat epoxy polymer decomposes completely.

Boric acid liberates water in an endothermic reaction during heating from 70 to 350 °C which leads to the dilution of combustible gases and provides heat sink. The temperature $T_{50\%}$ is 436 °C and higher by 28 °C for the sample filled with BA than for the neat epoxy polymer. The residue of the sample EB at 600 °C is 11.9 %.

In the case of the combination of Al NP and BA the temperature $T_{50\%}$ increases by 29 °C in comparison with the neat epoxy polymer, and the residual mass was 7.6 %.

DSC curves (figure 3) show three exothermic peaks for all samples. For the neat epoxy polymer E0 the first exothermic peak has maximum (T_{max1}) at 281 °C, the second peak has maximum (T_{max2}) at 410 °C and the third peak maximum (T_{max3}) at 506 °C. The introduction of all fillers results in shift of the exothermic peaks maxima T_{max1} and T_{max3} of the composites to lower temperature. However the shifting effect in T_{max3} for Al NP filled sample is insignificant. The peak maximum T_{max2} of the filled samples shifts to a higher temperature compared to that of the neat epoxy polymer.

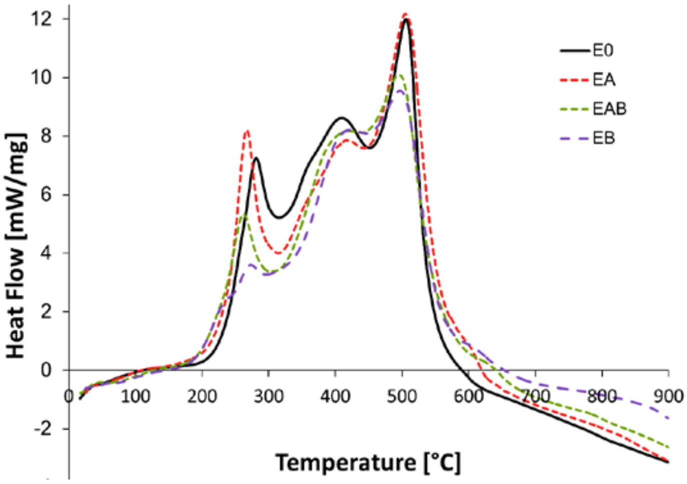

Figure 3. DSC curves of the epoxy composites.

The results of the mechanical tests are shown in table 2. The enhancement in flexural modulus is observed for all filled samples compared to that of the neat epoxy polymer. The flexural modulus for the composite filled with Al NP is 2.2 times higher than that of the neat epoxy polymer. The maximum improvement in flexural modulus is observed for the sample EAB. In the case of combination of Al NP with BA the flexural modulus is 2.4 higher than that of the neat epoxy polymer.

Table 2. The results of mechanical test.

Details	E0	EA	EAB	EB
Maximum Load [MPa]	36.1	50.9	36.5	29.0
Flexural Modulus [MPa]	569.3	1248.1	1380.2	901.5
Maximum stress at break [kgf]	8.9	11.9	11.1	8.7

The incorporation of nanosized aluminum particles in the epoxy resin provides the formation of finely crystalline structure of the polymer having fewer defects and leads to a restriction of molecular motions that result in enhancement of the thermal stability and mechanical properties. In addition, the presence of oxide hydroxide compounds on the aluminum nanoparticles surface and a high value of thermal conductivity of aluminum lead to the mentioned effects.

4. Conclusion

In the present paper, the epoxy composites filled with aluminum nanopowders, boric acid and aluminum nanopowders/boric acid were produced. The thermal stability of the epoxy composites was investigated by thermogravimetric analysis and differential scanning calorimetry. The mechanical test was carried out by three-point bending method.

The addition of all studied fillers increased the thermal stability and mechanical properties of the epoxy composites compared to the neat epoxy polymer. The epoxy composite filled with boric acid showed the best thermal stability. However, the combination of boric acid and aluminum nanopowders resulted in the highest flexural properties. The obtained results can be useful in developing the epoxy based composites with enhanced thermal stability and mechanical properties.

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