Effect of Iron Nanopowder on Flammability of Epoxy Composites

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***Abstract*—Reducing the flammability of polymeric materials is a serious problem that needs to be solved. The paper presents the results of a study of the effect of iron nanopowders, used as filler, on the flammability of epoxy polymers. Epoxy composites filled with 5 wt. % of iron nanopowder and 10 wt. % of boric acid separately, as well as in combination were prepared. The flammability of the prepared samples was evaluated by determining the ignition temperature and time-to-ignition**

Keywords—epoxy resin, flammability, filler, iron nanopowder

I. INTRODUCTION

Epoxy resins are used in various industries and in everyday life for the manufacture and repair of structural parts, as component of adhesives, paints and coatings, as well as sealing and impregnating compounds, etc. [1, 2]. The combination of unique properties, such as ease of curing, low viscosity, low shrinkage, high adhesive ability, high mechanical and electrical insulating properties, chemical resistance, promotes the widespread use of these materials. One of the main drawbacks of epoxy resins, limiting their field of application, is high fire hazard [3]. Therefore, the problem of reducing the flammability of polymers is topical.

To evaluate the flammability, an indicator such as the ignition temperature is used, by which is meant the lowest temperature of a substance, at which a substance emits combustible vapors and gases at such a rate that ignition is observed when exposed to an ignition source.

Reducing the flammability of polymers can be achieved by using such a method as the introduction of fillers, which have flame retardant properties [4, 5]. Fillers of different nature lead to changes in the character of the process of polymer destruction at the heating or blocking the combustion process by non-combustible or inhibiting substances. One of the inorganic compounds with good flame retardant properties is boric acid. At the heating, boric acid releases water in the endothermic process that reduces polymer temperature and degradation. In our previous works we found that the introduction of boric acid into epoxy matrix at percentage 10 wt. % has a positive impact on the thermal and thermo-oxidative degradation of the epoxy composites and does not lead to deterioration of the functional properties of the composites [6, 7]. In addition, boric acid can provide greater effect on the improvement of the thermal stability of the epoxy composites when it is used in combination with other materials.

The disadvantage of traditional flame retardants is that their effectiveness in reducing the flammability of materials is achieved, as a rule, at relatively high concentrations (50 wt. % and more). At the same time, structural and functional properties of polymer composites can significantly deteriorate. Nanodispersed materials, in contrast to conventional coarse flame retardants, can help to solve the problem of reducing the flammability of polymers at relatively low concentrations (< 5 wt. %) [8, 9]. It is assumed that the mechanism of action of nanodispersed fillers is the barrier effect.

The aim of this work was to evaluate the effect of iron nanopowder separately and in combination with fine boric acid powder used as fillers on the flammability characteristics of epoxy polymers.

II. EXPERIMENTAL

A. *Materials and Preparation*

The epoxy-diane resin grade ED-20 was used as polymer matrix; polyethylenepolyamine (PEPA) was used as hardener for preparation of the epoxy composites.

Iron nanopowder (Fe NP) was produced by the method of electrical explosion of wires (EEW) [10–13] in Tomsk Polytechnic University. EEW is a process of explosive destruction of a metal wire under the action of great density current ($>10^{10}$ A/m^2). To produce Fe NP, the argon was used as working ambient in the discharge chamber. Fe NP produced by EEW is pyrophoric material, has high reactivity and ignites on contact with air. Therefore, air-passivation was carried out by Ar+0.1 vol. % air directly after production in order to protect iron nanoparticles against oxidation.

Boric acid (BA) was milled in a mortar before the sample preparation. The particles with the size less than 64 μm were used for preparation of the epoxy composites.

For the preparation of epoxy composites the required amount of the fillers was added into epoxy resin. We have used for the composites preparation the following fillers percentage: 1) 5 wt. % of Fe NP, 2) 10 wt. % of boric acid, and 3) combination of 5 wt. % of Fe NP and 10 wt. % of boric acid. The formulations of the studied epoxy composites are given in Table I.

TABLE I. FORMULATIONS OF EPOXY COMPOSITES

Sample	**ED-20 (wt. %)**	**Fe NP (wt. %)**	**BA (wt. %)**
E0	100	0	0
E/Fe	100	5	0
E/BA	100	0	10
E/Fe/BA	100	5	10

The epoxy resin with the fillers was mixed by hand for 5 min at room temperature. After that PEPA was added into

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mixture and mixed again for 3 min. The ratio of epoxy resin and hardener was 10:1 by mass. The obtained mixtures were cured in the silicone molds at room temperature for 24 h. The images of the prepared samples are shown in Fig. 1.


a) b) c) d)

Fig. 1. Images of the prepared samples: a) E0; b) E/Fe; c) E/BA; d) E/Fe/BA.

B. Characterizations

The phase composition of the Fe NP was determined by X-ray diffraction (XRD) analysis using a diffractometer Shimadzu XRD-7000 with CuKα radiation. The size and morphology of the studied samples were investigated using scanning electron microscope (SEM) TM-3000. The infrared spectra of the samples in the spectral range 4000-400 cm^{-1} were recorded using Nicolet 5700 Fourier transform infrared (FTIR) spectrometer.

The flammability of the prepared epoxy composites was evaluated by the standard method of experimental determination of the ignition temperature of solid substances and materials in accordance with GOST 12.1.044-89 “Occupational safety standards system. Fire and explosion hazard of substances and materials. Nomenclature of indices and methods of their determination”. The ignition temperature of the epoxy composites was determined using the installation consisting of a vertical electric furnace with two coaxially located cylinders made of quartz glass, a container for placing the samples and a holder, an electric heater, a gas burner, and an air ejector. The principle of operation of this installation is based on setting the temperature mode in the reaction chamber and the effect of the burner flame, and controlling the temperature parameters after adding the studied material to the reaction chamber. The epoxy samples in this test were of cylindrical shape with a diameter of 45±1 mm. The weight of each sample was 3±0.1 g.

III. Results and Discussion

Fig. 2 shows the XRD patterns of the Fe NP.

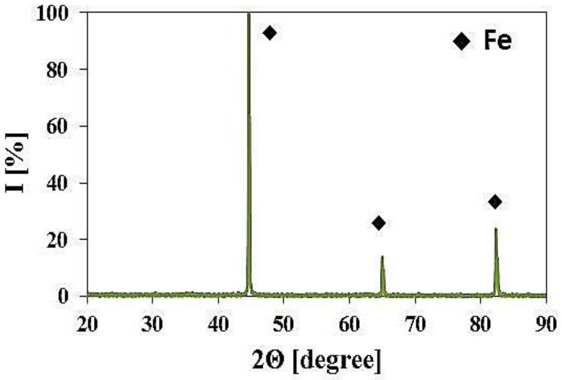

Fig. 2. X-ray diffraction pattern of Fe NP.

All the reflections correspond to metallic iron. The crystalline iron oxide phases as part of the protective layer formed during passivation were not detected in the XRD patterns of the Fe NP sample due to their amorphousness.

Fig. 3 shows the SEM image of the Fe NP. The Fe NP consists of micron-sized and nanosized fractions. The average diameter of the micron-sized particles is about 1–3 μm and of the nanosized particles is about 80–150 nm. The particles of both powder fractions have the shape closed to spherical.

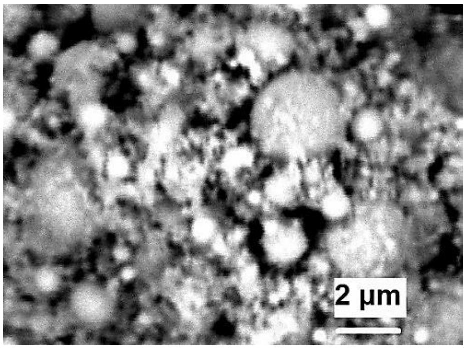

Fig. 3. SEM image of Fe NP.

The chemical functional groups on the surface of the iron particles were identified using the FTIR spectroscopy. Fig. 4 shows the FTIR spectrum of the Fe NP.

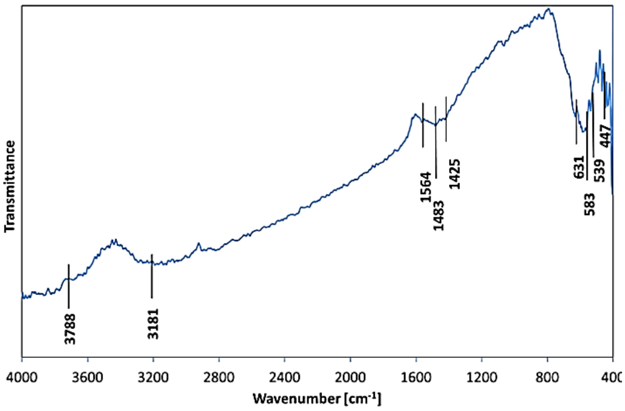

Fig. 4. FTIR spectrum of Fe NP.

The several absorption bands in the range of 635–430 cm^{-1} corresponding to the Fe–O vibrations modes were observed in the FTIR spectrum of Fe NP. Thereby, it can be assumed that the surface layer of the Fe NP particles contains oxide phases γ-Fe_2O_3 and Fe_3O_4. The presence of two absorption bands at 1425 and 1483 cm^{-1} indicates that as a result of CO_2 chemisorption, carbonate structures were formed on the Fe NP particles surface. The broad band in the range of 3300–3100 cm^{-1} and the band at 1564 cm^{-1} are due to the vibrations of hydrogen-bonded water molecules adsorbed on the Fe NP particles surface.

The results of the experimental determination of the ignition temperature and the time-to-ignition of the epoxy samples are shown in Table II. The time-to-ignition is

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defined as the minimum exposure time required for the sample to ignite and sustain flaming combustion.

TABLE II. IGNITION TEMPERATURE AND TIME-TO-IGNITION

Sample	**Ignition temperature (°C)**	**Time-to-Ignition (s)**
E0	305	342
E/Fe	314	354
E/BA	317	343
E/Fe/BA	322	314

Figure 5 depicts the change of the ignition temperature of the studied epoxy composites. The incorporation of Fe NP and boric acid in epoxy resin individually, as well as of their combination leads to an increase in the ignition temperature of the samples compared to the control sample E0. Nanodispersed iron powder contributes to the formation during burning of a strong and dense char layer on the surface of the epoxy sample that acts as a barrier to oxygen and combustible gases. In addition, formed iron oxide on the surface of the sample contributes to the protection of the epoxy sample from further decomposition as it was shown in [14]. The maximum ignition temperature was observed for the sample E/Fe/BA. The endothermic process of BA decomposition with the release of water leads to cooling of the composite surface. Moreover, the boron oxide glassy layer on the surface of epoxy matrix formed as a result of BA decomposition acts as heat barrier [15] and increases the ignition temperature of the epoxy composites.

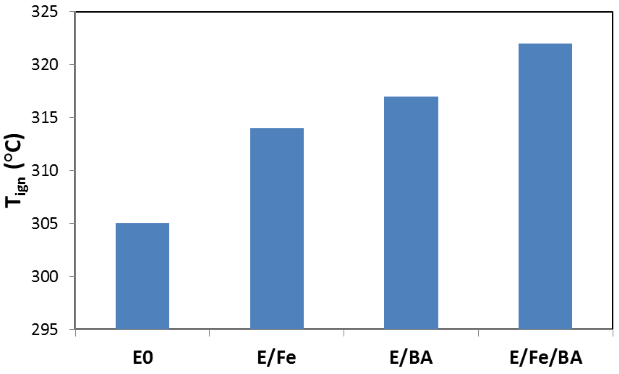

Fig. 5. Ignition temperature of epoxy composites.

The sample E/Fe showed the maximum value of time-to-ignition. These results can be attributed to the active role of Fe NP in the formation of protective carbon chair residue.

IV. CONCLUSION

In this work, the effect of iron nanopowder separately and in combination with fine boric acid powder used as fillers on the flammability characteristics of epoxy polymers was evaluated. The flammability characteristics of the produced epoxy composites were determined: the ignition temperature and time-to-ignition. It was found that in the case of the addition of 5 wt. % Fe NP to the epoxy matrix the ignition temperature increased by 2.9 % in comparison with that of the unfilled epoxy resin. In the case of combination of 5 wt. % Fe NP and 10 wt. % boric acid the ignition temperature of the epoxy composite increased by 5.6 % compared to the unfilled epoxy resin.

Thus, the data obtained indicate the effectiveness of the use of nanodispersed iron powders separately, and especially in combination with boric acid as filler for epoxy resin in order to improve the fire hazard characteristics of the epoxy composites.

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REFERENCES

[1] H. Lee and K. Neville, Handbook of Epoxy Resins. 1st ed., New York: McGraw-Hill; 1967, 960 p.

[2] F.-L. Jin, X. Li, S.-J. Park, “Synthesis and application of epoxy resins: a review.,” J. Ind. Eng. Chem., 2015, vol. 29, pp. 1–11.

[3] D.J. Irvine, J.A. McCluskey, I.M. Robinson, “Fire hazards and some common polymers,” Polym. Degrad. Stab., 2000, vol. 67, pp. 383–396.

[4] C.A. Wilkie and A.B. Morgan, Fire Retardancy of Polymeric Materials. 2nd ed. Boca Raton: CRC Press; 2010, 856 p.

[5] A. Dasari, Z.Z. Yu, G.P. Cai, Y.W. Mai, “Recent developments in the fire retardancy of polymeric materials,” Prog. Polym. Sci., 2013, vol. 38, pp. 1357–1387.

[6] P.M. Visakh, O.B. Nazarenko, Yu.A. Amelkovich, T.V. Melnikova, “Thermal properties of epoxy composites filled with boric acid,” IOP Conf. Ser.: Mater. Sc. Eng. 2015, vol. 81, 012095.

[7] P.M. Visakh, O.B. Nazarenko, Y.A. Amelkovich, T.V. Melnikova, “Effect of zeolite and boric acid on epoxy-based composites,” Polym. Adv. Technol., 2016, vol. 27, pp. 1098–1101.

[8] F. Laoutid, L. Bonnaud, M. Alexandre, J.M. Lopez-Cuesta, P. Dubois, “New Prospects in Flame Retardant Polymer Materials: from Fundamentals to Nanocomposites,” Mater. Sci. Eng. R., 2009, vol. 63, pp. 100–125.

[9] Y. Arao, “Flame retardancy of polymer nanocomposite,” in Flame Retardants: Polymer Blends, Composites and Nanocomposites; P.M. Visakh and Y. Arao, Eds. Cham: Springer International Publishing, 2015, pp. 15–44.

[10] Y.S. Kwon, A.P. Ilyin, D.V. Tikhonov, O.B. Nazarenko, G.V. Yablunovskii, “Current status and future development of the electroexplosive technology,” in Proceedings of the 7th Korea-Russia International Symposium on Science and Technology KORUS’2003. Ulsan, 2003, vol. 1, pp. 175–178.

[11] A.P. Ilyin, O.B. Nazarenko, D.V. Tikhonov, V.Ya. Ushakov and G.V. Yablunovskii, “Structural and energy processes in electrically exploded conductors,” Russian Phys. Journal. 45 (12), 2002, pp. 1176–1180.

[12] Y.S. Kwon, J.S. Kim, H.T. Kim, H.K. Lee, O.B. Nazarenko, A.P. Ilyin, “Preparation of nano metal carbide powders by electric explosion of conductors in liquid hydrocarbons,” J. Ind. Eng. Chem., 10 (6), 2004, pp. 949–953.

[13] O.B. Nazarenko, “Electroblasting technology for producing nanopowders of high-melting nonmetallic materials,” Glass Ceram., 2005, vol. 62(11-12), pp. 364–367.

[14] X.L. Chen, C.M. Jiao, Y. Wang, “Synergistic effects of iron powder on intumescent flameretardant polypropylene system,” Express Polym. Lett., 2009, vol. 3, No.6, pp. 359–365.

[15] S. Balci, N.A. Sezgi, E. Eren, “Boron oxide production kinetics using boric acid as raw material,” Indian Eng. Chem. Res., 2012, vol. 51, pp. 11091–11096.