Thermal properties of epoxy composites filled with boric acid

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Abstract. The thermal properties of epoxy composites filled with boric acid fine powder at different percentage were studied. Epoxy composites were prepared using epoxy resin ED-20, boric acid as flame-retardant filler, hexamethylenediamine as a curing agent. The prepared samples and starting materials were examined using methods of thermal analysis, scanning electron microscopy and infrared spectroscopy. It was found that the incorporation of boric acid fine powder enhances the thermal stability of epoxy composites.

1. Introduction

Epoxy resins are one of well-known thermosetting polymers and used as construction material, for coating and adhesive applications, which can also be reinforced with additives for obtaining high strengths and good chemical resistances. However, they are intrinsically combustible. Since environmental concerns using the halogenated and brominated flame retardant arose from the daily consumer products, new approaches for the developments of non-halogenated flame retardants has been initialized and flourished at both academics and industries. Mineral fillers are considered to be the most suitable flame retardants.

In a study performed by Ollier et al. [1], the author incorporated 5 wt. % of bentonite in unsaturated polyester (UP) matrix. They noted that the addition of bentonite increases the thermal stability of the UP resin. Carrasco and Pagès [2] showed that, at low clay contents (up to 5 wt. %) the addition of clay had no effect on the thermal stability of the epoxy matrix, whereas for higher concentration (10 wt. %) a clear increase on this parameter was observed. In addition, Lakshimi et al. [3] reported an improvement in the thermal stability of epoxy resins with the incorporation of montmorillonite (MMT). Saitoh et al. [4] found that the phosphonium cations used to obtain the organoclays influenced the thermal resistance of the resulting epoxy/clay nanocomposites. The explanation for this behavior is that the dispersed MMT-Clay nanolayers can act as barrier protecting the epoxy polymer matrix from volatilizing gaseous products of degradation. Régnier et al. performed a kinetic study on the thermal degradation of carbon fibre/epoxy composites, both in air and in inert atmosphere. The thermal degradation of the composites occurred in three stages [5]. Brnardic et al. studied the thermal stability of nanocomposites based on organically modified MMT and an epoxy resin [6]. Compared to the neat resin, small changes in the thermal stability were observed in the case of nanocomposites.

The thermal stability of epoxy resin/TiO_2 nanocomposites was found to be dependent on the nanoparticles loading, as well as on their dispersion state [7]. At a very low TiO_2 loading into the matrix, the nanoparticles were dispersed uniformly and formed a barrier to heat and oxygen, due to their ceramic nature. The incorporation of the hybrid TiO_2-SiO_2 nanofillers into an epoxy resin increased the thermal stability of the neat resin [8]. Also the char yield increased from 0% for the neat

resin to 25% for the nanocomposites. These phenomena are a consequence of the hybrid nanoparticles which acted as thermal stabilizers for the epoxy resin. The addition of multi-walled carbon nanotubes (MWCNTs) leads to a decrease of the thermal stability of epoxy matrices [9, 10]. This effect is caused by the increase of the polymer thermal conductivity as a consequence of MWCNTs addition. Kuan et al. reported that the incorporation of the MWCNTs functionalized with vinyltriethoxysylane into an epoxy resin increased its thermal stability [11]. The same effects were obtained in the case of MWCNTs grafted with triethylenetetramine [12] and MWCNTs functionalized with silane. Mehmet et al. reported [13] on their work on solid particle erosion behavior of glass fibre reinforced boric acid filled epoxy resin composites.

Boron compounds, including boric acid, are known as effective flame retardant additives [14, 15]. As a rule, boric acid is used in cellulosic products and coatings: wood, plywood, particle board, wood fibre, paper, cotton. Boron compounds reduce the flame spread of wood but may have diverse effects on hygroscopicity. Wood treated with inorganic flame-retardant salts is usually more hygroscopic than untreated wood, particularly at high relative humidity. Increases in the equilibrium moisture content of such treated wood will depend upon the type of chemical, level of chemical retention, and size and species of the wood involved.

To the best our knowledge no systematic work has been reported on the use of boric acid as reinforcement in epoxy resin, although these composites can be used for many applications. The objective of this work was the investigation of effect of the boric acid fine powder with different percentage as flame-retardant filler of epoxy resin on the thermal properties of the composites obtained.

2. Experimental

2.1. Physical properties of starting materials
The materials were used in this study: the epoxy-diane resin ED-20 (GOST 10587-84), the molecular weight of 390-430, the content of epoxy groups 20.0-22.5%, the viscosity 12-18 Pa·s; boric acid H_3BO_3, the molar mass 61.83 g/mol, the density 1.48 g/cm^3 (25 °C), the melting point 171 °C.

2.2. Preparation of composites
For the preparation of epoxy composites the epoxy-diane resin ED-20 was used and hexamethylenediamine (HMDA) as an epoxy resin curing agent. Boric acid fine powder having 45% of particles less than 40 microns was used as flame-retardant filler. The preparation of epoxy composite samples was performed as follows. The surface of boric acid was modified by a hardener to improve the adhesion of the particles with the epoxy resin. Then, the required amount of filler was added into epoxy resin. The filler content in the compositions was 1; 2.5; 5 and 10 wt. %. The epoxy resin was mixed by hand with the filler for 5 min at room temperature. After that HMDA 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 sample coding is given in table 1.

Table 1. The compositions (wt. %) of the specimens.

Samples	ED-20	Boric acid
H_3BO_3 Boric acid powder	0	100
Epoxy resin + 1 wt. % H_3BO_3	99	1
Epoxy resin + 2.5wt% H_3BO_3	97.5	2.5
Epoxy resin + 5wt. % H_3BO_3	95	5
Epoxy resin + 10wt. % H_3BO_3	90	10
Epoxy resin	100	0

2.3. Characterizations
The obtained samples and starting materials were examined using methods of thermal analysis (TA instrument SDT Q600), scanning electron microscopy (Hitachi TM-3000). The parameters of thermooxidative degradation in air atmosphere and thermal decomposition in argon were investigated at a linear heating rate of 10 °C/min in the temperature range 20-1000 °C.

3. Results and discussion

3.1. Scanning electron microscopyr
According to the scanning electron microscopy data (figure 1), boric acid powder is polydisperse systems. The analysis of the dispersed composition revealed that 45 % of the particles have a size less than 20 mcm. The powder particles are scaly crystals composed of the planar layers of thickness about100 nm.
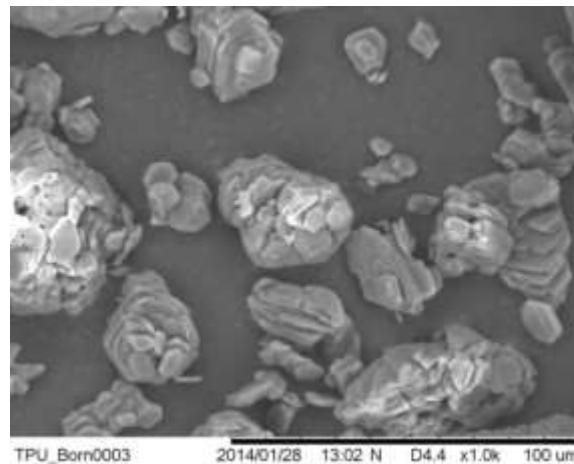

Figure 1. SEM micrograph of the boric acid powder.

3.2. TGA results in air
Figure 2 shows the TGA analysis results of boric acid powder, neat epoxy polymer and epoxy composites at different percentage of boric acid done in the presence of air.
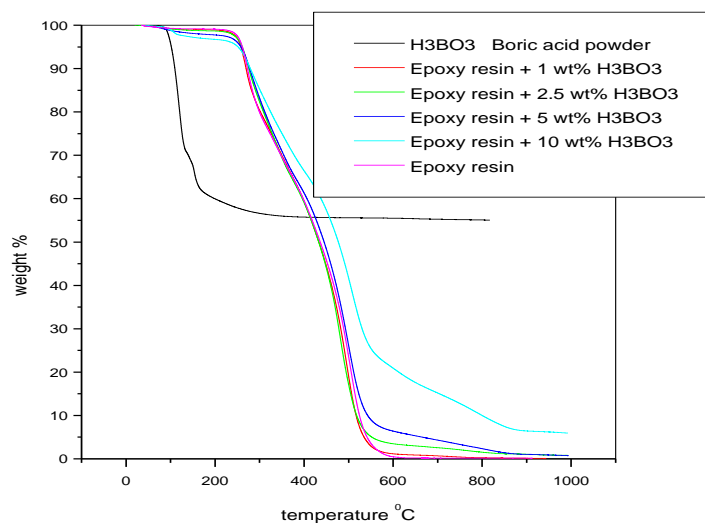

Figure 2. TGA plots of boric acid, neat epoxy and their composites at the heating in air.

Thermo-oxidative degradation of the samples occurs in several stages. The onset temperature of degradation is between 250-260 °C for all samples, steadily shifted between 550-560 °C. The process of thermooxidation for neat epoxy polymer ends at 600 °C. Using the TGA results we determined the values of temperature for a fixed weight loss - 10, 30, 50, 70 and 90 % (table 2). Introduction of the filler has a positive effect on the thermal stability the filled samples. The temperature corresponding to 50 % weight loss for the sample with a filler content of 10 wt. % is higher by 40 °C than the neat epoxy polymer.

Table 2. Degradation temperature at different weight loss levels of composites.

Samples	Degradation temperature (°C)				
	$T_{10\%}$	$T_{30\%}$	$T_{50\%}$	$T_{70\%}$	$T_{90\%}$
H_3BO_3 Boric acid powder	109	139	-	-	-
Epoxy resin + 1 wt. % H_3BO_3	269	349	433	482	516
Epoxy resin + 2.5wt% H_3BO_3	276	347	432	478	518
Epoxy resin + 5wt. % H_3BO_3	277	354	444	492	542
Epoxy resin + 10wt. % H_3BO_3	279	377	476	530	799
Epoxy resin	272	348	436	488	524

It is found that the thermal stability increases with increasing amount of boric acid content, and the decomposition temperature of the composites at different stages increased upon the addition of boric acid. Increased thermal stability of the composites with increased boric acid content may be explained by the more uniform distribution of boric acid in epoxy matrix and decreased mobility of epoxy phase in the vicinity of the boric acid particles.

3.3. TGA results in argon

Figure 3 shows the TGA analysis results of boric acid powder, neat epoxy polymer and epoxy composites at different percentage of boric acid done in the presence of argon.
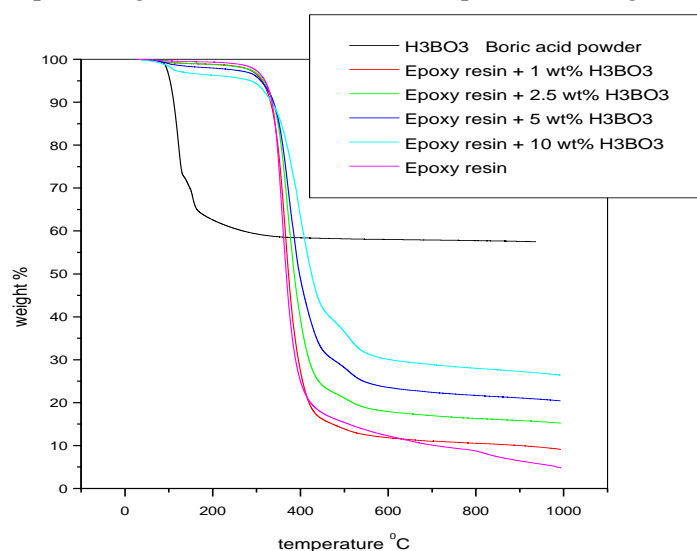

Figure 3. TGA plots of boric acid, neat epoxy and their composites at the heating in argon.

The process of thermal degradation of the studied samples occurs in several stages. We can see from figure 3, the onset temperature of degradation is between 200-400 °C for all samples, steadily

shifted between 400-600 °C. From this figure also we can say that thermal stability increases with increasing boric acid content. The decomposition temperature of the epoxy composites at different stages increased upon the addition of boric acid. From the figure, neat epoxy and 1 % boric acid composites are not very difference in thermal degradation, but 2.5, 5 and 10 % boric acid based composites shows very good improvements in the thermal degradation, these results show, the boric acid content effect in epoxy composites.

   The temperature values for a fixed weight loss (10, 30, 50, 70 and 90 %) at the thermal degradation are presented in table 3. It can be seen that the temperature corresponding to a fixed weight loss increases with the increasing the filler content. The best result was obtained for the sample with a filler content of 10 wt. %. The temperature of 50 % weight loss for this sample is higher by 58 °C than that for the neat epoxy polymer.

Table 3. Degradation temperature at different weight loss levels of composites.

Samples	Degradation temperature (°C)				
	$T_{10\%}$	$T_{30\%}$	$T_{50\%}$	$T_{70\%}$	$T_{90\%}$
H_3BO_3 Boric acid powder	111	148	-	-	-
Epoxy resin + 1 wt. % H_3BO_3	331	357	372	395	899
Epoxy resin + 2.5wt% H_3BO_3	338	366	385	419	-
Epoxy resin + 5wt. % H_3BO_3	338	371	397	475	-
Epoxy resin + 10wt. % H_3BO_3	334	389	425	604	-
Epoxy resin	335	354	367	388	707

   The decomposition of boric acid takes place in two steps and is accompanied by the release of water. The first stage begins at temperature of 70 °C, the second stage - at 130 °C and finishes at 400 °C. Boric acid decomposition reaction is endothermic, resulting in cooling of the polymer matrix.

4. Conclusion

The effect of the addition of boric acid fine powder in the epoxy polymer on the thermal stability of epoxy composites at the heating in the atmosphere of air and argon was studied. It is shown that the influence of boric acid as a filler depends on its content. The temperature of 50 % weight loss in the process of thermo-oxidative degradation at the heating in air and thermal degradation at the heating in argon increases; the yield of the residue also increases. The results obtained demonstrate the effectiveness of using the fine powder of boric acid as the additive in the epoxy resin for reducing the flammability.

References
[1] Ollier R, Rodriguez E, Alvarez V 2013 Unsaturated polyester/bentonite nanocomposites: influence of clay modification on final performance *Composites Part A* **48** 137-143
[2] Carrasco F, Pagès P 2008 Thermal degradation and stability of epoxy nanocomposites: influence of montmorillonite content and cure temperature *Polym. Degrad. Stab.* **93** 1000-1007
[3] Lakshmi M S, Narmadha B, Reddy B S R 2008 Enhanced thermal stability and structural characteristics of different MMT-Clay/epoxy-nanocomposite materials *Polym. Degrad. Stab.* **93** 201-213
[4] Saitoh K, Ohashi K, Oyama T, Takahashi A, Kadota J, Hirano H, Hasegawa K 2011 Development

of high-performance epoxy/clay nanocomposites by incorporating novel phosphonium modified montmorillonite *J. Appl. Polym. Sci.* **122** 666-675

[5] Régnier N, Fontaine S 2001 Determination of the thermal degradation kinetic parameters of carbon fibre reinforced epoxy using TG *J. Therm. Anal. Calorim.* **64** 789-799

[6] Brnardic I, Macan J, Ivankovic H, Ivankovic M 2008 Thermal degradation kinetics of epoxy/organically modified montmorillonite nanocomposites *J. Appl. Polym. Sci.* **107** 1932–1938

[7] Chatterjee A, Islam M S 2008 Fabrication and characterization of TiO_2–epoxy nanocomposite *Mater. Sci. Eng. A* **487** 574-585

[8] Omrani A, Afsar S, Safarpour M A 2010 Thermoset nanocomposites using hybrid nano TiO_2–SiO_2 Mater. Chem. Phys. **122** 343-349

[9] Zhou Y, Pervin F, Lewis L, Jeelani S 2007 Experimental study on the thermal and mechanical properties of multi-walled carbon nanotube-reinforced epoxy *Mater. Sci. Eng. A* **452-453** 657-664

[10] Ma P C, Kim J K, Tang B Z 2007 Effects of silane functionalization on the properties of carbon nanotube/epoxy nanocomposites *Compos. Sci. Technol.* **67** 2965-2972

[11] Kuan C F, Chen W J, Li Y L, Chen C H, Kuan H C, Chiang C L 2010 Flame retardance and thermal stability of carbon nanotube epoxy composite prepared from sol–gel method *J. Phys. Chem. Sol.* **71** 539-543

[12] Yang K, Gu M 2009 The Effects of triethylenetetramine grafting of multi-walled carbon nanotubes on its dispersion, filler-matrix interfacial interaction and the thermal properties of epoxy nanocomposites *Polym. Eng. Sci.* **49** 2158–2167

[13] Bagci M, Imrek H 2011 Solid particle erosion behavior of glass fibre reinforced boric acid filled epoxy resin composites *Tribology International* **44** 1704–1710

[14] Awoyemi L, Westermark U 2005 Effects of borate impregnation on the response of wood strength to heat treatment *Wood Science and Technology* **39** 484-491

[15] Shen K K, Kochesfahani S H, Jouffret F 2009 Boron based flame retardants and flame retardancy *Fire Retardancy of Polymeric Materials* 2nd ed C A Wilkie and A B Morgan (Baco Raton: CRC Press) pp 207-237