Epoxy-based Flame Retardant Nanocomposite Coatings: Comparison Between Functions of Expandable Graphite and Halloysite Nanotubes

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ABSTRACT

*T*his work presents a study on the flammability of epoxy coatings containing two types of nano-scale fillers as potential flame retardants: expandable graphite (EG) and halloysite nanotubes (HNTs). Both nanocomposites are prepared by incorporation of the same amount of nanofiller into the epoxy resin for the sake of comparison. Fire retardant nanocomposite coatings are cured through a two-stage procedure in a mold and oven, respectively. The cone calorimeter test is performed to investigate the effect of using these flame retardants on the peak of Heat Release Rate (pHRR), Total Heat Release (THR), Total Smoke Production (TSP) and Time-To-Ignition (TTI). It was found that the thermal behavior of blank epoxy and epoxy/EG was quite different and loading EG leaded to a significant fall in pHRR. In the presence of EG, the thin layer of residue was formed at first stages of ignition, grown rapidly and became denser acting as a strong barrier against fire. This barrier could retard the burning and doubled the total time of burning. By contrast, HNTs could not affect as an efficient flame retardant in the epoxy-based coating. Even by high loading level of 9 wt.%, HNT could not influence pHRR, TTI and THR parameters. Prog. Color Colorants Coat. 10 (2017), 245-252© Institute for Color Science and Technology.*

1. Introduction

Epoxy is well-known as one of the most applicable thermosetting polymers widely utilized in different industries such as adhesive, coating, laminating, casting, and electrical insulator [1-3]. Epoxy represents an acceptable hardness, flexibility, high chemical resistance and dielectric properties, the main advantageous features making the epoxy resin versatile [4-9]. Although epoxy resin has unique chemical and

mechanical properties, it has some inherent shortcomings in thermal properties [2, 10]. Since epoxy burns easily, numerous approaches have been carried out to reach a flame retardant epoxy with improved thermal properties which can fit some applicable industries [11-13]. The corresponding mechanism of flame retardancy in composite material consists of the formation of protective layers on the surface of the polymer during the burning [14-17]. Addition of protective layered inorganic additives limits the heat

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transfer to the pyrolysis surface [18, 19] and thereby reduces the transport of volatiles into the flame zone. The efficiency of flame retardancy is highly depended on the nature (chemical composition) and structure of the protective layer. A dense and compact layer of residue can make the effective protection [20].

The use of layered additives, even in small quantities, is an efficient way to overcome high heat release rate (HRR) of polymers [21]. One of the most effective layered carbon materials with unique mechanical, electrical and thermal properties as well as reasonable cost [22] is expandable graphite (EG), which is well-known for its flame retardant character [23, 24]. In each layer of EG, the carbon atoms are covalently bonded, while different layers of graphite are interconnected to each other with van der Waals interactions [22]. A number of studies have demonstrated that the use of EG as a flame retardant in polymers can reinforce the char and improve the thermal stability [18]. Moreover, EG has the ability to migrate to the surface of the polymer at the beginning of combustion process and acts as a physical barrier [23]. There is a general agreement that flame retardancy of epoxy can significantly be enhanced by introduction of carbon materials [1, 25], hence, it was decided to study the effect of EG on flame retardancy of epoxy resin. On the other hand, recent studies reveal that halloysite nanotubes (HNTs) can enhance thermal stability and flame retardancy of polymers [26]. HNTs are one-dimensional nano-scale additives considerably used in nanocomposites because of their good thermal stability, mechanical strength and reasonable price [27, 28]. Chemically saying, HNTs are alumina-silicate clay-like structures having the formula $(Al_2Si_2O_5(OH)_4.nH_2O)$ similar to Kaolin [28, 29]. Thanks to their micro-tubular hollow structure with the inner diameter of 10-30 nm and the outer diameter of 50-70 nm, they are expected to retard flammability [30]. HNTs have a high aspect ratio because of their length changes in the range of 1-15 µm [30]. Previous studies have demonstrated that fire properties and flame retardancy of polypropylene, poly(vinyl alcohol), nylon 6 [31], low-density polyethylene [27, 32], ethylene propylene diene monomer [33], polyamide [34] and epoxy resin [35, 36] could remarkably be enhanced with incorporation of HNTs in nanocomposites. From a mechanistic viewpoint, HNTs create a thermal insulation layer at the top surface of nanocomposite during combustion and act as a physical barrier which can at even double the total

time of burning [26]. In addition, recent works of flame retardancy have demonstrated that HNTs can improve the thermal degradation of epoxy based intumescent fire retardant coatings [37].

In this study, the performances of HNTs and EG nano-scale additives on flame retardancy of epoxy have been discussed. It was attempted to provide a comparative angle over flame retardancy of epoxy/EG and epoxy/HNTs nanocomposite coatings by comparing their effectiveness with blank epoxy coating. The cone calorimeter test was used to investigate the effect of additives on the thermal stability and flame retardancy of epoxy coatings, as featured in changes in the peak of Heat Release Rate (pHRR), Total Heat Release (THR), Total Smoke Production (TSP) and Time-To-Ignition (TTI). Based on the obtained results, the effect of EG and HNT on the flame retardancy of epoxy was mechanistically explained.

2. Experimental

2.1. Materials

Epoxy resin (diglycidyl ether of bisphenol A, EPON1001) and polyamidoamine hardener (NT-1541) were used to prepare epoxy coatings after complete cure. The solid content of the epoxy resin and the hardener were 80%, and 85%, respectively. Expandable graphite (EG) grade SFF was supplied by Chuetsu Graphite Works. According to the manufacturer data, the specific surface volume of EG was 180 cm^3/g and its size was around 180 µm. The solvent used in this study was dimethylformamide (DMF) from Sigma Aldrich. Moreover, halloysite nanotube (HNTs) (having outer diameter 50 to 200 nm, internal diameter 15-70 nm, length 1-3 µm, specific surface area ca. 26.29 $m^2.g^{-1}$ and pore volume of 0.122 $cm^3.g^{-1}$) was purchased from Hunan Province, China. The chemical structures of the used nanoparticles (EG and HNTs) are illustrated in Figure 1.

2.2. Sample preparation

First, epoxy resin was mixed with DMF solvent for the sake of dispersion enhancement. Then, EG was slightly added into the solution at room temperature under stirring at 750 rpm until the weight fraction of EG in epoxy matrix reached 9 percent by weight. Then, the speed of stirrer increased up to 1400 rpm, and mixing was continued for about 30 min (Figure 2). The

hardener with weight ratio 100/105 was added to the mixture. The mixture was poured into the preheated steel mold with Teflon coating at 100 °C for about 30 min and then thermally cured for 6 h at 100 °C in an air convection oven (Figure 3). The samples were cooled to room temperature. These steps were followed for preparing epoxy/HNT nanocomposites, too. Also, the unfilled epoxy was prepared under the same condition, for comparison. The samples' name and composition are given in Table 1.
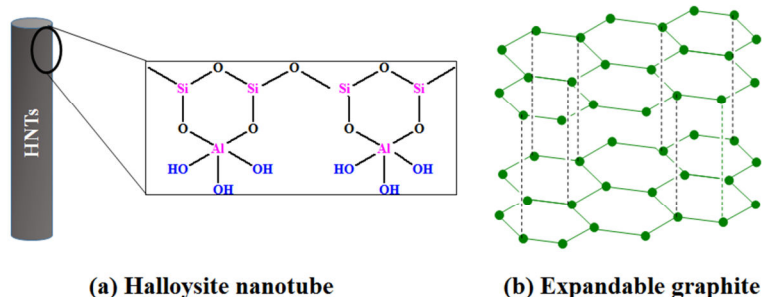

(a) Halloysite nanotube   (b) Expandable graphite

Figure 1: Chemical structure of the used nanoparticles.

Ep   EpEG9   EpH9

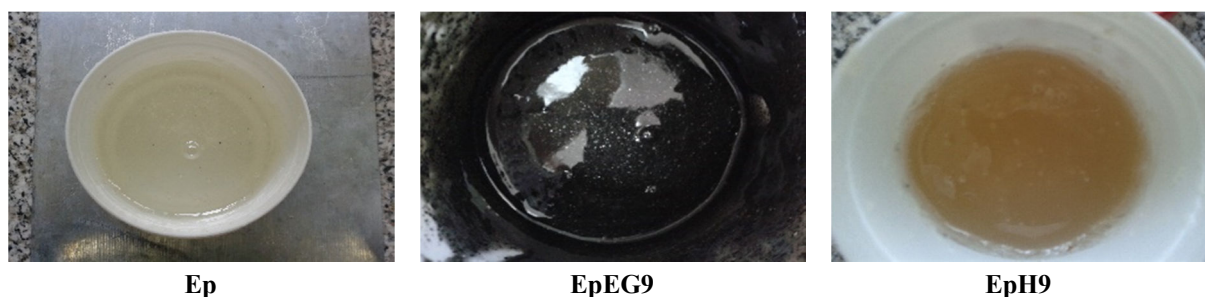**Figure 2:** The mixture of specimens before curing.
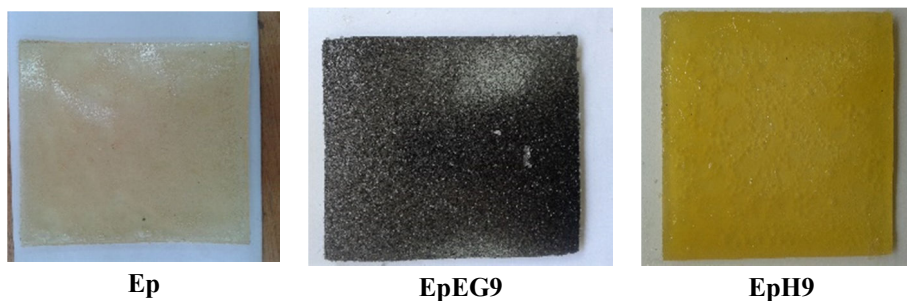

Ep   EpEG9   EpH9

Figure 3: Prepared samples after curing.

Table 1: Name and composition of samples prepared in this study

Sample Code	Epoxy Resin (wt.%)	EG (wt.%)	HNT (wt.%)
Ep	100	0	0
EpEG9	91	9	0
EpH9	91	0	9

2.3. Instruments

The flame retardancy of prepared nanocomposites and unfilled epoxy was measured with cone calorimeter test (FTT Company) according to ISO 5660 with the external heat flux of 50 kW.m^{-2} on a $100\times100\times4$ mm^3 sheet. The samples were put on a load cell and a radiant electrical heater with a conical shape uniformly irradiated the sample. Various parameters such as Total Heat Release (THR), peak of Heat Release Rate (pHRR), Total Smoke Production (TSP), and Time-To-Ignition (TTI) can be measured through cone calorimeter test. Also, the residual chars were observed by a digital camera to see the char surface and its integrity. The test was performed three times for each sample and the experimental error value is estimated to be around ±5%.

3. Results and discussion

One of the most important parameter for investigating the flammability of polymers is heat release rate. It shows the intensity of the fire and the ability of fire growth through the polymer [31, 38]. The heat release rate (HRR) of three prepared samples as a function of time is presented in Figure 4. Also, the obtained parameters from HRR curve are summarized in Table 2.

The efficiency of each flame retardant material is characterized by its ability to decrease the peak of Heat release rate. As shown in Figure 4, by adding EG into the epoxy resin, the pHRR decreased remarkably. The pHRR of EpEG9 reaches to 152 kWm^{-2} and reduces

about 85% in comparison with unfilled epoxy. According to Figure 2, the shape of HRR in unfilled epoxy and EpEG9 is completely different. This difference in their thermal behavior can be explained accordingly. At first step of ignition a thin layer of residue is formed on the surface of nanocomposites. In the case of EpEG9, the char grows and become denser and tougher and so does not break down in the combustion process. This thick layer of char, act as an insulating layer between the polymer and flame zone [39]. As a result, the heat transfers between these two regions become more difficult. So the rate of polymer decomposition reduces and makes the pyrolysis process slow. Thus, the role of EG in flame retardancy of epoxy is related to the insulating properties of its char, which reduce the mass and heat transfer to the flame zone [31]. However, the correlation between fire performance (such as pHRR) and the structure of final residue was challenging and if the layer of char develops at the first stages of the test it makes sense [19].

The flame retardant mechanism of EG/epoxy composite is shown in Figure 5. As mentioned, when fire applied to the composite, the external graphite expanded fast into a low-density materials, and the volume of this intumescent flake graphite increased even more than 200 times. This structure could barrier the heat penetration, limit the oxygen diffusion and prevent mass transfer from epoxy nanocomposites matrix to the heat source, thus restrict the matrix from further degrading.
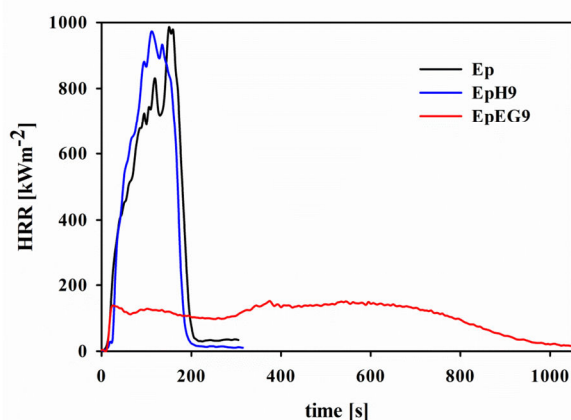

Figure 4: Heat Release Rate (HRR) curves of unfilled epoxy, graphite-epoxy and HNTs-epoxy composites, irradiance: 50 kW.m^{-2}.
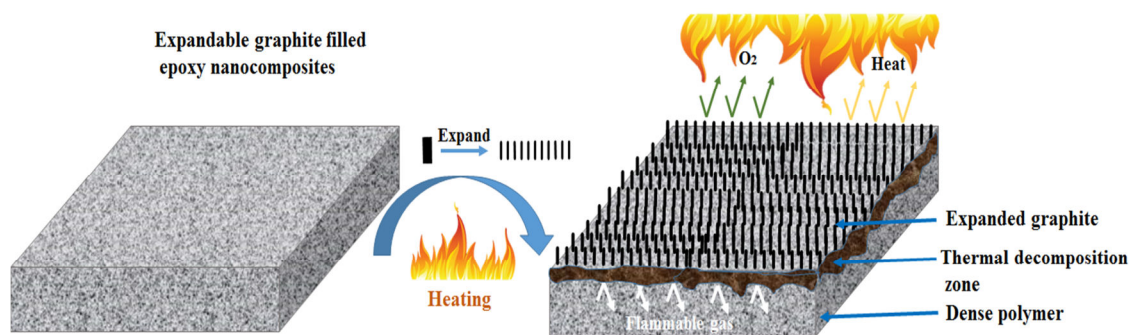
Figure 5: Flame retardant mechanism of EG/epoxy composites.

Table 2: Cone calorimeter data of blank epoxy and epoxy/EG and epoxy/HNTs composites at 9 wt.% cured during 6 h at 100 °C.

Sample code	TTI [s]	pHRR [kW.m^{-2}]	THR [MJ.m^{-2}]	TSP [m^2]	Residue [%]
Ep	5	986	113	34	0
EpEG9	10	152	110	59	9.6
EpH9	5	969	110	36	4.3

While EG has a positive effect on pHRR, it has no influence on THR. Also, the TTI of unfilled epoxy is doubled by incorporation of 9 wt.% EG. Such significant increase of TTI can be considered as the second positive effect of EG in epoxy resin. Another important parameter which is considered in this study is total smoke production. As the smoke increases the risk of suffocation and can be significantly fatal. As shown in Table 2, the TSP of unfilled epoxy is increased by addition of EG, indicating the smoke suppression is deteriorated in presence of EG. Comparison between the shape of HRR curve of unfilled epoxy and HNT-epoxy nanocomposite, reveals that their behavior during burning is relatively similar. By incorporation of 9 wt.% HNTs in epoxy resin, the pHRR slightly decreased but the influence was not obvious. It can be deduced that a thin layer of char is formed on the surface of composite which is not condensed enough to withstand against volatile gases and break down easily. So addition of HNT couldn't significantly reinforce the char and in comparison with unfilled epoxy, just the amount of residue increased.

Also, other obtained results in Table 2 show that incorporation of HNTs has no influence on TTI, TSP, and THR. Maybe better performance achieve on loading much more HNTs.

The images of remaining char after cone calorimeter test are presented in Figure 6. Unfilled epoxy burned without any remaining residue. Two types of residue could be observed for two filled-specimens. In the case of epoxy/HNT nanocomposite, a thin and brittle layer of residue was formed. But for epoxy/EG sample, the char was somehow thick, dense and smooth which indicated that the char forms at the first stage of ignition, grow and become tougher. Much higher amount of residue in EpEG9 was reported in Table 2 which proved that presence of EG considerably promoted the formation of char residue.

The comparison of the results demonstrated that EG performs much better on enhancing the flame retardancy parameters of epoxy resin than HNTs. This fact can be attributed to the thicker char layer and prevention against heat and mass transfer to the flame zone during burning and improving the barrier effect.
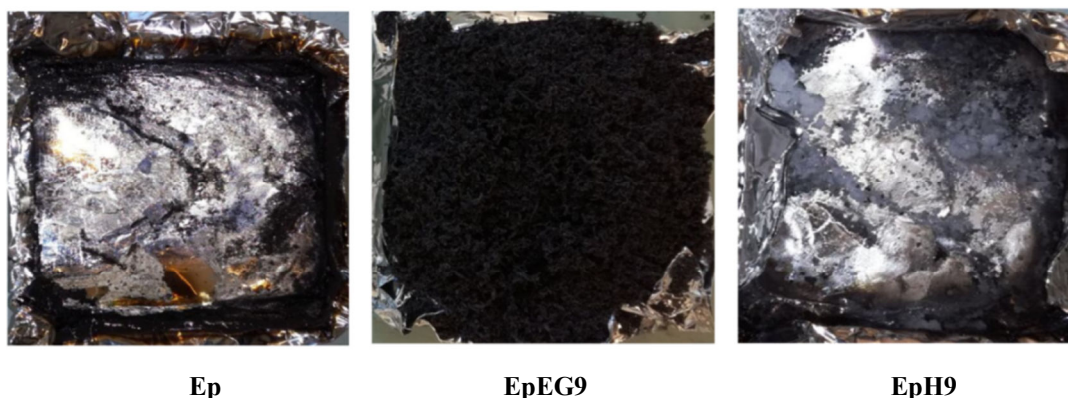
| Ep | EpEG9 | EpH9 |

Figure 6: Unfilled epoxy, Graphite-epoxy and HNTs-epoxy composites remaining char after cone calorimetric test.

4. Conclusion

Expandable graphite (EG) and halloysite nanotube (HNT) were used to prepare flame retardant epoxy composite. By introduction of EG into the epoxy coating, the pHRR decreased remarkably. This significant reduction in pHRR is probably attributed to the thick char formed onto the surface of epoxy coating. The strong interfacial interaction between different carbon atoms increased the char layer thickness and improved the barrier effect as well. It is believed that such a thick layer of residue could withstand against pressure caused by volatile gases and wouldn't break down. Furthermore, EG delays ignition due to its high thermal conductivity but it has no significant effect on THR of epoxy resin. In comparison, incorporation of HNTs has no influence on pHRR, TTI, THR and TSP due to formation of thin layer of char which couldn't act as an insulating barrier. Maybe much more HNTs were needed to achieve better performance.

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