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Flame retardant epoxy/halloysite nanotubes nanocomposite coatings: Exploring low-concentration threshold for flammability compared to expandable graphite as superior fire retardant

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A B S T R A C T

Epoxy nanocomposites containing halloysite nanotubes (HNTs) were developed and their low-concentration thresholds for thermal stability and flame retardancy were compared with that of epoxy system containing expandable graphite (EG), as a reference with superior flame retardancy. The effects of HNTs and EG on the peak of Heat Release Rate (pHRR), Total Heat Release (THR), and Time-To-Ignition (TTI) of the prepared samples were subsequently discussed. At low loading level of 3 wt.%, HNTs appeared more effective, as signaled by an enhanced thermal stability compared to the EG-incorporated composite at an identical loading, because of hindered mobility of epoxy chains in a well-cured epoxy network. At higher loadings (6 and 9 wt.%), however, exfoliation of EG because of heat build-up in the system was dominantly hindered the crosslinking of epoxy it the presence of HNTs, which consequently deteriorated thermal stability of epoxy. This was featured by the formation of intumescent flake on the surface of the epoxy that played the role of a physical barrier, and assisted in reduction of the value of pHRR, while it doubled the TTI value. Different functions of HNTs and EG in regard with thermal stability and flame retardancy of epoxy/amine systems were discussed experimentally and mechanistically.

Keywords:
Epoxy
Flame retardancy
Nanocomposites
Halloysite nanotubes
Expandable graphite

1. Introduction

Epoxy resins are known as the most versatile thermosetting polymers with appropriate chemical and corrosion resistance, adhesion properties, curability, low shrinkage and mechanical properties [1–6]. Epoxy resins can be crosslinked together with a wide variety of curing agents under different curing circumstances [4,5,7]. Noticeably, however, they suffer from poor thermal stability, high flammability and poor fracture toughness, which limit their use in engineering applications [1,8]. In this sense, different kinds of fillers/additives have been examined to gain high-performance epoxy systems. Epoxy composites are receiving much more attention every day because of the properties of epoxy-based composites being manipulatable for desired applications.

When used as coating materials, epoxy suffers from inadequate potential for protecting the underlying substrate against fire [9–11]. However, in electronic devices such as printed wiring boards and cable industry, fire retardancy of epoxy resins is of premier importance [12]. For such purposes, the coating should be designed so as to minimize heat transfer across the coating thickness during the combustion process [13]. Moreover, one would be wise to develop eco-friendly flame retardants for epoxy prior to the time a coating is expected to retard burning. The fire retardancy of epoxy can be enhanced by the incorporation of flame retardant additives or chemical reactive flame retardants into the resin [14,15]. Combustion is a complex process through which physical and chemical mechanisms take place simultaneously. This hardens prospective identification of the combustion process and determination of the main mechanism that dominantly controls over flame retardancy of composites [16–18]. Classically saying, four important zones have been identified in the combustion process: flame zone, char layer, molten polymer and underlying polymer. Char layer is known as the most critical zone which mainly controls over the heat and mass transfer phenomena. Typically, char decelerates the release of heat by formation of a protective layer against heat flux source [16,19]. This layer with its low thermal conductivity hardens heat transfer leading to polymer degradation rate reduction

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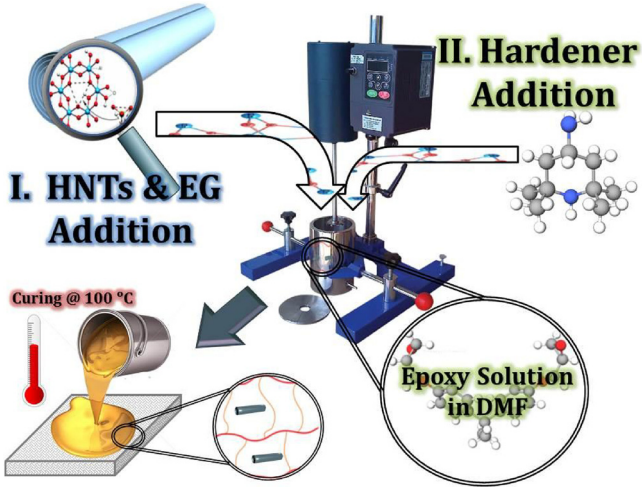

Fig. 1. Schematic of procedure applied in sample preparation.

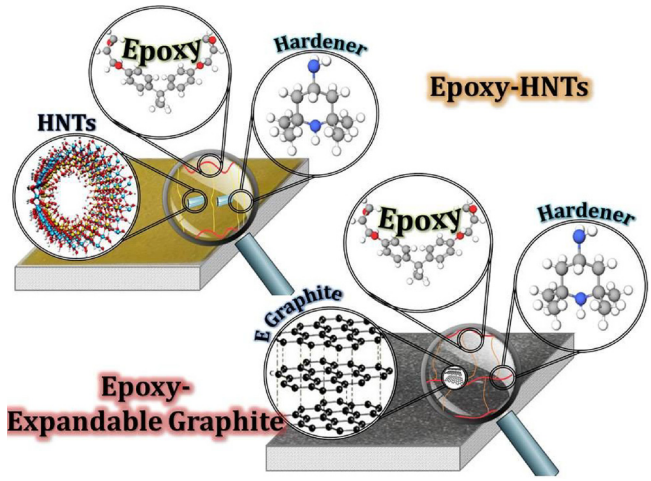

Fig. 2. Schematic of chemical structure of EG/epoxy and HNTs/epoxy composites.

[16]. The effectiveness of a flame retardant system is highly pertinent to its capacity to form a protective layer during the combustion. Overall, a dense and compact layer of char residue is required for a proper heat barrierity [9,20,21].

The use of nano-scale additives has been practiced as a profound solution for the poor flame retardancy of polymers. Nanoparticles not only can improve the fire performance, but they can also improve to a desired level mechanical properties of polymer matrix [19]. Formation of nanoparticle-rich char layer could effectively reinforce its cohesiveness. As a result, the rate of mass loss decreases, which is reflected in a fall in the peak of heat release rate (pHRR), while nanoparticles could limitedly improve the total heat release (THR). Moreover, the broadness of the heat release rate (HRR) curve could be a signature of appropriateness of nano-scale additives when used as flame retardant in polymers. Graphite in both micro- and nano-scale size is known as a superior flame retardant because of its covalently bonded hexagonal structure [22]. Pristine graphite can hardly be used as a flame retardant for polymers due to the compactness of carbon flakes in the natural graphite structure, which prevent penetration of polymers into the galleries of graphite sheets [16]. The chemically modified graphite (expandable graphite, EG), however, appears as a superior flame retardant benefiting from its exfoliation potential [16]. There are numerous examples demonstrating the excellence of EG as a commercially available flame retardant for various polymeric matrices [16,21–27]. It has been mechanistically explained that in the course of combustion EG expands hundred times leading to formation of a worm-like char layer

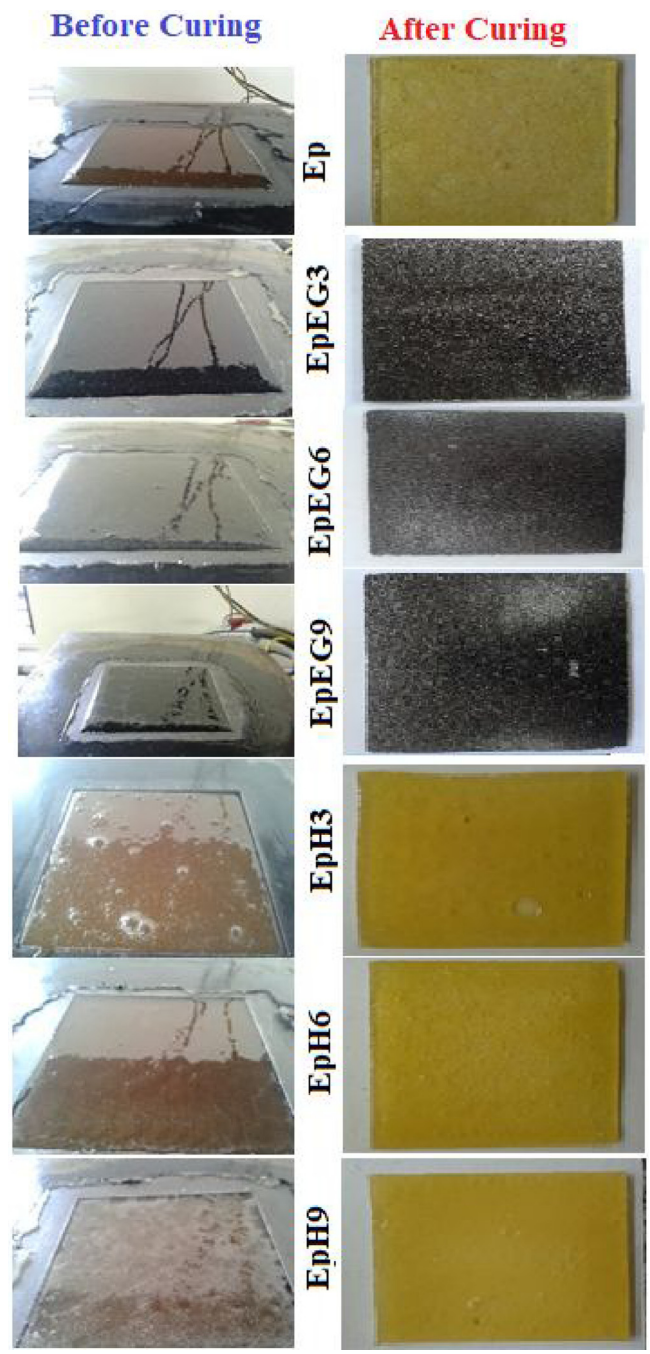

Fig. 3. Samples' appearance right before and after curing process.

on the surface of polymer, which acts as a barrier against heat and mass transfer [28,29]. There is a general agreement that flame retardancy of epoxy can significantly be improved by incorporation of such carbonous materials [30–32].

The use of inexpensive, one-dimensional nano-scale additives such as halloysite nanotubes (HNTs) has received a particular attention in recent years [33–37]. Thanks to its tubular nanostructure and high aspect ratio in addition to its natural availability, HNTs resembles carbon nanotube (CNTs) – the reason why HNTs exhibit unique properties such as good biocompatibility and acceptable mechanical strength – and can be considered as an alternative to CNTs for high-performance applications [38–40]. HNTs with molecular formula ($Al_2Si_2O_5(OH)_4{\cdot}nH_2O$) are similar to kaolin, but their hollow structure gives reason to hope that it can be considered as a flame retardant additive [39,41]. Previous studies have uncovered the fact that addition

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

Sample Code	Epoxy Resin (wt.%)	EG (wt.%)	HNTs (wt.%)
Ep	100	0	0
EpEG3	97	3	0
EpEG6	94	6	0
EpEG9	91	9	0
EpH3	97	0	3
EpH6	94	0	6
EpH9	91	0	9

of HNTs at high loading levels (more than 20 wt.%) and/or in combination with conventional flame retardants to polypropylene [42], poly (vinyl alcohol) [43], polyamide 6 [44,45], low-density polyethylene [38,46], ethylene propylene diene monomer [47], and epoxy resin [48,49] could to a large extent improve flame retardancy of polymers. Moreover, recent studies have shown that incorporation of HNTs has a positive effect on thermal degradation of epoxy-based intumescent fire retardant coatings [50]. From a coating point of view, however, it is important to find the low concentration threshold for additives in order to prevent deterioration of mechanical and anti-corrosion properties of nanocomposites. In this regard, study of curing behavior and cure kinetics of nanocomposites with variable filler content is crucial to understanding structure-flame retardancy correlation in epoxy/HNTs, which is the subject of a future investigation. All in all, a compromise between the amount of additive used in coating and the efficiency of thermal stability of composite is currently an important challenge.

The present study is aimed to find HNTs low-concentration threshold at which appropriate thermal stability and flame retardancy of epoxy nanocomposite could be achieved, but a rigorous analysis would be possible over a full range of concentration of HNTs. The thermal efficiency of HNTs is compared with EG as a reference additive known for its superior flame retardancy varying the concentration of fillers within the epoxy matrix. For samples having 3, 6, and 9 wt.% filler (EG or HNTs), the thermogravimetric analysis (TGA) measurements were performed to study thermal decomposition behavior of composites. Moreover, cone calorimeter test was used to investigate the effect of additives on the flame retardancy parameters including pHRR, THR, and TTI. The effect of HNTs and EG on the flame retardancy of epoxy was mechanistically explained as well. It is believed that the current study opens promising windows to researchers working in the realm of organic coatings, particularly those seeking inexpensive flame retardant epoxy nanocomposites for engineering applications.

2. Experimental

2.1. Materials

EPON™ 1001-B-80 epoxy resin was purchased from Hexion (USA). This epoxy is a 80 percent solid solution of diglycidyl ether of bisphenol A of EPON™ 1001F in methyl ethyl ketone solvent with an EEW of 450–550 g/eq. An unmodified polyamide-based hardener having trade name of Cardolite NT-1541 was provided by EM Sullivan (USA) to cure epoxy. The solid content of the hardener was 95 percent, its AHTW was 198 g/eq, and its viscosity was above 10^5 cps at 25 °C. Expandable graphite (EG) grade SFF was supplied by Chuetsu Graphite Works Co., Ltd. According to the manufacturer data, the specific surface volume of EG was 180 $cm^3.g^{-1}$ and its length of sheets was ca. 180 µm. The solvent used in this study was dimethylformamide (DMF) from Sigma Aldrich. Moreover, halloysite nanotube (HNTs) (having outer diameter 50–200 nm, internal diameter 15–70 nm, length 1–3 µm, specific surface area ca. 26 $m^2.g^{-1}$ and pore volume of 0.122 $cm^3.g^{-1}$) was purchased from Hunan Province, China.

2.2. Sample preparation

Epoxy composites comprising EG (or HNTs) were prepared through the following procedure: (1) Epoxy resin was mixed with DMF solvent for the sake of dispersion enhancement; (2) A specified amount of nanoparticles was slightly added into the solution at room temperature under stirring at 750 rpm; (3) The speed of stirrer increased up to 1400 rpm, and mixing was continued for about 30 min; (4) Hardener with weight ratio of 100/105 was added to the mixture; (5) 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; (6) The samples were cooled to room temperature. The neat epoxy was prepared under the same condition, for the sake of comparison. The sample preparation and chemical structure of samples are schematically shown in Figs. 1 and 2, respectively. The situations and appearance of samples before and after curing are shown in Fig. 3. In addition, the samples' names and compositions are given in Table 1.

2.3. Instruments

The fire characteristics of the prepared composites and neat epoxy are measured with a cone calorimeter, FTT Company (UK), according to the international standard ISO 5660. A horizontal sample sheet with

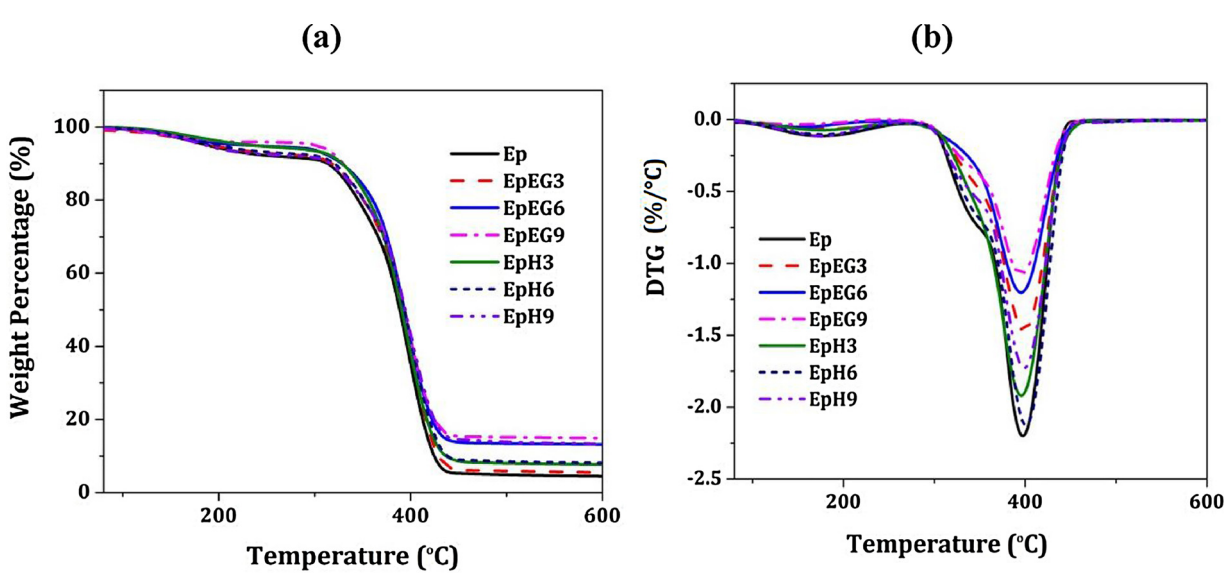

Fig. 4. (a) TGA and (b) DTG curves of all samples at heating rate of 10 °C.min-1 under nitrogen.

Table 2
TGA parameters obtained under nitrogen ($T_{10\%}$: Temperature at 10% weight loss; T_{max}: Maximum degradation rate temperature from DTG.).

Sample code	$T_{10\%}$ (°C)	T_{max} (°C)	Residue (wt.%) at 600 °C
Ep	313	188–435	4
EpEG3	317	194–439	6
EpEG6	328	232–436	13
EpEG9	330	302–439	15
EpH3	327	235–436	8
EpH6	319	199–438	8
EpH9	315	186–440	13

dimension 100 × 100 × 4 mm^3 subjected to a conical heater with an external heat flux 50 $kW.m^{-2}$ was selected to simulate a well-developed fire. The heat release rate (HRR) is obtained by measuring the oxygen concentration and gas flow. In addition, the total heat released (THR) is calculated by integration of HRR curve versus time. The test also enabled to calculate the peak of heat release rate (pHRR) (as one of the most important parameters in flame retardancy of polymers), and time-to-ignition (TTI). Furthermore, the residual chars were observed by a digital camera to see if the char surface has integrity. Thermal decomposition was conducted on a Setaram Labsys Evo thermogravimetric analyzer (France). All measurements were performed on a sample having the weight of 30 ± 2 mg under the nitrogen atmosphere and a heating rate of 10 °C.min^{-1}.

3. Results and discussion

3.1. Thermal stability assessment

The thermal stability of the neat epoxy and its composites containing EG or HNTs was studied through TGA. Fig. 4a and b show TGA and Derivative TGA (DTG) curves of the neat epoxy and epoxy-based composites. The parameters obtained from these curves are summarized in Table 2. According to Fig. 4a, the samples were decomposed in two stages taking place in the range of 110–440 °C. First, degradation step began at ca. 110 °C and continued to 300 °C. It is probably related to the release of water containing in the filler and polymer. Furthermore, the degradation of the intercalant in the EG structure led to a drastic fall in the mass loss curve [51,52].

The main peak of degradation in DTG is around 400 °C, but the intensity of degradation was decreased by incorporation of nanoparticles in epoxy resin (Fig. 4b). The data in Table 2 indicates that neat epoxy has the lowest amount of residue. The amount of residue at 600 °C was increased by the introduction of EG and HNTs into the resin/hardener system, but the results showed that expandable graphite

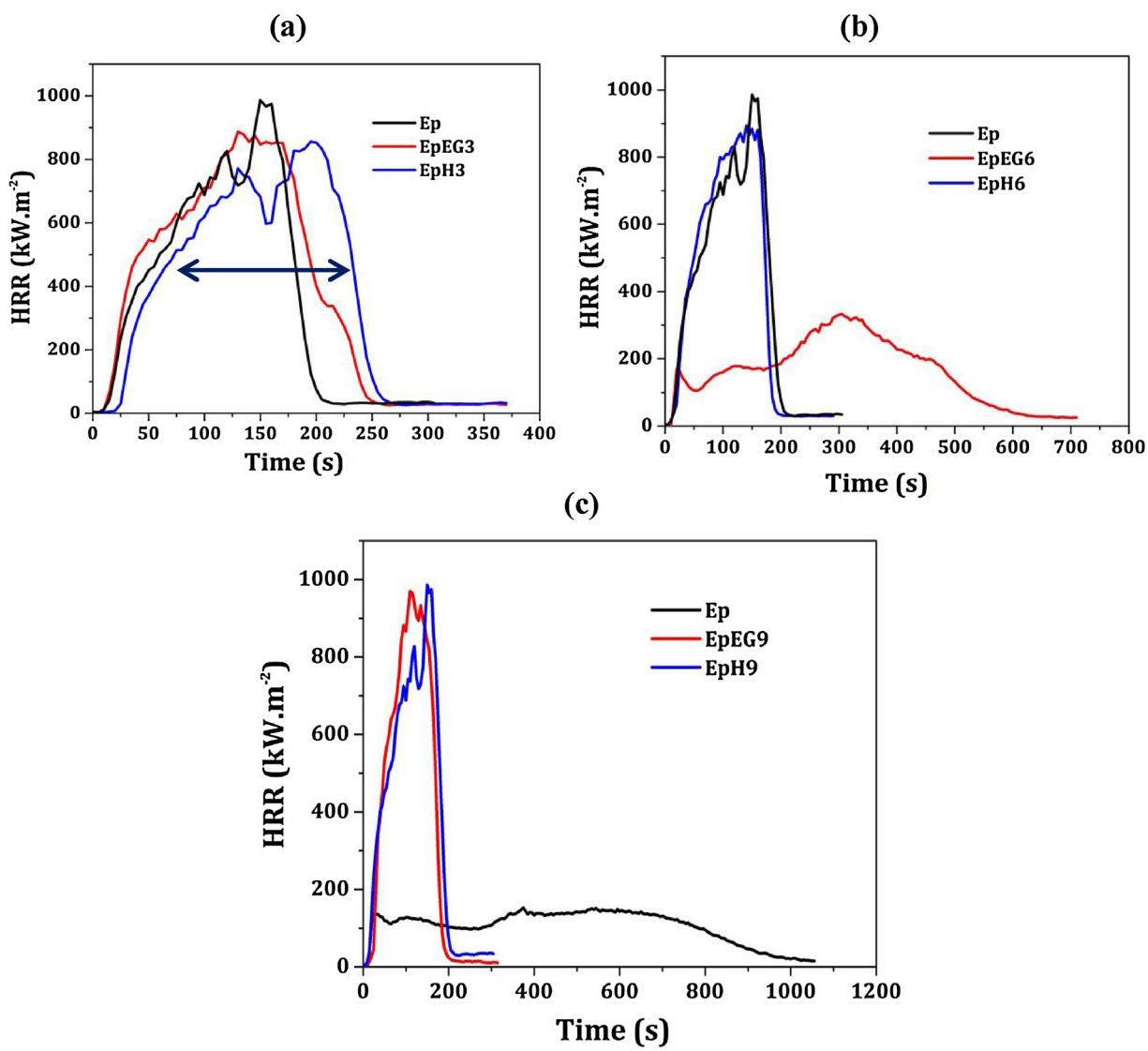

Fig. 5. Heat Release Rate (HRR) curves of (a) Ep, EpEG3, EpH3; (b)Ep, EpEG6, EpH6; and (c) Ep, EpEG9, EpH9.

Table 3
Cone calorimeter parameters of neat epoxy and epoxy-based composite at different loading of EG and HNTs (3, 6 and 9 wt.%).

Sample code	TTI [s]	pHRR [kW m^{-2}]	THR [MJ m^{-2}]	Residue [%]
Ep	5	986	113	0
EpEG3	5	887	136	0
EpEG6	10	333	114	4.4
EpEG9	10	152	110	9.6
EpH3	10	855	136	0
EpH6	5	893	111	3.6
EpH9	5	969	110	4.3

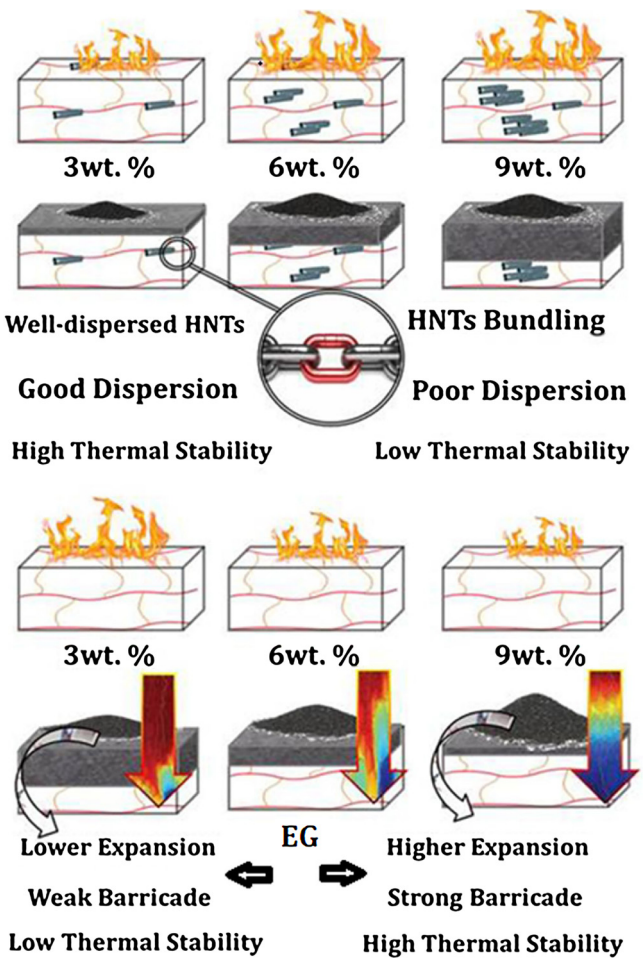

Fig. 6. Flame retardant mechanism of EG/epoxy and HNTs/epoxy composites.

slightly promoted charring from 6 wt.%. As in Fig. 4, EG more effectively boosted thermal stability of epoxy compared to the HNTs. This happened due to the fact that EG could expand hundred times during heating to form a protective insulation layer against heat. In the case of EpH3 sample, the onset degradation temperature, defined as the temperature at which 10% mass loss takes place, was surprisingly higher than that of EpEG3. The improvement of thermal stability of polymers in the presence of HNTs has already been reported and probably related to the high volume percentage of the lumen of HNTs. The internal cavity of HNTs enables this molecule to trap the degraded molecules and therefore increases the thermal stability [53,54].

3.2. Flame retardancy analysis

The effect of varying amounts of EG and HNTs on the HRR curve shape is shown in Fig. 5a–c. In order to compare the effects of different types of particles on HRR, samples with similar weight percentage are presented separately in one figure and compared with the neat epoxy. Moreover, all the obtained parameters (pHRR, THR, and TTI) from the cone calorimeter test are summarized in Table 3. According to Fig. 5a and Table 3, incorporation of 3 wt.% EG and HNTs could not significantly reduce pHRR (by a limited success in lowering 10 and 13%, respectively) and revealed no significant effect on the THR. On the other hand, TTI value was increased to 10 s for EpH3 sample. Furthermore, the HRR curve of this sample revealed a different behavior (double-headed arrow in Fig. 5a). The alteration of the shape of this curve could be explained based on the possibility of the formation of much more char during combustion, which is here accompanied by a collapse of the formed char on the surface of polymer after 150 s [55]. Further addition of EG (6 and 9 wt.%) considerably reduced the pHRR due to the formation of much more char residue. According to Fig. 5b, the thermal behavior of EpEG6 was considerably changed. Two steps can be distinguished according to the shape of the HRR curve. The first peak is appeared at around 120 s, while the second happened at 310 s. The EG is expanded rapidly during combustion making an intumescent flake on the surface of the composite. This structure acts as a physical barrier, which could prevent heat and mass transfer and limit oxygen diffusion. Since this layer of char was not so compact, it was cracked due to the pressure of flammable gases and the second peak was appeared in HRR curve. When the amount of EG increased in the composite to 9 wt.%, pHRR decreased about 85% and the second peak somehow vanished from the HRR curve. The presence of 9 wt.% EG in epoxy increased the char compactness and made it much thicker and denser, which could withstand the pressure imposed by the released gases. The comparison between the shape of HRR curves of the neat epoxy and epoxy/HNTs nanocomposite suggested that their thermal behavior is more or less similar. Neat epoxy and epoxy/HNTs composites burn intensely. Addition of EG reduces the speed and the intensity of burning at 6 and 9 wt.% loading, while the effect EG at 3 wt.% loading is not significant. The comparison between HRR curves of EpEG6 and EpEG9 shows that the formation of an efficient char with addition of 9 wt.% EG lead to pHRR reduction down to ca. 120 kW.m^{-2} after 300 s. Furthermore, the total combustion time was extended from 700 to 1000 s upon addition of 6 and 9 wt.% EG, respectively. Therefore, epoxy/EG composites burn over a longer period. The addition of 9 wt.% HNTs to epoxy resin slightly reduced the pHRR. It can be concluded that the char layer formed during combustion in the epoxy/HNTs was not compact enough to resist against volatile degradation products.

The TTI of the neat epoxy is doubled in EpH3, EpEG6 and EpEG9 with respect to epoxy. Such phenomena happened because of the enhanced thermal conductivity of polymer and much more heat transfer through the surface of the sample. Such significant rise in TTI value is considered as a positive effect of such nanoparticles, which could delay the ignition time and retard the flame growth. In the case of HNTs, an increase in TTI at low loading level (EpH3) supports TGA results. TTI value obtained for EpH3 sample was 10 s in cone calorimeter test, which is more than those of Ep and EpEG3 samples. In TGA, onset temperature ($T_{10\%}$) was higher for EpH3 (327 °C) than those of EP and EpEG3 (313 and 317 °C, respectively) (Table 2). This result revealed the effect of HNTs on thermal stability at low loading level. The flame retardancy mechanisms of expandable graphite and HNTs in the epoxy system are demonstrated in Fig. 6.

The top and front view images of the char after cone calorimeter test are presented in Figs. 7 and 8. Three forms of residues can be observed. A layer of compact and dense char with a worm-like structure is formed at the surface of the polymer by incorporation of 6 and 9 wt.% EG. As expected, the residue of EpEG9 is thicker than that of EpEG6, due to the presence of more expandable graphite exfoliated against the heat. The residue of samples containing HNTs is powder-like without any cohesion, which can hardly act as a physical barrier. As discussed earlier, the pHRR of epoxy/HNTs composites did not change meaningfully

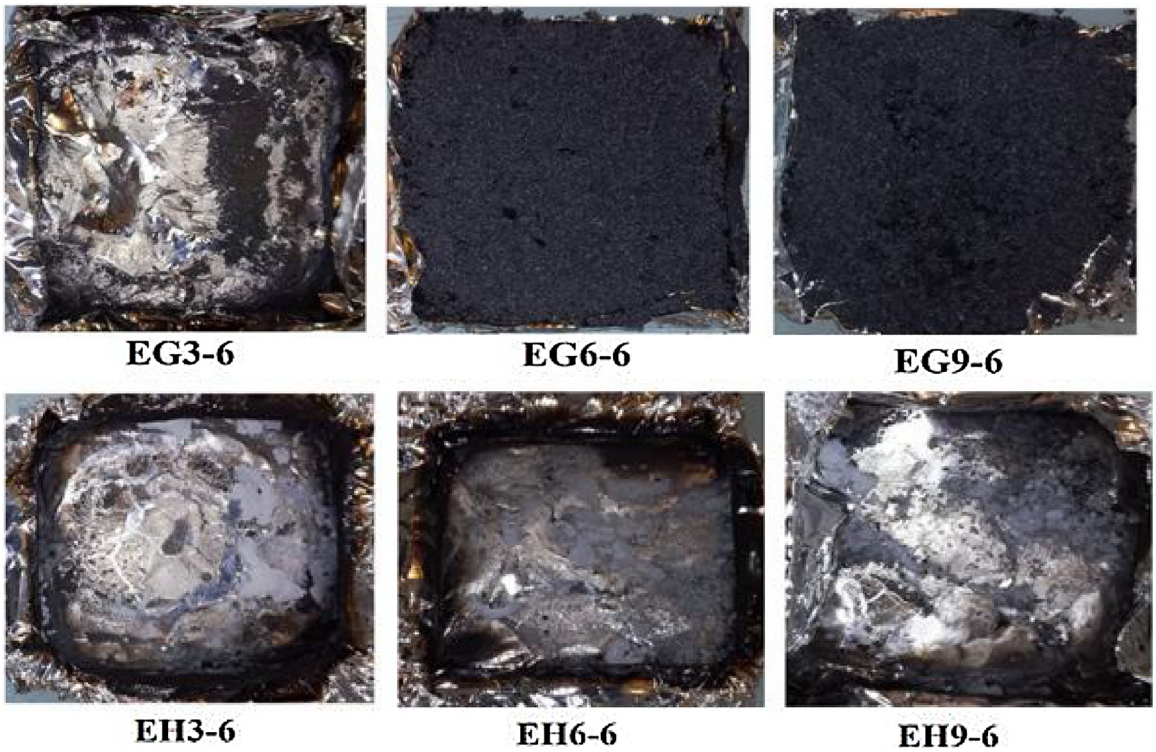

Fig. 7. Top view of remaining char after cone calorimetric test of epoxy and epoxy-based composites.

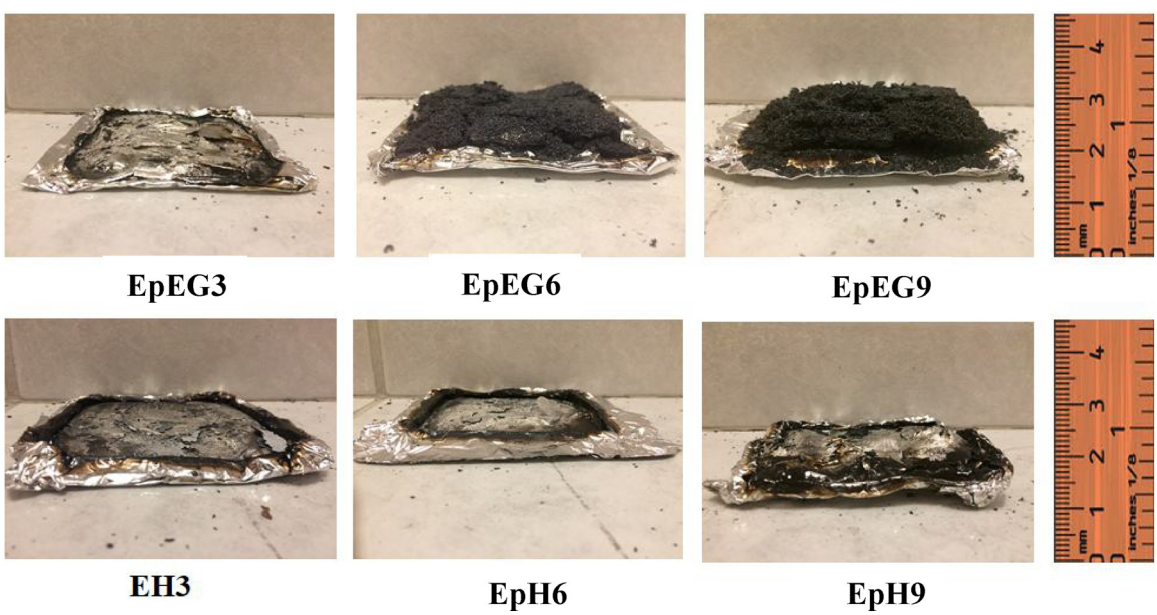

Fig. 8. Front view of remaining char after cone calorimetric test of epoxy and epoxy-based composites.

considering its brittle, thick, and non-cohesive char layer. Therefore, HNTs were not effective as a flame retardant additive for epoxy due to the formation of non-cohesive char residue. All in all, low concentration threshold for a proper flame retardancy effect of HNTs in the studied concentration range could be 3 wt.%.

4. Conclusions

Halloysite nanotubes (HNTs) were used at low loading level to improve thermal stability and flame retardancy of epoxy resin. The obtained results were compared with that of expandable graphite (EG), as a well-known superior flame retardant additive for polymer systems. Thermal stability and flame retardancy of the obtained composites were studied using TGA and cone calorimeter measurements. The results showed that HNTs can more effectively boost thermal stability of epoxy than EG at low concentration of 3 wt.%. However, at 6 and 9 wt.%, EG promoted the charring potential of the epoxy by play the role of physical barrier and blocking the heat and mass transfer to the flame zone. About fire retardancy, a thick layer of char with good compactness formed on polymer surface controlled the thermal behavior of epoxy/EG composites and reduced pHRR value from 986 to 152 $kW.m^{-2}$. Moreover, high thermal conductivity of expandable graphite could delay the ignition time and retard the burning process. HNTs did not significantly changed the pHRR value because of its powder-like and

brittle residue, even at 6 and 9 wt.% loading. However, HNTs improved the thermal stability and gave better results in term of its higher flame retardancy compared to EG at an equivalent loading of 3 wt.%

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