

Effects of Halloysite Nanotube Reinforcement in Expandable Graphite Based Intumescent Fire Retardant Coatings Developed Using Hybrid Epoxy Binder System

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Abstract In this study, the effects of halloysite nanotubes (HNTs) reinforcement in expandable graphite based intumescent fire retardant coatings (IFRCs) developed using a polydimethylsiloxane (PDMS)/phenol BA epoxy system were investigated. Intumescent coating formulations were developed by incorporating different weight percentages of HNTs and PDMS in basic intumescent ingredients (ammonium polyphosphate/melamine/boric acid/expandable graphite, APP/MEL/BA/EG). The performance of intumescent formulations was investigated by furnace fire test, Bunsen burner fire test, field emission electron microscopy (FESEM), thermogravimetric analysis (TGA), transmission electron microscopy (TEM), and Fourier transform infrared analysis (FTIR). The Bunsen burner fire test results indicated that the fire performance of HNTs and PDMS reinforced intumescent formulation has improved due to the development of silicate network over the char residue. Improved expansion in char residue was also noticed in the formulation, SH(3), due to the minimum decomposition of char carbon. FESEM and TEM results validated the development of silicate network over char layer of coating formulations. A considerable mass loss difference was noticed during thermal gravimetric analysis (TGA) of intumescent coating formulations. Reference formulation, SH(0) with no filler, degraded at 300 °C and lost 50% of its total mass but SH(3), due to synergistic effects between PDMS and HNTs, degraded above 400 °C and showed the maximum thermal stability. XRD analysis showed the development of thermally stable compound mullite, due to the synergism of HNTs and siloxane during intumescent reactions, which enhanced fire performance. FTIR analysis showed the presence of incorporated siloxane and silicates bonds in char residue, which endorsed the toughness of intumescent char layer produced. Moreover, the synergistic effect of HNTs, PDMS, and other basic intumescent ingredients enhanced the polymer cross-linking in binder system and improved fire resistive performance of coatings.

Keywords Polydimethylsiloxane (PDMS); Halloysite nanotubes (HNTs); Intumescent fire retardant coatings (IFRC); Thermogravimetric analysis (TGA); Transmission electron microscopy (TEM)

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INTRODUCTION

In recent years, incorporation of nano-clays in intumescent fire retardant coating system has drawn a great deal of attention in the flame retardant industry. Polymers along with nano-clays possess better thermal properties as well as reduced flammability^[1–4]. A good chemical affinity between clay and polymer is the governing parameter in dispersion phenomena. Recently, halloysite ($\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4 \cdot 2\text{H}_2\text{O}$) has been reported as a new potential nano-clay filler to reinforce in polymers^[5–8]. Halloysite, commonly known as hydrated oxides of Si–Al, possesses a hollow tubular structure. The interesting fact in halloysite structural chemistry is a mismatching alignment of its basic elements (oxides), silica, and alumina; silica has tetrahedral sheet structure in

halloysite clay while alumina lies in form of octahedral sheets^[9]. Siloxane groups (Si–O–Si) lie on the external surface of halloysite nanotubes but their inner surface consists of aluminol groups (Al–OH)^[10]. These two groups exhibit higher tendency to crosslink within the polymer during char forming process of intumescence reaction. Many researchers have recently reported improved thermal stability and enhanced flame retardancy of polymeric materials in the presence of HNTs^[11–14].

Lately, a group of polymeric organosilicon compounds called polydimethylsiloxane (PDMS) has been introduced in different polymers to enhance their thermal stability and mechanical properties^[15–17]. PDMS is optically transparent, and, in general, non-toxic, and non-flammable in nature^[18]. In addition, this polymer shows distinguished mechanical properties *i.e.* high modulus, tensile yield strength and impact strength^[19]. Among the wide variety of flame retardant additives, halloysite nanotubes (HNTs) have been

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recognized as a promising filler for intumescence formulation^[20]. Polydimethylsiloxane has its own potentials in flame retardancy industry due to its high thermal stability and low flammability.

In this context, phenol BA was modified with PDMS to reduce toxicity and enhance thermal stability. The modified epoxy mixture was used to develop intumescent fire retardant formulation and reinforced with HNT. The coating formulations were evaluated in terms of thermal performance and char expansion.

The aims of the present study are to investigate the synergistic effects of HNTs and PDMS on the thermal stability and flammability performance of intumescent fire retardant system based on expandable graphite as a carbon source.

EXPERIMENTAL

Materials and Methods

Halloysite nanotubes (HNTs), polydimethylsiloxane (PDMS), melamine (MEL), ammonium polyphosphate (APP), expandable graphite (EG), and boric acid (BA) were purchased from Sigma Aldrich (M) Sdn Bhd. Malaysia. Binder system bisphenol An epoxy resin BE-188 (BPA) and ACR Hardener H-2310 polyamide amine were bought from Mc-Growth chemical Sdn Bhd. Malaysia. Structural steel A36M, used as the substrate, was provided by TSA industries (Ipoh) Sdn. Bhd. Malaysia. FESEM analysis was conducted to confirm the size and orientation of halloysite nanotube used in intumescent formulation and the micrograph is presented in Fig. 1.

Preparation of Coating Samples

First, epoxy (BPA) resin was heated for 15 min at 50 °C to be prepared for PDMS incorporation. Preheated epoxy (BPA) resin and PDMS in 3:2 (*W:W*) were taken into a flask fitted with a thermometer and magnetic stirrer. The reaction

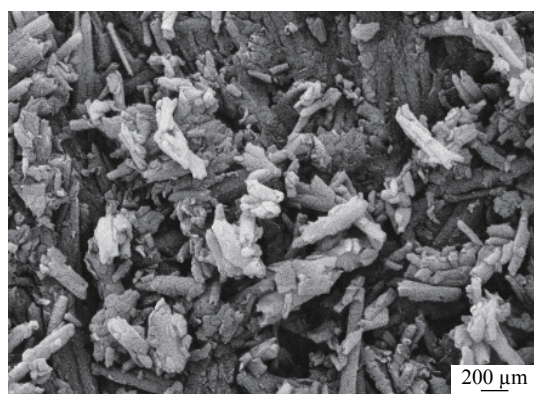


Fig. 1 FESEM micrograph of HNTs used in studied formulations

mixture was continuously stirred at 45 °C for 15 min. All intumescent ingredients, except curing agent, polyamide, were ground for 1 min to homogenize using a grinder (Table 1).

The shear mixer was used for the homogeneous dispersion of a ground mixture of materials with hybrid epoxy for 60 min at 50 r/min. After that polyamide was added in coating formulation and mixed again for 10 min. The sandblasted structural steel plates of area 100 cm² were used as a substrate. The coating was applied using a brush on the steel substrate and an average thickness of coating samples was maintained at approximately 2 mm and it was measured by the thickness measuring gauge. The coated substrates were cured for 24 h at room temperature. Table 1 shows five intumescent coating formulations prepared to study the effects of HNT reinforcement on bisphenol/PDMS epoxy based IFRC on heat shielding and char expansion.

The char morphology was characterized by FESEM and TEM. The thermal stability of developed intumescent formulations was investigated by using thermogravimetric analysis (TGA) and DTG analysis. Functional groups present in char residue were studied by FTIR analysis. Compound analysis of char residue was conducted with the help of X-ray diffraction.

Characterization of Intumescent Coating and Char

Fire test

The fire test was conducted for each coating formulation to evaluate the penetration of heat from fire to the steel substrate. A portable Bunsen burner was used to perform the fire test of the coating on the steel substrate and the distance between the coated substrate and burner was kept 7 cm. Three thermocouples (type K) were connected to Anarittsu Data logger, Input Channel 6 Model AM-8000K with Anarittsu software with the other ends of three thermocouples attached to the back of the coated substrate. The temperature of the steel plate was recorded for 60 min at an interval of 1 min as shown in Fig. 2.

The butane gas was used during Bunsen burner test and temperature of flame was determined using K type thermocouple and the temperature was recorded by Data Logger. The butane gas has a maximum temperature of 1350 °C. Fire test setup is presented in Fig. 2.

Furnace test

Furnace test was performed to examine the char properties such as char expansion and char structure after fire test. The intumescent coatings were burnt in a Carbolite furnace model rapid heating chamber RWF 11/13. The total time was 90 min to reach 500 °C ambient temperature. This temperature was maintained for 60 min to ensure the complete degradation of coating^[21]. Then, the samples were

Table 1 The mass percentage of HNTs and PDMS reinforced coating formulations

Formulation	Mass percentage (wt%)							
	APP	MEL	BA	EG	HNTs	BPA epoxy resin	BPA/PDMS epoxy resin	Hardener
SH(0)	11.36	5.50	11	5.5	–	44.44	–	22.22
SH(1)	11.36	5.50	11	5.5	–	–	41.00	25.64
SH(2)	11.36	5.50	11	5.5	0.5	–	40.50	25.64
SH(3)	11.36	5.50	11	5.5	0.7	–	40.52	25.42
SH(4)	11.36	5.50	11	5.5	1.0	–	40.50	25.14

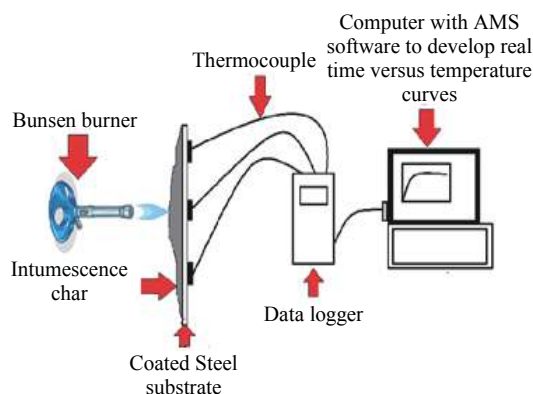


Fig. 2 Bunsen burner fire test set up for developed intumescent coating formulations

cooled in the furnace for approximately 120 min to avoid thermal cracking of char. The char expansion was measured using digital Vernier calliper at four locations of the char and an average char expansion value for each formulation was reported.

Field emission scanning electron microscopy (FESEM)

Integrity and morphological structures of char obtained from each formulation were studied and analyzed by SUPRA 55VP FESEM. The FESEM micrographs were taken at $500\times$ to $5000\times$.

Transmission electron microscopy (TEM)

Transmission electron microscopy was used to investigate the presence of halloysite nanotubes in char residue. Small particles from char residue were dissolved in isopropanol solution and sonicated for one hour before TEM analysis. TEM images were obtained on a JEOL JEM-100SX transmission electron microscope with an acceleration voltage of 100 kV at 8000 , 2.0×10^4 , and 3.1×10^4 magnifications.

Thermogravimetric analysis (TGA)

The thermogravimetric analysis of intumescent coating samples (approximately 10 mg) was carried out at $10^\circ\text{C}/\text{min}$ under N_2 , over the whole range of temperature (25 – 800°C) by TGA Q50 Perkin Elmer. The characterization was performed to determine the residual weight of the char for each coating formulation.

Fourier transform infrared spectroscopy (FTIR) analysis

The FTIR spectra were recorded with EQUINOX55 FTIR spectrometer (Bruker Co., Germany) using KBr pellet technology over the wave number ranges from 4000 cm^{-1} to 400 cm^{-1} .

X-ray photoelectron spectroscopy (XPS) analysis

XPS was used to analyse the elemental composition and possible compounds formed in char residue of intumescent coating formulation. The samples of the char were examined by XPS on a LEYBOLD spectrometer using $\text{Al K}\alpha$ radiation (1486.6 eV). The spectrometer was run in a fixed analyzer transmission mode at the pass energy of 50 eV with an X-ray power source of 300 W . Char samples were mounted by pressing onto the indium holder and introduced in a pre-chamber to obtain a pressure of 10^{-5} Torr .

X-ray diffraction (XRD) analysis

XRD was used to analyse the compounds present in the residual char of the intumescent coating after the fire test.

These measurements were carried out on a Bruker Diffractometer AXS D8 Advance using Cu K radiation and a nickel filter ($k\ 1/4\ 0.150595\text{ nm}$) in the range ($10^\circ < 2\theta < 90^\circ$).

RESULTS AND DISCUSSION

Fire Performance of HNTs-reinforced IFRCs

Bunsen burner fire test has been carried out to investigate the thermal insulation property of developed intumescent formulations according to ASTM E-119. Fig. 3 presents the results of Bunsen burner fire test performed on the intumescent coating samples with different weight percentages of HNTs and PDMS. SH(0) formulation did not contain any filler and was developed using BPA/hardener, thus showed poor fire performance. After 60 min of Bunsen burner test, SH(0) showed 270°C steel substrate temperature. It was found that all samples containing HNTs and PDMS/phenol epoxy exhibited much-improved fire resistance as compared to reference coating without HNTs and PDMS, indicating that the presence of HNTs in PDMS/phenol epoxy can significantly enhance the fire performance of intumescent coating formulations.

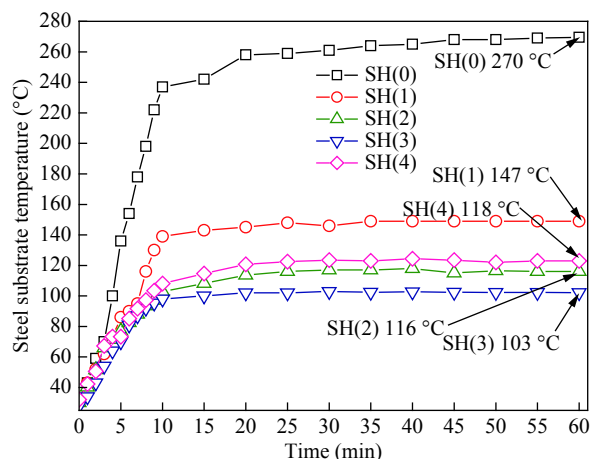


Fig. 3 Steel substrate temperature versus time curves obtained from Bunsen burner test of studied IFRCs

SH(1) formulation was PDMS/BPA epoxy system and without HNT but SH(2) formulation contained PDMS/BPA and halloysite nanotubes. After 60 min of Bunsen burner fire test, SH(1) established the fragile char that can limit the steel substrate temperature up to 145°C . This showed that the presence of PDMS in epoxy binder reduced substrate temperature from 270°C to 145°C , 53% reduction in substrate temperature. This was considered due to the fact that attachment of siloxane particles over the char surface enhanced the heat shielding effect.

However, SH(2), which contained PDMS and HNT ($0.5\text{ wt\%}$), exhibited the further decrease of 8% in steel substrate temperature, from 145°C to 116°C . It showed the effective interaction between HNTs and PDMS contents in intumescent coating formulations. Subsequently, with increasing weight percentage of HNT ($0.7\text{ wt\%}$) in SH(3) in intumescent formulations, insulation property of coated steel

substrate became better. SH(3) showed substrate temperature 103 °C after 60 min of Bunsen burner test. During degradation, siloxanes and HNTs have developed a silicate network over char surface which prevented the carbon in char residue from further degradation. This enhanced the overall fire protection of intumescent coatings by solidifying the insulation layer and hindering the heat transfer. Later, when HNTs quantity was further increased in SH(4) (HNT 1 wt%), an increase in substrate temperature 118 °C was noticed. It indicates that the excessive amount of silica contents could produce delicate char which would increase heat penetration[22]. It is assumed that higher amount of silicates might damage the crosslinking of burning polymer during combustion reaction, thus fail to produce spongy char structure[23].

Analysis of Char Expansion

The microstructure of the residual chars after furnace test was carefully examined to investigate the effects of halloysite nanotube in PDMS/BPA epoxy binder on retardancy of the intumescent coating formulations on the flame. Fig. 4 presents the physical appearances of SH formulation before furnace test.

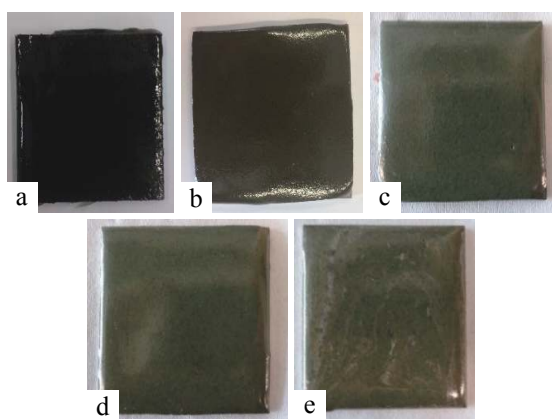


Fig. 4 The physical appearances of (a) SH(0), (b) SH(1), (c) SH(2), (d) SH(3), (e) SH(4) formulation before furnace test

Top view of optical photographs of intumescent formulation char samples after furnace test are shown in Figs. 5(a)–5(e) while the cross-sectional view is presented in Fig. 5(f). HNTs reinforcement in PDMS/BPA resulted in better char expansion with increasing weight percentage of HNT in intumescent coating formulations. Fig. 6 presents the char expansion observed in HNTs reinforced intumescent coating formulations. SH(0) with no filler (BPA/PA) showed the minimum expansion among all coatings samples. Sample SH(0) entirely burnt out and produced vague and fragile char residue (shown in Fig. 5a). Burning behavior of all intumescent samples was the same due to the similar intumescent reaction.

Char residue started to swell in the early stage of combustion after the release of gasses. Complete cellular charred layers were developed after a condensed phase of combustion over the intumescence samples, as discussed earlier. However, significant differences were noticed in

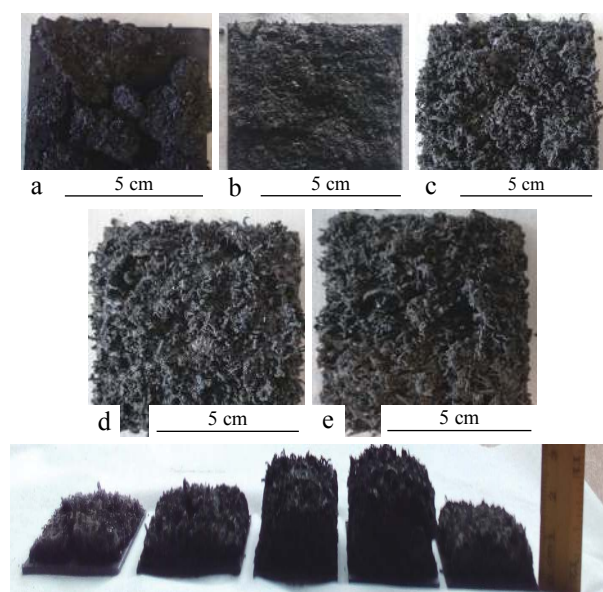


Fig. 5 Top view of HNT and PDMS reinforced intumescent coating samples after furnace test for (a) SH(0), (b) SH(1), (c) SH(2), (d) SH(3), (e) SH(4) and (f) cross-sectional view

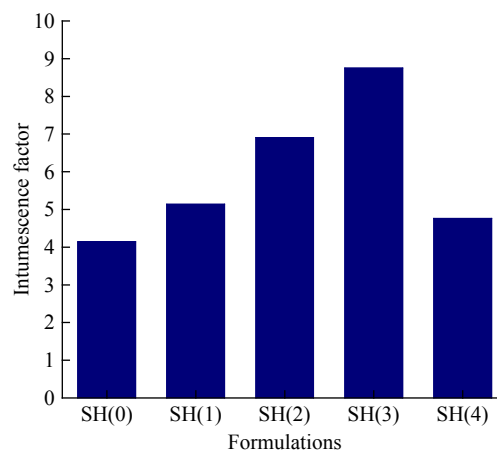


Fig. 6 Intumescence factor recorded in HNTs and PDMS reinforced IFRC samples

thermal behavior of these char layers and with increasing amount of HNTs in coating samples, char expansion increased as shown in Fig. 6. HNTs contributed alumina and silica contents during the intumescent reaction, which successfully filled up the porous structure of char, ensuring the maximum entrapping of gas bubbles with the char residue. Development of spongier char also endorsed the participation of silica and alumina contents in development of char.

Later, in sample SH(4), a sudden decrement was noticed in the expansion of char due to excessive filler quantity. This reduction in char expansion was attributed to crowding of silicates in char residue, which hindered the expansion phenomena[24]. Addition of HNTs and PDMS in the coating formulations resulted in better heat shielding developed silicate network over the char surface, and captured the evolving gasses within char structure, resulting in improved expansion. Table 2 shows the details of char expansion measured and calculated during furnace test in SH

Table 2 Char expansion calculated during furnace test of SH formulations

No.	Thickness after furnace test d_2 (mm)	Coating thickness without substrate before furnace test (mm)	Coating thickness with substrate before furnace test d_1 (mm)	Thickness of steel substrate d_0 (mm)	Intumescence factor IF [*]
SH(0)	9.1	1.82	3.27	1.45	4.25
SH(1)	10.2	1.67	3.12	1.45	5.11
SH(2)	13.5	1.75	3.20	1.45	6.88
SH(3)	16.5	1.72	3.17	1.45	8.75
SH(4)	10.5	1.90	3.35	1.45	4.76

* IF = $(d_2 - d_0)/(d_1 - d_0)$

formulations.

Char Morphology of HNTs and PDMS-reinforced IFRCs

The quality of char layer developed was measured to determine the insulation property of intumescent formulation^[25]. In order to examine the quality of char layer developed over the burnt samples, field emission scanning electron microscopy (FESEM) was used. Homogeneous distribution of HNTs was expected in intumescent formulations due to their tubular structure.

Morphological analysis of HNTs reinforced siloxane epoxy base intumescent formulations showed that the quality of char was improved with the incorporation of HNTs in PDMS-based intumescent ingredients. Figs. 7(a) and 7(b) show the micrographs obtained from FESEM analysis of SH(0) formulation. Since SH(0) had no HNT or PDMS content to support the formation of quality char, micrographs showed poor quality of char with cracks. Cracked surface char cannot offer effective heat shielding during fire situation^[26] as it provides a venue for faster heat transfer to the substrate.

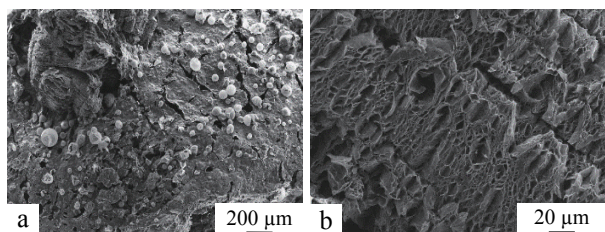


Fig. 7 Nonhomogenous and cracked char structure of SH(0) shown in (a, b) at different magnifications

Figs. 8(a) and 8(b) present micrographs obtained from char residue of SH(1) formulation at different magnifications. Nano size siloxane attachments were clearly visible in these micrographs. It was noted that these siloxanes were helpful to establish their own shielding network over the char layer and provide a complete insulation effect. This insulation layer offered a hindrance to heat flow to the steel substrate, resulting in the improved fire performance^[17].

Figs. 9(a) and 9(b) present the micrographs obtained from char residue of SH(2) formulation at different magnifications. The attachment of siloxane over the char surface became more prominent in these images due to the presence of HNTs in SH(2) formulation. Because of HNTs, the alumina contents also participated in the intumescent reaction and developed Al—O—Si bonding with other ingredients, which successfully enhanced the attachment of

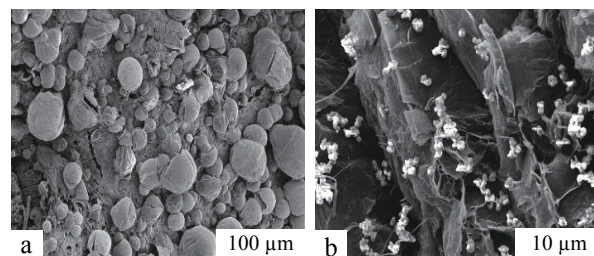


Fig. 8 Nonhomogenous and siloxane attached char structure of SH(1) shown in (a, b) at different magnifications

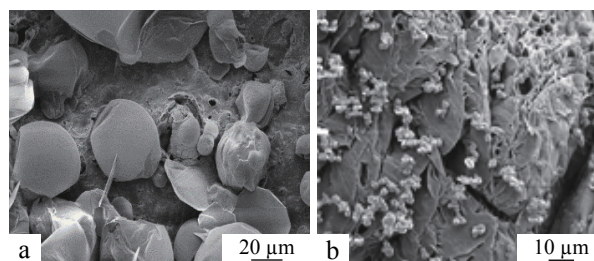


Fig. 9 Homogenous and siloxane attached char structure of SH(2) shown in (a, b) at different magnifications

more siloxane contents over char surface, thus strengthened the protective layer^[27]. It was noticed that with the incorporation of HNT in PDMS base epoxy, the quality of char was enhanced in SH(1), SH(2), SH(3) formulations.

Figs. 10(a)–10(d) show the micrographs obtained from char residue of SH(3) formulation at different magnifications. Highly dense and compact intumescent char layers with small pore sizes were observed in samples SH(3) as shown in Fig. 10(b). HNTs due to its nanostructure

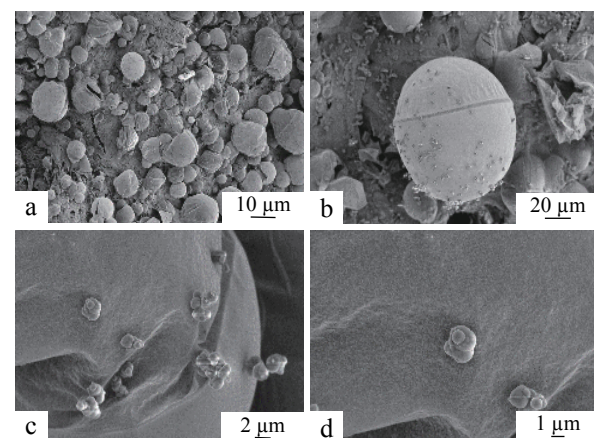


Fig. 10 Siloxane attached char structure of SH(3) shown in (a, b, c, d) at different magnifications

completely filled all the pores and cracks present in char layer, developing smooth char surface and ensuring better insulation^[28]. Ullah *et al.* reported that the char of 0.4% CNTs reinforcement decreased the evaporation of the gaseous products and char delivered an effective thermal barrier to reduce the rate of heat transfer to the underlying substrate^[29]. These nano size siloxanes (Figs. 10c and 10d) had a tendency to block up the smallest crack and pores present in char layer and provide enhanced heat shielding effect. Intumescent phenomena and expansion of char depend upon the entrapment of gas bubbles in spongy char layer during volatile burning^[30, 31]. Fig. 11 shows the EDS analysis of SH(3) char, which confirmed the attachment of siloxane attached on the residual char.

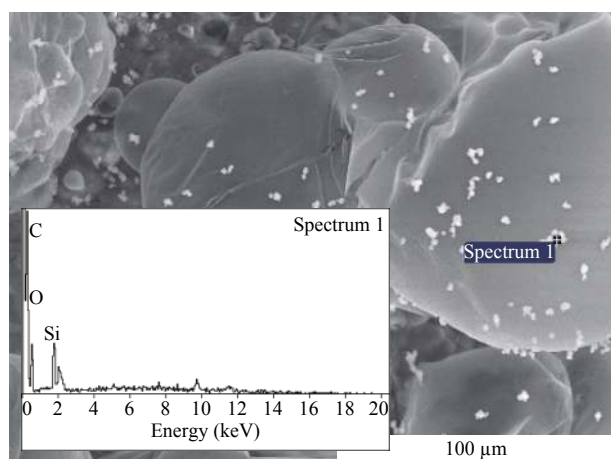


Fig. 11 EDS analysis of char residue of SH(3) char

In SH(4), when 1.0 wt% HNTs were loaded in siloxane epoxy base intumescent formulation, intumescent factor decreased as discussed in an earlier section. The abundance of siloxane contents in SH(4) formulation might block all the pores, resulting in futile capturing of gas bubbles and thus producing low quality char (Figs. 12a and 12b). PDMS-based epoxy resin offered nano siloxane particle to the char layer,

which not only played an important role in reducing the pore size of char layer but also developed a shielding silicate network over char surface (as shown in SH(3)). It was assumed that this silicate network protected residue carbon from further decomposition and enhanced the heat shielding property of intumescent formulation^[15, 32, 33].

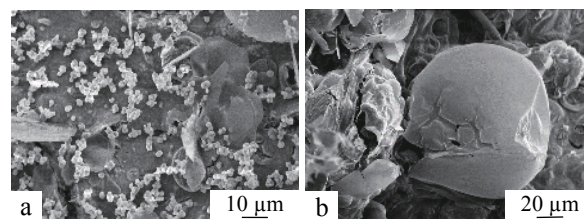


Fig. 12 Siloxane attached char structure of SH(4) shown in (a, b) at different magnifications

A quality char should have homogenous minimum pore size to entrap gasses and give char spongy effects along with proper silicate layer over the surface to offer enhanced heat shielding. In the case of SH(4), the pore size was uneven due to an excessive amount of silica in the formulation. EDX analyses of SH formulations are presented in Fig. 13.

TEM Study of HNTs and PDMS-reinforced IFRCs

The transmission electron micrographs were obtained with a JEM-1200EX electron microscope to examine intercalation states of the HNTs and siloxane in char residue after Bunsen burner test. The presence of HNTs and siloxane nanoparticle in char residue ensured the development of silicate network that has been discussed in earlier sections and we can reasonably assume that throughout the intumescent reaction, added content established their protection network over char surface and hindered heat transfer as expected. Fig. 14 shows the TEM images of SH(3) sample at different magnifications. Halloysite nanotube assembly is clearly visible at higher magnification (Fig. 14c and 14d). It was assumed that these nanotubes built up a silicate network over char residue which protected char carbon from further degradation and enhanced fire performance of intumescent coatings. In an epoxy-based

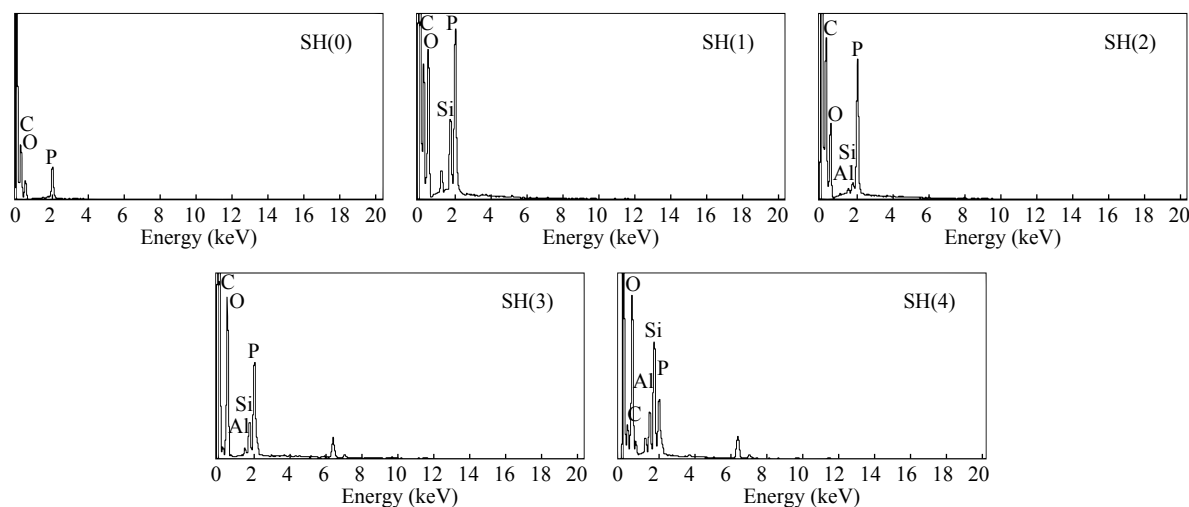


Fig. 13 EDX analysis of SH formulations

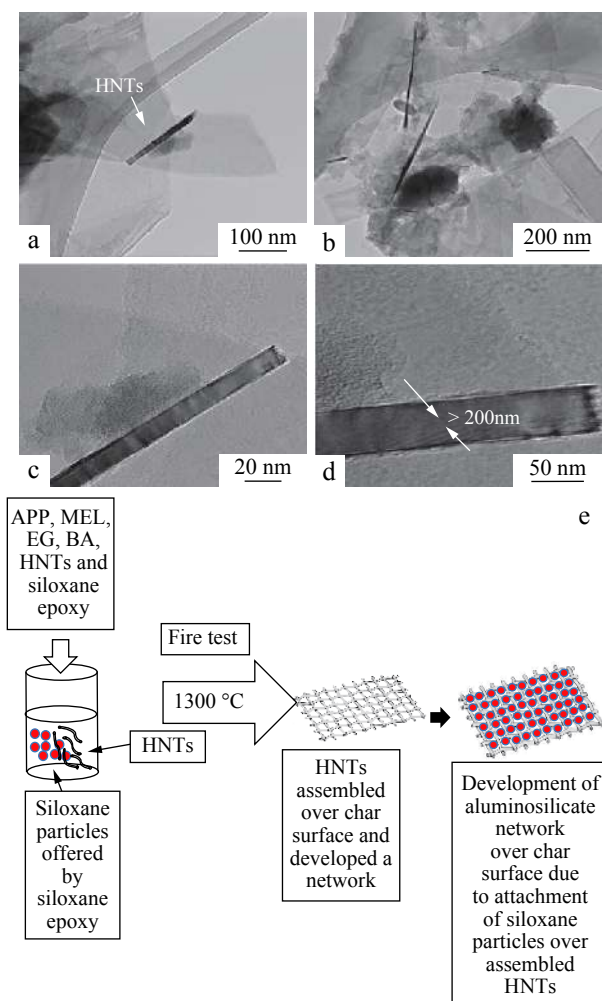


Fig. 14 TEM micrograph of SH(3) at (a) 8000, (b) 2.0×10^4 , (c) 3.15×10^4 and (d) 6.0×10^4 ; (e) Graphical representation of attachment of siloxane particles over HNTs network within intumescent coatings

intumescent system, it is essential to avoid dripping of the molten polymer so that further flame spread can be avoided. Incorporation of HNTs also played a vital role in this phenomenon by the development of tubular network over the char surface^[20]. This tubular network was further strengthened by attachment of siloxane particles offered by the epoxy binder. Dual effects of HNTs and siloxane epoxy binder exhibited a crucial effect on properties of intumescent coatings like thermal stability, inflammability, barrier properties and chemical resistance^[34]. The phenomena of attachment of siloxane particles over HNTs network within intumescent coatings are graphically explained in Fig. 14(e).

A homogeneous distribution of the HNTs in intumescent formulations can be seen in TEM micrographs. HNTs had an extra hydroxyl ion at their outer surface which enabled the formation of temporary hydrogen bonds with the siloxane groups offered by siloxane epoxy binder during the intumescent reaction. This phenomenon enhanced the overall thermal stability of SH(3) formulation^[35]. Moreover, the addition of HNTs in siloxane epoxy base intumescent formulation brought up an increase in the interlayer distance

of the silicate polymer matrix (used as an epoxy binder) when the coating was subjected to fire and enhanced the char expansion due to the development of aluminosilicate network over the char surface^[36].

Thermal Stability Analysis of HNTs and PDMS-reinforced IFRCs

Thermal gravimetric analysis of HNTs and PDMS-reinforced intumescent formulation was performed to investigate the thermal stability of designed formulations and results are presented in Fig. 15. The residual mass of the SH(0), SH(1), SH(2), SH(3) and SH(4) formulations was found to be 39%, 40%, 42%, 43% and 38.7%, respectively. It was noticed that samples SH(3), with 0.7 wt% of HNTs and 17% of PDMS, showed the maximum residual weight after 800 °C during TGA analysis. For a further understanding of thermal degradation of intumescent coating formulations, DTG analysis was also carried out and results are presented in Fig. 16.

In Fig. 15, all samples had the first degradation stage at

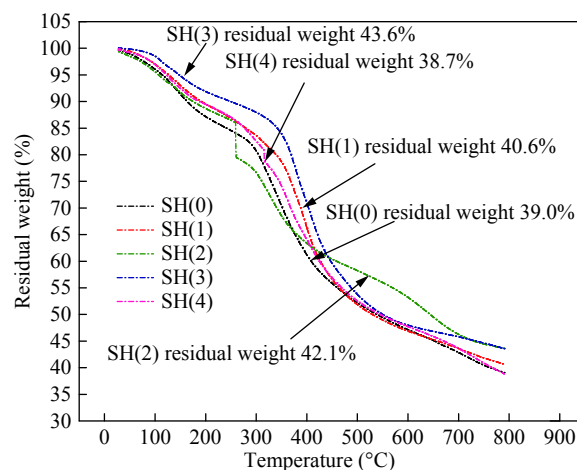


Fig. 15 TGA curves for HNTs reinforced IFRC formulations

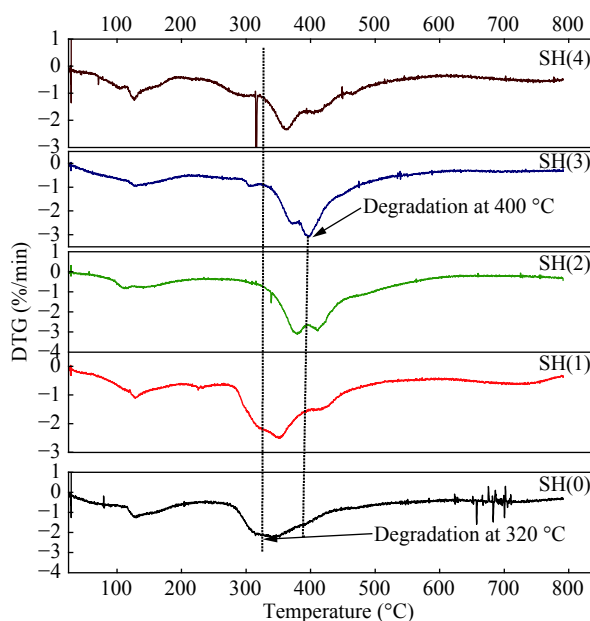


Fig. 16 DTG curves for HNTs reinforced IFRC formulations

150 °C except SH(3). At this stage, intumescent coating samples lost a very minimal weight (less than 2%) due to volatilization of residue solvent and partial decomposition of intumescent coatings^[37]. The major degradation occurred between 250 and 430 °C. At this stage, intumescent samples massively degraded and released gases, which further blew the developed char network and improved insulation. In SH(0) and SH(4), the second degradation occurred around 320 and 350 °C. This second major degradation delayed in SH(1), SH(2) and SH(3) samples. Sample SH(2) and SH(3) showed higher thermal stability and degraded around 400 °C as shown in Fig. 16. During the second degradation stage, the intumescent coating melted, releasing NH₃ and other volatile gases^[21, 38, 39]. The delayed degradation of intumescent samples resulted in the maximum release of gases and established spongier and stronger char. These volatile gases made the char surface more compact, firm and porous in structure.

After 500 °C, silicates from HNTs and PDMS developed silicate network over the char surface which secured the char carbon for further oxidation. In Fig. 16, SH(0) showed further degradation at a higher temperature, while SH(3) did not show any degradation after major degradation step at 400 °C. It was assumed that in SH(4), excessive release of silicates from HNT and PDMS during degradation stage affected the intumescent reaction and failed to develop a proper char to offer enhanced insulation.

X-ray Diffraction Analysis of HNTs and PDMS-reinforced IFRC

In order to analyse the compound present in the char residue, XRD analysis of SH formulation was conducted and results are presented in Fig. 17. During XRD analysis two peaks were observed in all SH formulation at 24.6° and 26.54°. The first peak at 24.6° was assigned to sassolite ($d = 74\text{-}1169$) which is a borate mineral, released due to degradation of boric acid^[40]. The second peak at 26.54° observed in XRD patterns was for borophosphate ($d = 30\text{-}0620$)^[41]. It is expected that during the intumescent reaction, ammonium polyphosphate degraded and released phosphoric acid, which

further reacted with borate ions offered by boric acid and produced borophosphate. Similarly, at 40.53° ($d = 77\text{-}1060$), a small peak assigned to carbon was observed in all formulations. The presence of this peak was attributed to hydrocarbon compounds produced during degradation of epoxy binders^[37]. In XRD patterns of SH(2), SH(3) and SH(4), another peak was observed at 28.05° ($d = 45\text{-}0510$) which was assigned to a compound named “mullite”. Mullite is a rare silicate mineral of post-clay genesis. Its chemical formula is $3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ and it is considered to be thermally stable due to intercalated bonding between alumina and silica^[42, 43].

HNTs in SH formulations offered alumina and SiO₂, which were released by degradation of silicon epoxy, to react with each other during the intumescent reaction and form the alumino-silicate layer (mullite) over the char surface with enhancing the stability. This new alumino-silicate network was also confirmed by HRTEM analysis, discussed in pervious section. It was believed that formation of mullite (alumino-silicate network) improved the strength of the charring layer, made the charring layer hard to subside and increased the flame-retardant performance^[20].

Fourier-transform Infrared Analysis (FTIR) of HNTs and PDMS-reinforced IFRC

Fig. 18 shows FTIR spectra of the internal char samples of SH(0), SH(1), SH(2), SH(3) and SH(4) after furnace test. Nearly similar peaks were observed in all samples that except SH(0). SH(0) did not show any peak between silicon regions, 1000–1300 cm⁻¹, due to the absence of Si bonding in the sample^[44]. All char samples, except control formulation, exhibited stretching peaks in silicon region which validated the presence of Si bonding in samples. Siloxane from PDMS and silicon from HNTs decomposed during the intumescent reaction and generated compounds with silicon bonding. Peaks at 1185 and 1079 cm⁻¹ were assigned to Si–O–Si, Si–CH₃ bonds, respectively^[30].

Boric acid present in char samples degraded with

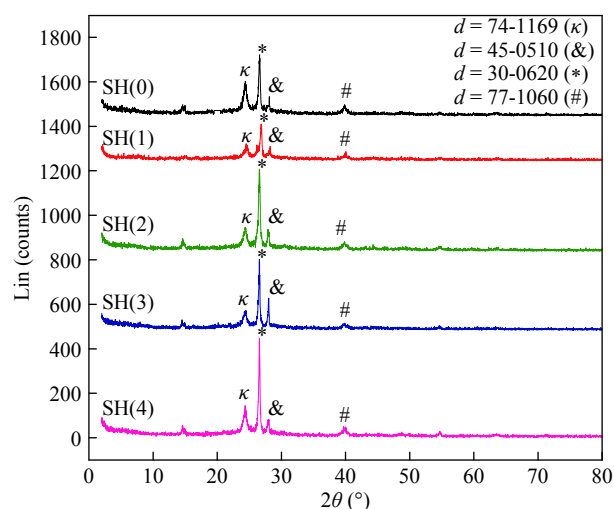


Fig. 17 XRD patterns developed in this study intumescent coating formulations

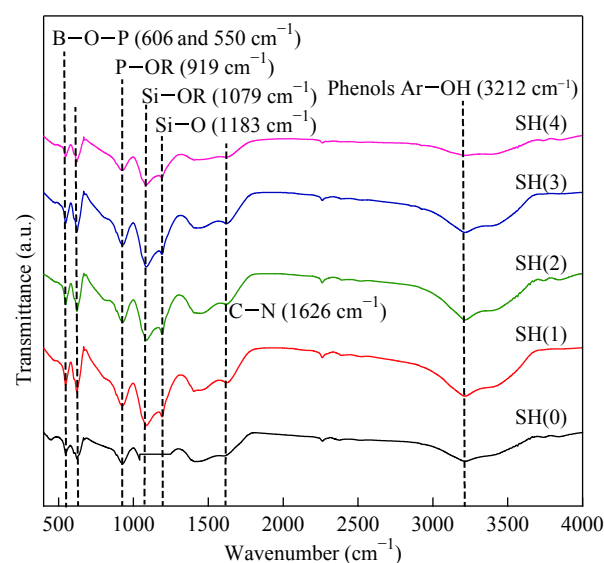


Fig. 18 FTIR spectra of HNTs and PDMS-reinforced IFRC samples

ammonium polyphosphate and produced borophosphate in all char samples. The peak at 606 cm^{-1} represented B—O—P bonding, confirming the presence of borophosphate^[45, 46]. All samples contained ammonium polyphosphate as an acid source, which degraded and produced phosphate bonding in the char. FTIR spectra showed one stretching peak at 919 cm^{-1} which represented the presence of P—O—P bonding^[47]. The stretching peak observed at 3212 cm^{-1} was attributed to carbon peaks for phenols Ar—OH bonding^[48]. The strong synergism between APP, siloxane, and HNTs was confirmed from the FTIR results due to the presence of P—O—P, Si—CH₃ and B—O—P bonding present in intumescent char residue. Moreover, the presence of Si—O—Si bonds validated the development of silicate network over char surface which enhanced the insulation effect during Bunsen burner test. The char residue with strong silicate network shield protected char carbon from further decomposition^[24].

Elemental Composition Analysis of HNTs and PDMS-reinforced IFRCs

In order to analyse the elemental composition present in the char residue, XPS analysis of SH formulation was conducted and results are presented in Table 3.

Table 3 Elemental compositions and XPS analysis of HNTs reinforced coatings

Elements	Atomic percentage (wt%)				
	SH(0)	SH(1)	SH(2)	SH(3)	SH(4)
N1s	4.2	1.2	3.08	5.27	5.08
O1s	56.36	56.06	43.64	43.73	41.86
C1s	37.14	38.09	47.51	45.06	47.15
P2p	2.3	2.56	3.56	2.94	3.90
Si2p	0	2.1	2.21	3.00	2.01

Table 3 shows the increase in carbon contents in char residues of intumescent coating formulations with the increasing amount of PDMS in formulations. SH(0) contained 37.14% carbon contents while in char residue of SH(4) the carbon content was increased up to 47.15%. This confirmed the stable structure of char. Char accumulation degree and oxidation degree can be judged by the quantity of carbon content and oxygen contents present in residual char, respectively. A higher quantity of carbon contents represents the strength of char formed during intumescence reaction. And the low degree of oxidation shows an anti-oxidation rate of carbon content present in char residue.

The phosphorus and nitrogen contents in the residual char of HNTs and PDMS reinforced coating formulations respectively were also increased upon increasing the quantity of HNTs in formulation. Phosphorus acted as char former in the condensed phase reaction of intumescence phenomena. Nitrogen was responsible for blowing that char network. A higher percentage of phosphorus and nitrogen contents confirmed the development of spongy and strong char structure in intumescent coatings formulations.

As SH(0) did not contain any silicon base additives, Table 3 shows no quantity of Si content for SH(0). However, for SH(1), halloysite nanotubes were introduced. HNTs are

basically Si—Al powder which can offer a small amount of silica for carbon stabilization during the intumescent reaction. In SH(2), SH(3) and SH(4), due to the presence of PDMS in these coatings, higher siloxane contents were exhibited in XPS analysis. Siloxane contents could develop proper silicate network over char residue which prevented carbon from further degradation. This may be the reason that carbon contents in SH(3) were higher as compared to those in SH(1) and SH(0).

CONCLUSIONS

For the first time, HNTs as a potential synergistic agent was investigated in new intumescent system having siloxane epoxy resins along with traditional intumescent ingredients (APP-EG-MEL). The incorporation of HNTs had a significant influence on the fire performance of intumescent fire resistive coatings. The noticeable improvement in fire performance of intumescent coating formulation was observed. Backside steel substrate temperature was decreased from $270\text{ }^{\circ}\text{C}$ to $102\text{ }^{\circ}\text{C}$ when 0.70% HNTs were incorporated into PDMS-based intumescent formulations, SH(3). This phenomenon was attributed to the development of silicate network over char residue, and the decreased thermal decomposition rate of residue carbon during the intumescent reaction. Subsequently, SH(3) showed the highest expansion among all formulations due to low degradation rate during combustion. FESEM and TEM images revealed that dense and compact intumescent char layer covered by silicate network was obtained using HNTs and PDMS as the additives in intumescent coating formulations, which provided better assistance to hinder heat penetration. Thermal stability of intumescent coating formulations was also improved by HNTs and PDMS incorporation in the intumescent formulation. Due to the development of strong silicate network, decomposition of coating formulations was delayed from $300\text{ }^{\circ}\text{C}$ to $400\text{ }^{\circ}\text{C}$. XRD analysis confirmed the development of aluminosilicate compound mullite. Mullite is highly thermally stable and it enhanced the fire performance of intumescent formulation. FTIR results revealed the presence of Si—O—Si and Si—CH₃, which endorsed good synergism between PDMS, HNTs and other intumescent ingredients. XPS analysis demonstrated that HNTs and PDMS contributed physically to the mechanical reinforcement of the intumescent char through the formation of a “skeleton-frame” for the siloxane-carbon structure. The bridging effect of the nanotubes allowed the development of a denser and tougher char, inhibiting heat and mass transfers between the flame zone and the condensed phase. To sum up, halloysite nanotubes can be considered as a proper synergistic agent in intumescent coating which contains siloxane epoxy resin as a binder system. The developed intumescent fire retardant coating system is highly recommended for high temperature applications.

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