Flame Retardant Effect of Nano Fillers on Polydimethylsiloxane Composites

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Polydimethylsiloxane has exceptional fire retardancy characteristics, which make it a popular polymer in flame retardancy applications. Flame retardancy of polydimethylsiloxane with different nano fillers was studied. Polydimethylsiloxane composite fire property varies because of the shape, size, density, and chemical nature of nano fillers. In house made carbon and bismuth oxide nano fillers were used in polydimethylsiloxane composite. Carbon from biochar (carbonised bamboo) and a carbon by-product (carbon soot) were selected. For comparative study of nano fillers, standard commercial multiwall carbon nano tubes (functionalised, graphitised and pristine) as nano fillers were selected. Nano fillers in polydimethylsiloxane positively affects their fire retardant properties such as total smoke release, peak heat release rate, and time to ignition. Charring and surface ceramization are the main reasons for such improvement. Nano fillers in polydimethylsiloxane may affect the thermal mobility of polymer chains, which can directly affect the time to ignition. The study concludes that the addition of pristine multiwall carbon nano tubes and bismuth oxide nano particles as filler in polydimethylsiloxane composite improves the fire retardant property.

Keywords: PDMS, Carbon Nano Tubes, Carbon Soot, Carbonised Bamboo Biochar, Bismuth Oxide.

1. INTRODUCTION

Flame retardancy becomes a critical issue in a variety of issues including, but not limited to protection of life and properties. Halogen free, recyclable, environment friendly systems that do not release toxic gases have recently become preferable.[1] Many polymers are known for their high flammability.[2] The significant use of fillers in polymers is remarkable because of their fire retardant characteristics and overall in their combination of properties. Some of the attractive properties of the polymer filler composite include: ignition ability, flame extinction, flammability of the volatiles, amount, and rate of heat released, flame spread, smoke toxicity, and density are few of them.[3] Ignition of organic polymers is a complex event involving several physical and chemical changes. Flaming ignition of polymer occurs when the gas phase concentration of fuel, produced by thermal decomposition of macromolecules, reaches the lower flammability limit.[4] The environment and safety are major concerns for flame retardant

materials. It is necessary to develop high performance and environmental friendly flame retardant materials to decrease pollution and toxic waste effects.

Conventional flame retardants need a high amount ($\sim$60 wt.%)[5] of filler within the polymer to achieve suitable results. Main disadvantages of this high concentration of filler in composite are the density and the lack of flexibility that may compromise the mechanical performance. This makes composite not suitable as flame retardant in many applications such as electrical cable applications. Non halogen flame retardants such as phosphorus, boron, and silica are some of the popular fillers studied in flame retardancy.[6, 7] One of the major research efforts in the field is to use nano structured particles. They includes nano clays, graphite, carbon nano tubes, graphene, silica and POSS.[6, 8] Nano fillers can avoid the disadvantages of traditional flame retardant fillers in composite.[9] Nano composites are attractive because a limited amount of nano structured filler can lead to large improvement in fire retardancy properties. When incorporating nano particles in the polymer matrix, both the physical properties of the

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polymer (e.g., melt viscosity) and chemical decomposition mechanism significantly modify.[4] The fire retardant property of polymer depends on the adequate interaction and dispersion of nano fillers.[10] Nano fillers can influence the thermal decomposition of composite through the reduction of combustible products, the modification of properties such as thermal conductivity, viscosity etc.[11, 12] Nano fillers will pave the way for future materials by contributing not only to the mechanical performance, but also to the tailoring of physico-chemical performances.[13, 14] The contribution of nano particles to flame retardancy varies and depends on their geometry and chemical structure.[1, 6, 15]

High thermal conductivity and mechanical properties of carbon nano tubes apparently made them an ideal nano filler in composite for better fire retardancy.[16, 17] However, the use of nano tubes may lead to out-of-the market costs for the application. Hence we investigated alternative materials that are more cost effective, abundant, and with limited or no environmental issues. For instance, carbon from biochar, soot, and carbon waste are interesting candidates.

Considering nontoxic property,[18] cost[19, 20] and environmental regulations, bismuth oxide (Bi_2O_3) attracted the attention over silica and other commercial inorganic fire retardants.[21–23] Silicone based polymer such as PDMS is in demand for high temperature applications.[24, 25] PDMS has unusual rheology with nontoxic properties. The structural elements of PDMS have direct or indirect influence on their stability at high temperatures.[5]

This work is focused on the effect of different nano fillers in PDMS composites on fire retardant property of the composite. A unique approach in this research is the limited concentration of (1 and 3 wt.%) the nano fillers in composite.

2. MATERIAL AND METHODS

2.1. Materials
PDMS polymer (Sigma Aldrich) and different types of nano fillers (Table I) were used. Nano fillers from different sources were selected for a comparison. Commercial (cheap tubes) graphitised, functionalised, and pristine multiwall carbon tubes (MWCNT) were used. Carbonised bamboo biochar was prepared by pyrolysing bamboo at

Table I. Different nano fillers used in composite for fire retardancy study.

Filler	Notation	Source
MWCNT	MW1	Commercial
MWCNT-graphitised	MWG1	Commercial
MWCNT (–COOH) functionalised	MWF0	Commercial
Carbonised bamboo	CB	Bamboo
Carbon soot	CS	By-product in fullerene synthesis
Bismuth oxide	Bi_2O_3	Bismuth nitrate

800 °C for 1 h in argon atmosphere. Carbonised bamboo (CB) was subsequently grinded to a fine powder form. Bi_2O_3 was prepared by oxidation of bismuth nitrate pentahydrate salt (Sigma Aldrich) at 600 °C for 1 h in oxygen atmosphere. Carbon soot (CS) was the by-product of in fullerene synthesis.[26, 27]

2.2. Composite Preparation
PDMS nano filler composites were prepared in ambient conditions. Nano filler at 1 and 3 wt.% concentrations were used. The appropriate quantities of fillers were mixed with PDMS monomer with ultraturex (10,000 rpm) mixer. Cross linker was added after achieving the uniform dispersion of nano fillers in monomer. This step initiates the polymerisation in the composite. The composite mixture was sonicated (20 Hz) for 10 min and was kept under vacuum (133 Pa) for 10 min. This procedure ensures the elimination of gaseous bubbles generated in the polymerisation process. The composite mixture was moulded in prescribed ($50 \times 50 \times 3$ mm³) dimension. Moulded composite was maintained at 90 °C for 4 h to achieve the complete polymerisation. The fire retardant test was conducted and evaluated in a cone calorimeter according to ASTM E 1354-16a standard.

2.3. Characterisation
Field Emission Scanning Electron Microscope (FESEM, Zeiss Supra 40TM) was employed to study the morphology of nano materials. Nano particles were coated with 5 nm chromium layer to avoid the charging effect while FESEM analysis.[26] No coating was needed for carbon based fillers.

Forced combustion tests were performed according to ISO 5660 standard. A Fire Testing Technology (FTT) cone calorimeter apparatus was used. During this test, the composite samples ($50 \times 50 \times 3$ mm³) were subjected to a standard cycle in accordance with ASTM E 1354-16a defined parameters in the calorimeter. Heat flux (35 kW/m²) was applied on the top of the specimen. The material decomposed and released gases after ignition. Combustion products were aspirated in a duct leading to the instrument analysers. A laser device placed at the end of the cone duct, evaluated the amount and opacity of smoke released during the test. The test was repeated three times for each formulation.
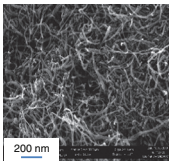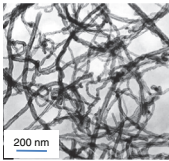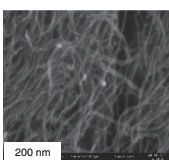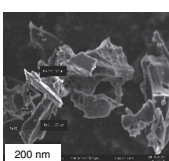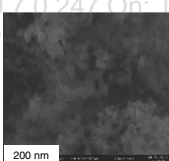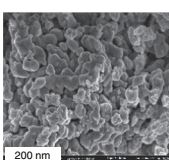
Time to Ignition (TTI), Peak of Heat Release Rate (PHRR), Total Smoke Released, and Specific Extinction Area (SEA) were studied. Average values and standard deviation of the various parameters were measured for each material.

3. RESULTS AND DISCUSSION

3.1. Nano Structural Analysis
FESEM analysis (Table II) confirms the size and morphology of the fillers. The MWCNT diameter were in the

Table II. FESEM of nano fillers used in composite.

Filler	Diameter (nm)	Length (μm)	FESEM of nano filler
MWCNT (MW1)	30–50	12–20	
MWCNT-graphitised (MWG1)	20–30	10–30	
MWCNT (–COOH) functionalised (MWF0)	30–50	10–20	
Carbonised bamboo (CB)	100–1000	20–50	
Carbon soot (CS)	100–200	–	
Bismuth oxide (Bi_2O_3)	100–300	–	

range of 30–50 nm with length in the range of 12–20 μm. Graphitised MWCNT were 20–30 nm in diameter and ∼10–30 μm in length. The carboxylic group (–COOH) functionalised MWCNT had diameter of 30–50 nm and length of ∼10–20 μm. CB had an irregular shape with thickness in the range of 100–800 nm and a length of 20–50 μm. The particle size is a function of the pulverisation process. CS has spherical cluster with diameter of 100 and 200 nm. CS particles are amorphous with presumably limited 2D arrangement.[27–29]
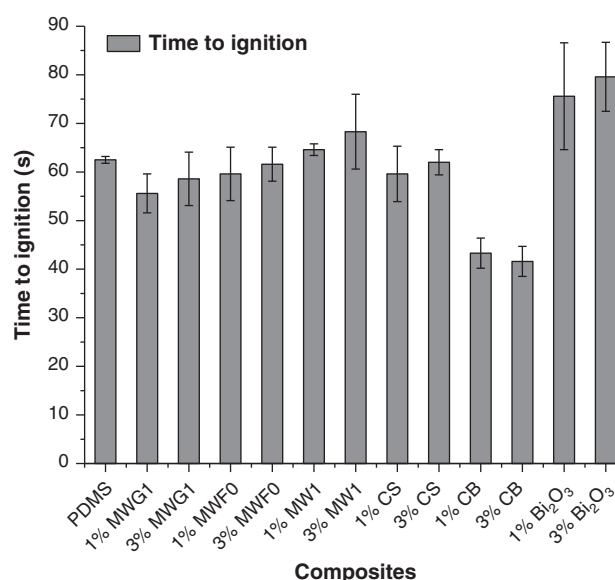
Bi_2O_3 nano particles are in agglomerated form having diameter 100–300 nm. The dimensions of nano particles can be one of the important factor for alteration in composite fire retardancy. Except surface modified MWF0, other

carbon based nano fillers were chemically inert. Bi_2O_3 and MWF0 nano particles may have the possibility to form chemical bonding with PDMS polymeric structure. The orientation of well-dispersed nano tubes in PDMS formed the network. It can influence the mechanical and thermal strength of the composite in fire retardancy. CB, CS, and Bi_2O_3 nano particles had random spherical agglomerated form, which was different from tubular MWCNT. This shapes might be interesting for localisation of thermal heat in the composite while fire retardancy.

3.2. Time to Ignition (TTI)

MWCNT (MW1) and Bi_2O_3 are the fillers that have a higher impact on the ignition time of the composite (Fig. 1). The other fillers did not show a noticeable impact on PDMS properties. TTI of Bi_2O_3 reinforced composites was increased by 15–20 s. In the case of MWCNT (MW1) the ignition is hindered by 3–5 s. These are rather noticeable changes. TTI values were affected by thermal stability of Bi_2O_3 nano particles in oxidation.[30] On the other hand, thermal conductivity of MWCNT[17, 30] may be one of the reason to show comparable TTI values (Fig. 1). MWCNT are in fact expected to significantly increase thermal conductivity.[31, 32] Thus, it is not surprising that composites showed a different ignition behaviour compared with blank PDMS. Composites with CS, and CB lowered the TTI value compared with blank PDMS. These fillers are having lower oxidation stability in fire retardancy.[34, 35]

Comparison among nano fillers, Bi_2O_3 nano fillers has lower thermal conductivity but higher thermal stability in air.[33–36] This is most probably the reason for the best performance of Bi_2O_3 nano particle in composite as far as TTI is concerned.

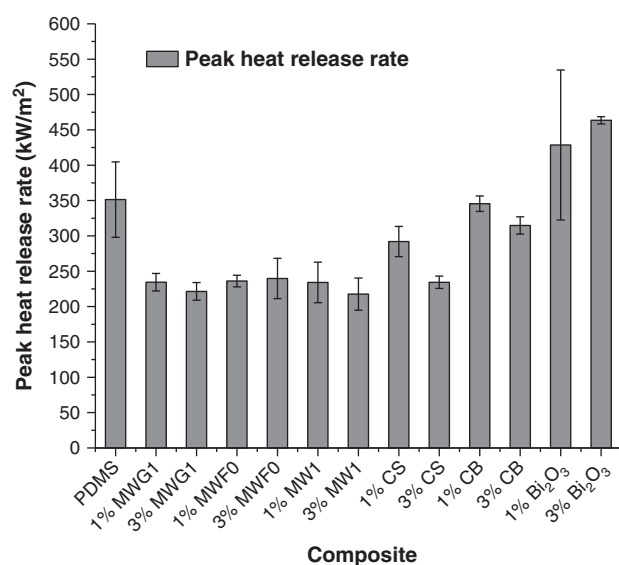**Figure 1.** Effect of nano fillers in composites on time to ignition.

Figure 2. Effect of nano fillers in composites on peak heat release rate.

3.3. Peak Heat Release Rate (PHRR)

A comparison of PHRR values (Fig. 2) shows that most of the carbon based nano fillers promote a reduction of the PHRR. The heat release rates (Fig. 3) of the MW1-PDMS composites are much lower than that of pristine PDMS. The above results indicate that the MWCNT-PDMS composites release the heat much slower than pristine PDMS. CS and CB had similar behaviour like MWCNT in composites. This may be due to chemical and/or physical processes in the condensed phase instead of in the gas phase.[36] On the contrary Bi_2O_3 nano filler composite showed higher heat release rate. It indicates that Bi_2O_3-PDMS composites burn much faster than pristine PDMS. Bi_2O_3 nano particles have higher thermal stability but lower thermal conductivity.[34, 37, 38] This may lead to increase the localised heating, which may lead to destroy the chemical structure

of PDMS. It can raise the PHRR of the composite as compared with pristine PDMS. HRR cone test (Fig. 3) helps to analyse the combustion behaviour of the nanofiller composite in detail. Composite with MWCNT fillers (Fig. 3) are more efficient in combustion behaviour. MW1 filled composite shows major alteration in combustion performance. HRR halved in respect to neat PDMS. There are no significant differences in the combustion behaviour observed with increase percentage of filler (3 wt.%). Only CS seems to have a decrease of HRR peak with the increase of amount of filler. Further detailed studies are required to understand this phenomenon.

3.4. Total Smoke Release

All kind of MWCNT-PDMS composites (Fig. 4) lead to a significant decrease in smoke release compare to pure PDMS (760 m^2/m^2). Graphitised MWCNT (MWG1) composite shows the lowest value of smoke release (300 m^2/m^2) among all. The nano tubes network layer may emit radiation from the material surface and acts as a barrier against the decomposed gas supplied from the bulk polymer and against oxygen diffusing from the air into the material, hence hindering polymer decomposition. The nano tubes network layer must be smooth, crack free, and opening free so that it may act as an effective gas barrier.[39] This may be due to the higher thermal stability of filler in air.[40] Observation indicates the graphitisation of the carbon impact on the thermal oxidation, which is influencing the total smoke release of composite. Other carbon fillers demonstrate variation in smoke release, which may be due to enhancing in thermal oxidation rate.[41] The composite reinforced with Bi_2O_3 nano particles shows an increase in total smoke release with respect to pristine PDMS. Additionally, the Bi_2O_3 particles sponsor a rapid degradation of polymer chain after ignition. Bi_2O_3 nano particles has high thermal stability,[37] which may play an important role to increase the total smoke release.
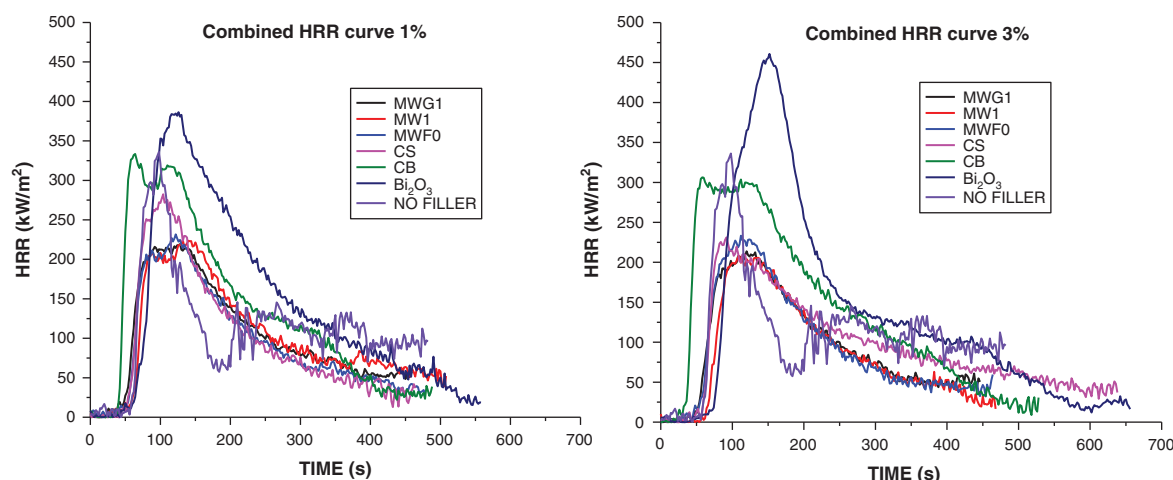

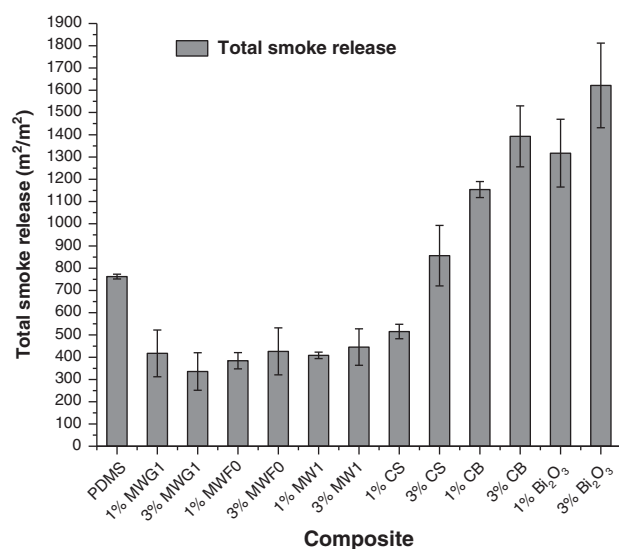**Figure 3.** Heat release rate cone test graphs.

Figure 4. Effect of nano fillers in composites on total smoke released.

3.5. Specific Extinction Area

Pure PDMS produced dense smoke (6100 m^2/kg) (Fig. 5). All type of MWCNT in PDMS composite decreased smoke density around 5–65% as compared with pure PDMS. 3 wt.% of MWF0 showed lower smoke density. 1 wt.% of Bi_2O_3 nano particles in composite reduced 25% of smoke density, whereas with 3 wt.% the smoke density enhanced as compared with pure PDMS. Composite with 3 wt.% of CB increased smoke density as compared with 1 wt.% and pure PDMS. CS had similar effect; additions of 1 wt.% decreased smoke density (5100 m^2/kg), whereas with 3 wt.% (5800 m^2/kg) of filler increased the smoke density. MWCNT, regardless of the concentration, has a positive effect by reducing the smoke density. Ultimately, the best candidate to reduce the smoke density is MWF0 with 3 wt.% in composite (1800 m^2/kg). This effect can
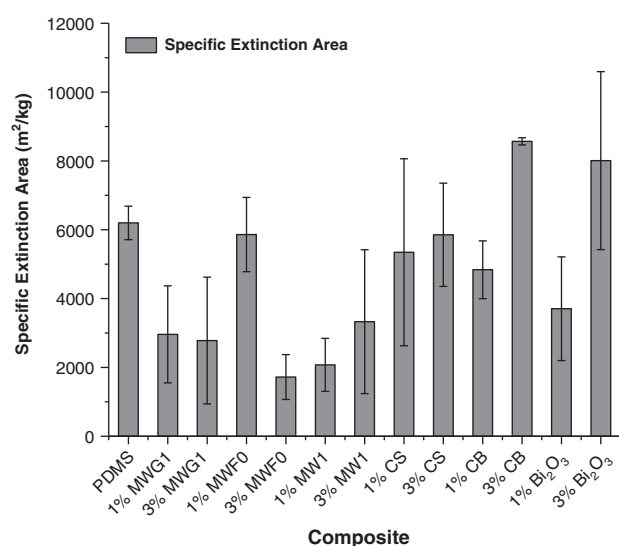
be attributed to the fact that MWF0 forms a protective layer on the composite surface. It may delayed the thermal oxidation of MWF0 composite in fire retardancy.

The results show the influence of 1 and 3 wt.% of MWCNT in the composite. It was observed that inclusion of MWCNT decreased total smoke released (∼50%), heat release rate (∼40%), smoke density (∼65%) compared with the pure PDMS. Most interestingly, lower concentration of MWCNT composite worked better as compared to conventional (∼40 to 50 wt.%) fillers with no detrimental impact on the mechanical properties.

Nano fillers in composite improved the flame retardancy of PDMS by forming a protective layer of ceramization and charring.[42, 43] The layer hindered the release of smoke and gas formed in the solid phase.[44] The exfoliated structure of nano fillers may limit the oxygen diffusion inside the nano composite. Bi_2O_3 nano fillers supported with positive effects in flame retardancy. It changed PDMS composite to a more oxidised more stable phase at high temperature. The steric effect may possible with nano fillers. More effective char production during thermal decomposition of polymer nano composites may be due to chemical interactions between PDMS and nano fillers during thermal degradation.

4. CONCLUSION

Different carbon and Bi_2O_3 nano fillers influence PDMS composite fire retardancy properties such as TTI, PHRR, total smoke release, and smoke density. Lower concentration (1 and 3 wt.%) of fillers in composite assures to keep the polymeric properties intact with cost effectiveness. MWCNT significantly increased the flame retardant properties of the PDMS composite, particularly in TTI. A major effect influencing the TTI properties of PDMS was thermal inertia. It is the product of specific heat capacity, particle density, and thermal conductivity. Carbon based nano fillers acted as barriers against gas flow and oxygen diffusion at the condensed phase. Bi_2O_3 nano particles can be a good choice to replace the conventional and toxic inorganic fillers where higher TTI values are expected. However, Bi_2O_3 nano fillers composite has highest smoke release rate with high PHRR value than other carbon based nano fillers.

Figure 5. Effect of nano fillers in composites on specific extinction area.

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