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Study of the fire resistant behavior of unfilled and carbon nanofibers reinforced polybenzimidazole coating for structural applications

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With increasing interest in epoxy-based carbon fiber composites for structural applications, it is important to improve the fire resistant properties of these materials. The fire resistant performance of these materials can be improved either by using high performance epoxy resin for manufacturing carbon fiber composite or by protecting the previously used epoxy-based composite with some fire resistant coating. In this context, work is carried out to evaluate the fire resistance performance of recently emerged high performance polybenzimidazole (PBI) when used as a coating material. Furthermore, the effect of carbon nanofibers (CNFs) on fire resistant properties of inherently flame retardant PBI coating was studied. Thermogravimetric analysis of carbon/epoxy composite, unfilled PBI and nano-filled PBI shows that the carbon/epoxy composite maintained its thermal stability up to a temperature of 400°C and afterwards showed a large decrease in mass, while both unfilled PBI and nano-filled PBI have shown thermal stability up to a temperature of 575°C corresponding to only 11% weight loss. Cone calorimeter test results show that unfilled PBI coating did not improve the fire retardant performance of carbon/epoxy composite. Conversely, nano-filled PBI coating has shown a significant improvement in fire retardant performance of the carbon/epoxy composite in terms of increased ignition time, reduced average and peak heat release rate and reduced smoke and carbon monoxide emission. These results indicate that addition of carbon nanofibers to inherently flame retardant coating can significantly be helpful for improving the fire resistance performance of composite materials even with low coating thickness.

Keywords: structural composite; fire resistant coating; carbon nanofibers

INTRODUCTION

The use of polymer-based composite materials is becoming significantly popular. They have an impressive and diverse range of applications in automotive, aviation, spacecraft, civil infrastructure and sports industries.[1–4] There has been a steady increase in the use of composite materials in both military and commercial aircraft. The weight percent of composite has increased to 50% in the newly developed Boeing 787 and A380 passenger aircraft.[3,5–7] The increasing interest in the use of composite materials is due to many advantages of composites materials over metallic materials. Some of these include high strength to weight ratio, good fatigue endurance, outstanding thermal insulation and low thermal expansion. However, there are some disadvantages of composite materials and these include poor impact damage resistance and poor performance under fire.[3] Although polymer-based composites are flammable at lower temperatures than aluminum, these materials possess some inherently useful properties which are not characteristic of metals. The rate of heat conduction of composite materials is much lower than that of metals [3]. The low heat conduction rate is significantly beneficial in slowing the rate of fire spread.

With increasing interest in polymer-based composite materials for structural applications, it is important to improve the fire resistant properties of carbon/epoxy-based composite materials. In this context, the objective of this study is to improve the fire retardant performance of currently used carbon/epoxy-based composite materials by utilizing polybenzimidazole (PBI) coating material. PBI is a heterocyclic thermoplastic polymer which exhibits the highest glass transition temperature T_g (425°C) of any commercially available organic polymer.[8] Due to its superior non-flammability, PBI has been used for firefighters' protective clothing, high-temperature gloves and astronaut flight suits.[9–12] These properties of PBI indicate its potential to be used as fire retardant coating. However, the potential of polybenzimidazole (PBI) as a fire resistant coating has not been

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explored yet. Therefore, present study will help to evaluate the performance of PBI as fire resistant coating.

In the past, many fire retardant studies were performed to improve the fire retardance of polymers and polymer-based composites by mixing the carbon nano-fillers into the resin, followed by the fire testing of specimens.[13–16] Improved fire retardance is observed due to the fact that polymers with carbon nano-fillers form a relatively uniform carbonaceous layer covering the entire sample surface without any cracks or gaps.[14] According to our knowledge, previous fire retardant studies were performed using commodity polymers to study the effect of nano-fillers on polymer flammability. However, the effect of these nano-fillers on the flammability properties of inherently flame retardant polymers has not been studied to date. Therefore, another objective of this work is to evaluate the performance of inherently flame retardant coating after adding carbon nanofibers (CNFs).

EXPERIMENTAL

Materials

Solution of polybenzimidazole (PBI) in N,N-Dimethylacetamide (DMAc) was supplied by PBI Performance Products. This solution was used as coating for carbon/epoxy composites. M21 epoxy-based unidirectional (UD) carbon fiber composite prepreg was supplied by Hexcel Corporation. Carbon nanofibers, with a diameter ranging from 70 nm to 200 nm and length ranging from 50 μm to 200 μm, were supplied by Pyrograf Products, Inc. with a trade name of PR-19-XT-LHT.

Preparation of composite laminates

Composite laminates with a thickness of 3.1 mm were prepared by stacking up 17 number of prepreg layers followed by curing in the autoclave. The laminate was cured in the autoclave by heating from room to 180°C at a heating rate of 5°C/min. During curing process, the pressure on the laminate was maintained at 7 bars. The laminate was held at 180°C and 7 bars for 2 h and afterwards, it was cooled down to room temperature at the rate of 5°C/min. At this point, the pressure was released and the laminate was removed from autoclave.

Plasma treatment of composite laminates

Composite surfaces were treated with atmospheric pressure plasma for better adhesion of coating with the composite laminate. Samples were plasma treated using TIGRES Plasma-BLASTER MEF equipment. The gas used for treatment was air at a pressure of 4.5 bars. Before performing the plasma treatment, the samples were first cleaned with methanol using ultrasonic cleaning to remove any contamination on the surface. After cleaning, the specimens were heated at 80°C under vacuum for 4 h to dry. The specimens were then placed under the atmospheric pressure plasma for surface treatment.

Contact angle measurement

Change in the surface energy after atmospheric pressure plasma treatment was determined in terms of contact angle value. A reduced value of contact angle indicates an improvement in surface energy of material which in turn improves the adhesion of the coating with the substrate.

Adhesion testing

Lap shear tests were performed to study the effect of atmospheric pressure plasma treatment on the adhesion properties of PBI. Specimens for lap shear testing were cut to the dimensions of $(100 \times 25 \times 3.1)\ \text{mm}^3$ and they were adhesively bonded for single lap shear tensile tests. Lap shear tests were performed at Zwick tensile testing machine using a test speed of 5 mm/min.

Preparation of PBI-coated samples

PBI solution was used as a coating material for composite laminates to produce a coating thickness of about 750–800 μm. Thickness of the coating was controlled using a doctor blade which has option of adjusting the thickness with screw gauges. Nano-filled PBI coating was prepared using 2 weight percent of carbon nanofibers (CNFs). CNFs were dispersed in PBI solution using bath sonication followed by mechanical stirring for 30 min. The mixture was then used as a coating material for composite laminates to produce a coating thickness of about 750–800 μm.

Thermogravemetric analysis (TGA)

Thermogravimetric analysis was used to characterize the thermal stability and decomposition of the unfilled PBI film, CNF-reinforced PBI film and carbon/epoxy composite. Analysis was performed using a Perkin Elmer Thermal Analysis Instrument. The mass of all the samples was maintained between 7 and 10 mg. The samples were heated in air from a temperature range of 25°C to 575°C at a heating rate of 10°C/min.

Cone calorimeter test

Cone calorimeter measurements were carried out on uncoated and PBI-coated UD carbon/epoxy composite laminates. Three samples for each material were cut to the dimensions of $100 \times 100\ \text{mm}^2$. Tests were performed using the standardized cone calorimeter procedure (ISO 5660). An external heat flux of $35\ \text{KW/m}^2$ was used to represent a well-ventilated, developing fire condition. Different fire properties including heat release rate (HRR), time to ignition (TTI), mass loss rate (MLR), CO and CO2 yield were measured.

RESULTS AND DISCUSSION

Thermogravimetric analysis (TGA)

TGA of epoxy-based UD carbon fiber composite, unfilled PBI and CNF-reinforced PBI was carried out to determine the thermal stability of all three materials in an oxidative environment. Figure 1 represents a comparison of thermal stability of three materials. Carbon/Epoxy composite has initially shown high thermal stability and only exhibits 2% mass loss by 350°C. Above this temperature, carbon/epoxy composite starts to show mass loss and a sharp decline in mass around 400°C is evident. Carbon/epoxy composite shows a mass loss of about 27% at 575°C. Almost all the epoxy resin decomposed up to this temperature and only carbon fibers are left in the residue. A sharp decline in the mass of carbon/epoxy composite around 400°C shows that epoxy resin starts to degrade quickly around this temperature. Therefore, the objective of this work is to provide a way which can prevent or delay the thermal degradation

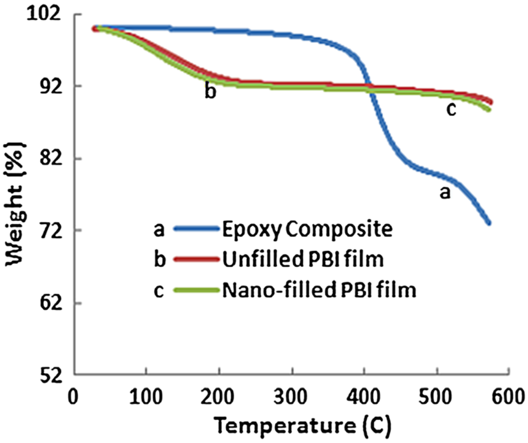

Figure 1. Comparison of thermal stability of carbon/epoxy composite, unfilled and Nano-filled PBI.

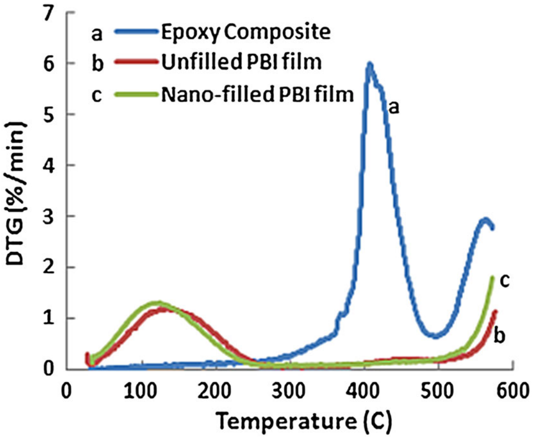

Figure 2. Comparison of mass loss rate of carbon/epoxy composite, unfilled and Nano-filled PBI.

of epoxy resin in carbon/epoxy composites at higher temperatures so that structural properties can be maintained for longer time.

The mass loss curves for unfilled PBI film and CNF-reinforced PBI film are shown in Fig. 1. Both unfilled and nano-filled PBI show initial mass loss around 70°C. This loss in mass continues up to a temperature of 200°C. The mass loss up to this temperature for both unfilled and nano-filled PBI is about 7.5%. This mass loss is due to evaporation of water present in the film. This fact is confirmed by drying the PBI film in the vacuum oven and then exposing it back to the ambient conditions. The coating again has shown similar gain in mass after exposure to the ambient conditions. After first degradation step, both unfilled PBI and nano-filled PBI films show a stable plateau and they exhibit a total of 11% mass loss up to a temperature of 575°C which is an indication of high thermal stability of PBI in air. PBI reinforced with carbon nanofibers shows a similar mass loss curve. However, carbon nanofibers are expected to improve the fire retardance properties of PBI through forming a stable char layer as studied by other researchers.[13–16] Both unfilled and nano-filled PBI show a high thermal stability and char yield as compared to epoxy resin and PBI does not show a sharp decline in mass which is evident for carbon/epoxy sample around 425°C. The high thermal stability of PBI is due to the presence of aromatic and heterocyclic rings in the backbone of the polymer chain [17].

Mass loss rate (MLR) is another important parameter to evaluate the response of a material during a fire. MLR of a material gives an indication of the rate at which fuel is supplied to the fire. The temperature at which significant mass loss occurs during decomposition in air provides information about the ignition temperature of the polymer.[18] A comparison of MLR of the three materials is shown in Fig. 2. The figure shows that the carbon/epoxy composite exhibits a very low MLR up to a temperature 350°C. Beyond 350°C, an increase in MLR is evident. The carbon/epoxy composite shows a peak in MLR around 400°C which is an indication that this composite reached its ignition temperature. This is the same temperature where a large decrease in the mass is evident in the TGA curve of carbon/epoxy composite. In comparison, PBI shows a small initial peak in MLR which is due to the evaporation of water, mentioned previously, and then remains stable and shows no further peak in MLR up to 575°C.

Atmospheric pressure plasma treatment of composite laminates and contact angle measurements

Very often, composite materials do not possess the surface properties needed to achieve better adhesion of the coating. Atmospheric pressure plasma treatment (APPT) is an efficient dry surface treatment method which offers a way to improve the surface energy of polymer-based composite.[19] APPT induces chemical changes at the surface of these materials. These chemical changes result in increased concentration of polar groups on the surface, thus increasing the polar component of the surface energy.[20] Motivated by these facts, APPT was used in the current study to improve the surface energy of carbon/epoxy composite. Change in surface energy was determined in terms of contact angle. Contact angle of water on composite surface was taken before and after the plasma treatment. Results show that APPT has reduced the contact angle of water on the carbon/epoxy composite surface from 72° to 17°. This decrease in contact angle has ultimately increased the surface energy of the material and hence increased the surface wetting.

Adhesion testing

Single lap shear tests were performed to study the effect of APPT on the adhesion properties of PBI. Lap shear tests for untreated and atmospheric pressure plasma-treated PBI adhesive bonded joints were performed. A comparison of lap shear strength of bonded joints of untreated and plasma-treated composite substrate is shown in Fig. 3. Results in Fig. 3 indicate that untreated carbon/composite has shown lap shear strength of about 5 MPa. After performing the atmospheric pressure plasma treatment on carbon/epoxy composite, lap shear strength increased from 5 MPa to 18 MPa – an improvement of about 250%. This increase in joint strength shows the effectiveness of performing APPT prior to the application of the coating material on composite surface. SEM micrographs of fractured joints of untreated and plasma-treated composite are shown in Fig. 4. The micrographs show that APPT has changed the mode of failure from adhesive to cohesive which further strengthens the effectiveness of using APPT.

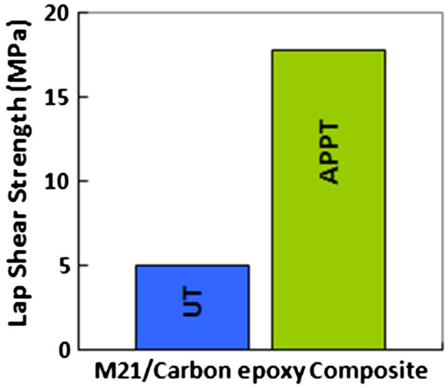

Figure 3. Lap shear strength of untreated and atmospheric pressure plasma treated composite bonded joints.

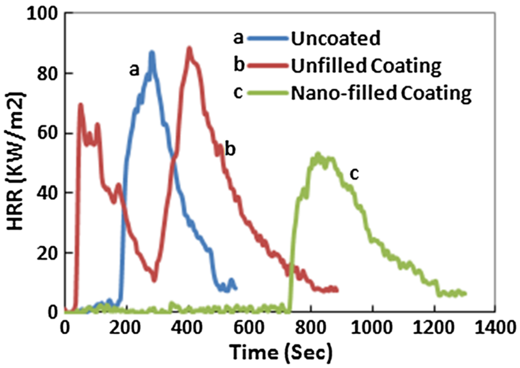

Figure 5. HRR of uncoated epoxy composite and composite with unfilled and nano-filled PBI coating.

Cone calorimeter test results

Heat release rates

A comparison of heat release rates (HRR) of uncoated carbon/epoxy composite and composite samples coated with unfilled and nano-filled PBI is shown in Fig. 5. There is an initial delay in the time to ignition for uncoated and PBI-coated epoxy composites. During this period, the material does not release any heat because the temperature of the material is below the pyrolysis temperature of the organic resin. When comparing the HRR curve of uncoated epoxy composite and composite with unfilled PBI coating, it can be observed that time to ignition (TTI) of uncoated epoxy composite is longer. The possible explanation of a shorter ignition time of carbon/epoxy composite with unfilled PBI coating is that PBI coating has a very low thickness compared to the carbon/epoxy composite underneath and also being on the surface, most of heat is absorbed by the PBI coating during the initial stages, and the coating quickly reaches its ignition temperature. Once ignition is sustained, there is a rapid increase in heat release rate, due to the combustion of organic material. At a certain point, the material releases maximum heat and then HRR starts to decrease. This maximum heat release rate is the peak HRR (PHRR) of the material. The uncoated composite showed a PHRR rate at 285 s. Unlike the carbon/epoxy samples without a coating, which show only one clearly defined peak heat release rate, samples with unfilled PBI coating show two HRR peaks. The first peak appears at 50 s after ignition and then there is a decline in HRR followed by another peak at 405 s, prior to the end of burning. This is characteristic of some thermally thick charring materials which show a HRR peak at the beginning until a thick char layer is formed which results in a decrease of HRR.[21] The occurrence of second peak could be attributed to the cracking of the char layer near the end of combustion process. However, this only applies if the material is homogenous, without any coating. In this study, the HRR curve of the composite sample with a thin unfilled PBI coating (compared to the epoxy/composite) absorbs most of the heat at the initial stages and quickly reaches the ignition temperature. Therefore, during the early stages, carbon/epoxy composite shows a peak in the HRR curve until char is formed which resulted in a decrease of HRR. The char formation also delays the decomposition of the underlying epoxy/composite. Once the underlying epoxy/composite reaches its ignition temperature, it burns with a similar HRR curve to the uncoated carbon/epoxy composite. However, the exact burning mechanism of the carbon/epoxy composite with unfilled PBI coating can be understood if the cone calorimeter is stopped at point of interest and then a visual inspection followed by mechanical testing is performed. A future work is planned to understand the burning mechanism of carbon/epoxy composite coated with unfilled PBI by performing the cone calorimeter test with different time intervals. Furthermore, fire resistant testing of PBI coating at different heat fluxes will also be the part of future work.

A comparison of different fire retardant properties of uncoated and PBI-coated carbon/epoxy composite is given in Table 1. Unfilled PBI coating did not improve the fire performance of

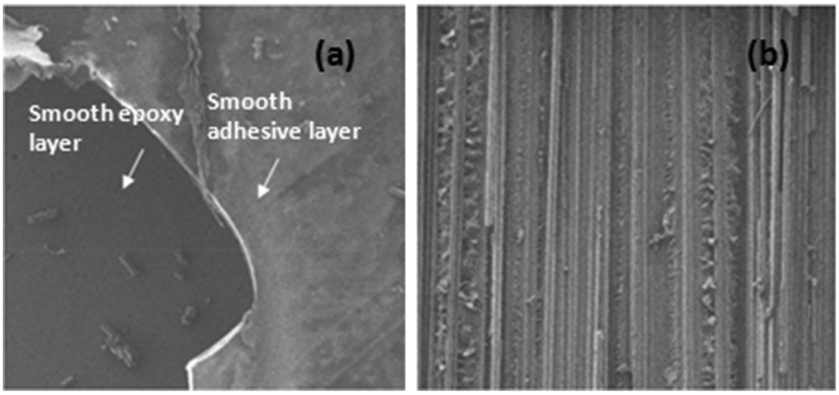

Figure 4. SEM micrographs of failed composite bonded joints before and after performing atmospheric pressure plasma treatment

Table 1. Comparison of fire resistant properties of uncoated and coated composite

Material	TTI[a] (s)	HRR^{a}_{300}[b] (KW/m^2)	HRR^{a}_{avg} (KW/m^2)	PHRR[a] (KW/m^2)	TTPHRR[a] (s)	THR^{a}_{300} (MJ/m^2)
Uncoated composite	165	27	28.51	86.98	285	8.03
Composite with unfilled coating	35	32.38	34.15	88.31	405	9.83
Composite with nano-filled coating	730	0.677	11.92	52.9	820	0.206

[a] TTI: Time to ignition, HHR_{avg}: Average heat release rate, PHRR: Peak heat release rate, TTPHRR: Time to peak heat release rate, THRR: Total heat release rate,
[b] Average for first 300 s

carbon/epoxy composite in terms of HRR, PHRR, THR and TTI. The reason of high values of HRR and PHRR with unfilled PBI coating is the low thickness (0.8 mm) of PBI coating.[3] The coating is thinner than many fire protective coatings which are commercially available,[22] including those of phenolic resins, which are well known for their outstanding fire retardant properties. These phenolic coatings do not perform well when applied as thin coating, demonstrating that even the inherently flame retardant materials are ineffective as thin fire protective barriers. Previous research shows that both thickness and thermal conductivity of a material have a great effect on fire retardant properties.[23,24] The performance of the PBI coating could be improved either by increasing the thickness of the PBI coating layer or by addition of a nano-filler. An objective of this study was to improve the fire resistant performance of the carbon/epoxy composite without adding any additional weight. Increasing the thickness of the coating increases its structural weight. Adding CNFs to the PBI coating improves its performance without adversely increasing its weight. The improved fire properties of CNF-reinforced polymers in previous work [13–16] motivated the author to evaluate the potential of CNFs with inherently flame retardant PBI polymer.

As expected, addition of 2% carbon nanofibers (CNF) to PBI coating shows a remarkable improvement in the fire resistant properties of underlying carbon/epoxy composite in terms of TTI, HRR and PHRR. Nano-filled PBI coating increases the TTI of the coated composite from 195 s to 730 s, giving a TTI which is three times longer. Dispersion of CNFs within PBI coating also reduced the heat release rate (HRR) which demonstrates the effectiveness of adding CNFs to PBI. The average HRR for the composite with nano-filled PBI coating, for first 300 s, is only 0.67 kW/m^2 which is almost negligible when compared to the average HRR_{300} of 27 kW/m^2 for uncoated epoxy composite. The composite with nano-filled PBI coating has also the lowest PHRR of the three materials and takes the maximum time to reach its PHRR value. The main reason for the improved performance of the nano-filled PBI coating is the formation of an effective char layer which acts as a barrier for the epoxy composite.

Digital photographs of uncoated and coated composites after fire testing are shown in Fig. 6. It can be observed that there is no char formed during the combustion of uncoated epoxy composite which means that the combustion process takes place in the form of boiling which led to the evaporation of the resin present in epoxy composite. On the other hand, a thick char layer is formed with both unfilled and nano-filled PBI coatings. However, the char layer formed with the unfilled PBI coating did not act as a shield for the underlying polymer and heat passed through quickly and decomposed the epoxy resin below. In contrast to unfilled PBI coating, a thick stable char layer is formed with nano-filled PBI coating which worked as a heat barrier for a longer period of time and thus the material showed a low HRR. Therefore, it is important that a continuous network structured layer is formed without the formation of cracks which can compromise the effectiveness of the char layer.

Total mass loss and mass loss rate in cone calorimeter test

Total mass loss (TML) and mass loss rate (MLR) of a polymer during fire show the extent to which a polymer decomposed and subsequent combustible volatiles added to the fire. A comparison of TML of the uncoated and coated samples is presented in Table 2. Results in Table 2 show that the carbon/epoxy composite with unfilled PBI coating and with nano-filled PBI coating has a higher TML during fire testing. The reason for this higher mass loss is because of higher resin content of the coated samples. As a result, more fuel was available to the fire which resulted in greater mass loss. However, we also have to

Figure 6. Digital photographs of three samples after fire testing (a) Uncoated composite (b) composite with unfilled coating (c) Composite with nano-filled coating.

Table 2. Comparison of total mass loss and average mass loss rate of uncoated and coated samples

Materials	TML (%)	Average MLR (g/s)
Uncoated carbon/ epoxy composite	17.35	0.020
Composite with unfilled coating	27.80	0.023
Composite with nano-filled coating	25.35	0.01

consider the fact that the mass loss of materials with nano-filled PBI coating occurred over a longer period. Therefore, it is important to also consider the MLR of different materials when comparing the TML of different materials.

A comparison of MLR for uncoated and coated samples is also presented in Table 2. Table 2 shows that both uncoated composite and the composite with unfilled PBI coating have shown almost same average MLR. In contrast to the unfilled PBI coating, the nano-filled PBI coating has reduced the average MLR by about 50%. The reason for a reduced average MLR with the nano-filled coating is the formation of a continuous char layer on the surface which has reduced the flow of heat deep into the specimen and ultimately slowed down the MLR. Hence, a continuous thick char layer with the nano-filled PBI coating worked well as compared to the char formed by the uncoated PBI with many cracks. Formation of cracks reduces the effectivenss of char.

Smoke and gas emission

A comparison of specific extinction area (SEA), average CO emission and average rate of CO emission for the uncoated carbon/epoxy composite and the coated composite is presented in Table 3. The values given in the table are averaged over the entire test duration. Table 3 shows that the unfilled PBI coating has a reduced value of SEA as compared to the uncoated composite which means that the unfilled PBI coating with a surface char layer has reduced the smoke emission to some extent. Better results are obtained with a nano-filled PBI coating. Nano-filled PBI coating with a continuous char layer has reduced the smoke emission to greater extent. Results in Table 3 show that samples with unfilled PBI coating show a 10% decrease in smoke emission whereas samples with a nano-filled PBI coating show a 70% reduction in smoke emission which is a significant improvement in the material performance in terms of smoke emission. The type and amount of gaseous products released by different organic materials during a fire can vary but all materials release CO and CO_2 on decomposition. CO yield is important because inhalation of CO is a major cause of death in fires.[25]

Table 3. Comparison of SEA, CO emission and CO emission rate of uncoated and coated samples

Material	SEA_{Avg}[a]. (m2/kg)	$CO_{Avg.}$ (g/g)	$CO_{Avg.}$ (g/s)
Uncoated carbon/ epoxy composite	429	0.0074	0.000363
Composite with unfilled PBI coating	394	0.0118	0.000464
Composite with nano-filled coating	126	0.0020	0.000140

[a]Average values for test duration

A comparison of average CO yield and the rate at which CO is evolved is given in Table 3. Results show that with unfilled PBI coating, a higher yield of CO is present when compared to the uncoated carbon/epoxy composite. On the other hand, nano-filled PBI coating reduces the yield of CO from 0.0074 (g/g) to 0.0020 (g/g); an improvement of about four times in terms of reduced CO emission. This is another significance of using nano-filled PBI coating material.

CONCLUSIONS

The purpose of this study was to improve the fire resistance of epoxy-based carbon fiber composite with unfilled and nano-filled PBI coatings. TGA results revealed that epoxy resin in the carbon/epoxy composite exhibited a large decrease in mass around 400°C and is totally decomposed at 550°C. Conversely, both unfilled and nano-filled PBI have shown high thermal stability even up to 575°C where only 11% mass loss occurred up to this temperature.

Cone calorimeter results show that the unfilled PBI coating could not improve the fire retardant properties of the carbon/epoxy composite. Contrary to unfilled PBI coating, carbon nanofiber-reinforced PBI coating showed a significant improvement in the fire retardant properties of the carbon/epoxy composite. Nano-filled PBI coating has reduced the average HRR of carbon/epoxy composite from 29 kW/m^2 to 12 kW/m^2; a reduction of about 60%. Nano-filled PBI coating has also reduced the peak HRR from 87 kW/m^2 to 53 kW/m^2; a reduction of about 40%. These results indicate that the performance of carbon/epoxy composite with PBI nano-filled coating has improved significantly.

The results of smoke and gas emission during fire testing reveal that nano-filled PBI coating has reduced the smoke and CO emissions up to 73% when compared to the uncoated carbon/epoxy composite. Hence, a significant outcome of this work is that carbon nanofibers, even when present in very small quantities, can be more effective in improving the fire performance of an inherently flame retardant material. Furthermore, addition of carbon nanofibers to inherently flame retardant coating material has significantly improved the composite fire resistance performance even with small coating thickness which is another outcome of this work.

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