

Effects of introducing bamboo charcoal on thermo-physical properties and combustion behavior of poly(ethylene terephthalate)

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Abstract The thermo-physical properties and combustion behavior of poly(ethylene terephthalate) (PET) composite formulations that contain bamboo charcoal (BC) fillers are studied. The experimental results showed that the volume resistance decreased sharply but with little effect on thermal conductivity, when PET was loaded with more than bamboo charcoal. Thermogravimetric analysis (TGA) revealed that higher bamboo charcoal loading was associated with a higher onset temperature of 50% degradation ($T_{d50\%}$). The SEM images and filter test results showed a strong coupling effect between bamboo charcoal and PET and uniform dispersion of bamboo charcoal in a PET matrix. A flammability test was performed using cone calorimetry, and 3 wt% bamboo charcoal filler in PET was found to give the best flame retardancy and the most effective smoke suppression. The rheological properties of dynamic viscosity, modulus and yield stress revealed that a higher bamboo charcoal loading was associated with greater shear thinning and thus viscosity at higher frequencies.

Keywords Bamboo charcoal · Poly(ethylene terephthalate) (PET) · Dispersion · Rheology · Flammability

Introduction

Polyethylene terephthalate (PET), one of the most important polyester resins, has been widely exploited because of its excellent mechanical and electrical characteristics in chemical resistance and heat resistance. PET is extensively used in textiles, industrial yarns, fibers, injection molding and soft drinks. The properties of PET are improved by incorporating inorganic fillers, such as silica, glass fibers or clay into the PET matrix to form PET composite. PET composites are widely used in automobile, household appliances, and electrical devices, for example [1–4].

Bamboo charcoal (BC), mainly bamboo, has been utilized for many years in every day life. In Taiwan, the several available kinds of bamboo include Moso bamboo, Makino bamboo, thorny bamboo, Ma bamboo, long-shoot bamboo and others. Generally, bamboo charcoal that is made from three to five year-old bamboo and carbonized at temperatures in the range 600~800 °C, has innumerable holes crosswise in its structure and an inner surface area up to 300 m²/g. Bamboo charcoal is widely used in humidity-controlling substances, the deodorization of gases, the treatment of water and the carrying of catalysts. Bamboo charcoal is also adopted as a functional additive in textiles and polymer owing to its mechanical, thermal and electric conductivity [5–8].

Recently, organic-inorganic hybrid materials have attracted considerable interest because of their unique hybrid properties, which are difficult to obtain from very few individual sources exhibit. This investigation explores the thermo-physical properties, rheological properties and combustion behavior characteristics of PET composite with different loadings of bamboo charcoal. PET composite is formed using a compounding technique. To disperse

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bamboo charcoal in PET, a milling method and a compatible agent were used. Scanning electron microscope (SEM) images and measurements of change in pressure associated with time provide useful data on the fiber spinning of functional PET filaments that contain bamboo charcoal.

Experimental

Raw materials

Poly(ethylene terephthalate) (PET) (intrinsic viscosity=0.8) resin was supplied by Nan Ya Plastics and dried at 130 °C for 4 h. The bamboo charcoal (BC) was Moso bamboo from Chiayi County in Taiwan, prepared by the carbonization of bamboo (at a carbonization temperature of around 700~750 °C), following by crushing and sieving to form micro-powder with a mean particle size of approximately 3.8 µm. The anionic surfactant, isobutene-maleic anhydride copolymer, was supplied by Pleasant and Best Chemical Co., Ltd. The wetting agent, polyoxyethylenated alcohol ethoxylates, was supplied by Evonik Tego Chemie GmbH. The compatible agent (wax), which was partially saponified ester wax, was supplied by Clariant.

Preparation of sub-micrometer bamboo charcoal slurry

The milling machine DRAIS Perl Mill PML 1.5 H/V from Buhler corp, was used to prepare a sub-micrometer powder. The bamboo charcoal slurry was prepared using bamboo charcoal powder, anionic surfactant, wetting agent and water. The slurry was milled until the average particle size of the bamboo charcoal was 268.3 nm and no cohesion was observed.

Preparation of PET/BC composites

First, the bamboo charcoal slurry was mixed with a compatible agent and then mixed with PET until the mixture appeared uniform. The mixture was put into the mechanical granulating machine at 105 °C for 30 min in a vacuum, and then melt-extruded at 240~270 °C using a twin-screw extruder. The extruded strand was cooled using a warm water (40 °C) bath and pelletized to form PET/BC composites. The PET composites that were loaded with various amounts of bamboo charcoal (1%, 3%, 5%, 10%, and 15% wt.) were denoted PET-X.

The PET/BC composites were dried at 105 °C for 48 h, and then compression-molded into 2 mm thick square plates of area 100×100 mm, or into circular disks (25 mm in diameter) at 100 kg/cm² for 1 hr at 285 °C.

Volume electric resistance

The resistances of PET/BC composites were measured using a Tokyo Electric Co. Volume Resistance Tester (SME-8000). Volume electric resistance values were as averages of three measurements.

Thermal conductivity

The thermal conductivities of PET/BC composites were measured using a Hot Disk TPS 2500. The specimens were disks with a diameter of $D=25.0$ mm and a thickness of 4 mm.

Thermal stability

TGA studies of the thermal stability of PET/BC composites, were performed using a TA Instrument (TGA Q-50), as the samples were heated from 20 to 600 °C at a rate of 10 °C/min in air or nitrogen (60 ml/min). The mass of each sample was about 10 mg.

Filter test

Delta pressure data were measured using a single-screw extruder with a filter die (Thermo Haake Rheomex252p). Its L/D ratio was 25 and the filter comprised four layers nonwoven structure, of thicknesses contained 800 µm, 260 µm, 100 µm and 40 µm. Before the filter test was carried out, the extruded pellets were dried at 105 °C for 4 h. The process was conducted using a barrel temperature of 285 °C and a screw speed of 150 rpm/min.

Scanning electron microscope (SEM)

The morphologies of PET-X were investigated by SEM (JEOL JSM 6510 FE-SEM).

Cone calorimeter testing

The cone calorimeter (Atlas Cone 2) was used to evaluate the flame retardancy of a material under an external heat flux of 50 kW/m², according to ASTM D2863/77. The tested composites were compression-molded into plates of 100×100×2 mm³. The heat release rate (HRR), time to ignition (TTI), and other parameters were measured simultaneously.

Rheological characterization

Rheological data were obtained using an Advanced Rheometrics Expansion System (ARES). A controlled rate spectrometer, equipped with a 200/2000 gcm dual range force rebalance transducer, was adopted in the dynamic tests along with parallel-plates with a diameter of 25 mm.

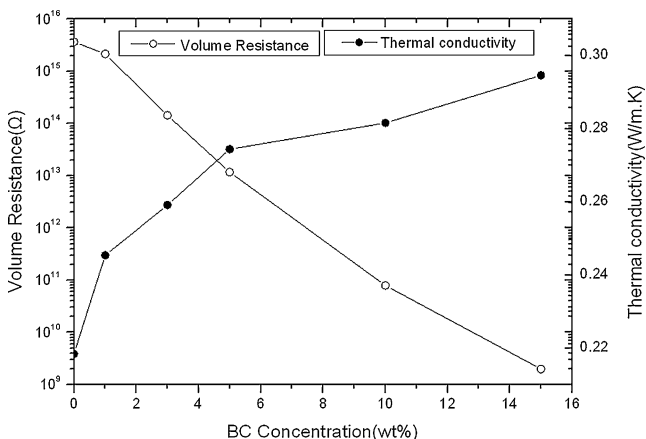
Table 1 Volume electric resistance and thermal conductivity of PET and PET-X

Sample Code	Volume resistance (Ω)	Coef of thermal conductivity(W/mK)
Pristine PET	3.63×10^{15}	0.2184
PET-1	2.15×10^{15}	0.2454
PET-3	1.43×10^{14}	0.2591
PET-5	1.17×10^{13}	0.2744
PET-10	7.89×10^{10}	0.2816
PET-15	1.98×10^9	0.2946

Result and discussion

Physical properties

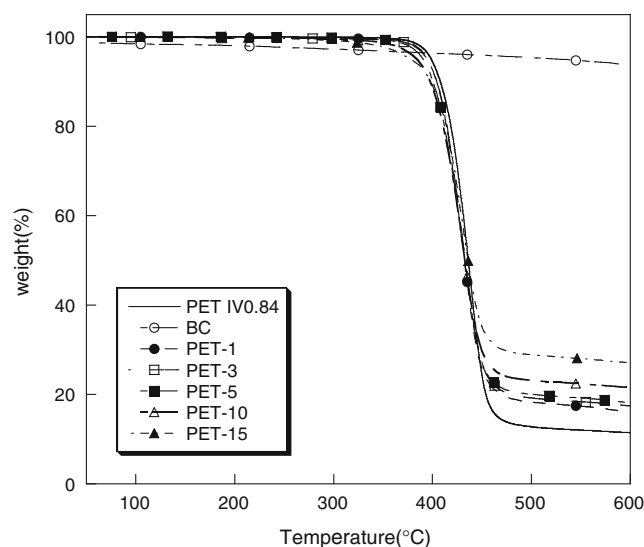
Table 1 and Fig. 1 plot the volume electric resistance and thermal conductivity of PET composites, influenced by the various loadings of versus loading of bamboo charcoal. The literature has established that the volume electric resistance of bamboo charcoal decreases as the carbonizing temperature of the bamboo charcoal increases, and the volume resistance of bamboo charcoal that is carbonized at 700 °C is 10^4 – $10^5 \Omega$ [9]. As shown in the Table 1 and Fig. 1, the volume electric resistance of PET composites declined sharply at an additive level of 3 wt%, and the thermal conductivity of PET composites increased slightly with the amount of bamboo charcoal additive. The thermal conductivity of PET composites was between 0.2946 and 0.2454, which values are similar to that for pristine PET. Li J et al. (2002) [10] found a thermal conductivity of a PET plastic film of 0.25 WmK^{-1} but in the present investigation, a 4 mm-thick pristine PET disk had a thermal conductivity of 0.2184 WmK^{-1} .

**Fig. 1** Plots of volume electric resistance and thermal conductivity versus bamboo charcoal concentration in PET

Thermal analysis

Thermal gravimetric analysis of pristine PET, bamboo charcoal powder and PET composite was conducted in a nitrogen or air atmosphere. As shown in Fig. 2, the pristine PET in the nitrogen atmosphere exhibited single-step degradation between temperatures of 428 and 481 °C, yielding approximately 11.44% (by weight) residue at 600 °C. The TGA curve of bamboo charcoal powder in the nitrogen atmosphere declined slightly as the temperature increased from 50 to 600 °C, and the powder yielded 93.46% residue at 600 °C. The small weight loss of bamboo charcoal observed in this temperature range was believed to be related to the evolution of incomplete carbonized residue or the absorption of water in the bamboo charcoal pore structure. PET/BC composites had higher char yield as than pristine PET at 600 °C. The residual weight of char from the PET/BC composites gradually increased with the amount of incorporated bamboo charcoal.

As shown in Fig. 3a, the thermo-oxidative degradation of pristine PET occurred in two consecutive steps. The first step was between 320 °C and 456 °C, which corresponded to the main degradation of the backbone and the formation of a char, with a weight loss of 81%. The second step was the thermo-oxidative of the char between 456 °C and 550 °C with loss of the remaining material. The residue detected at 600 °C was 0.2496% weight. The TGA curve of bamboo charcoal powder exhibited single-step degradation from 350 °C to 520 °C. The residue of bamboo charcoal that was detected at 600 °C was 2.765% weight, which significantly exceeded that of pristine PET. As shown in

**Fig. 2** Experimental TGA curves under nitrogen (10 °C/min) of PET, BC and PET-X

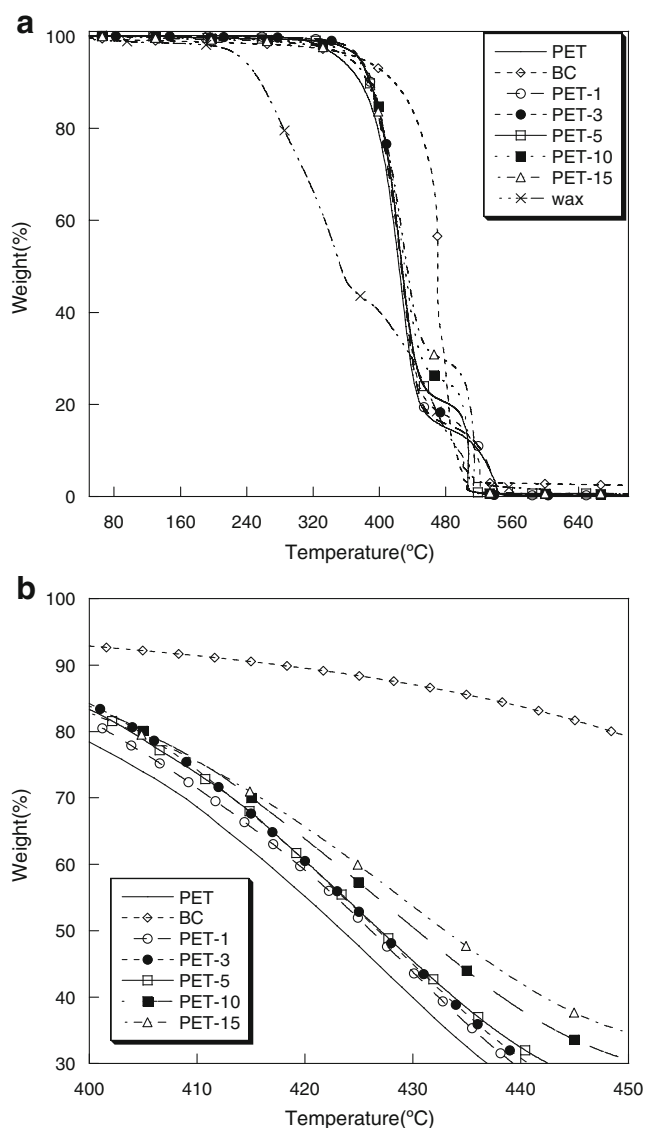


Fig. 3 **a** Experimental TGA curves under air(10 °C/min) of PET, BC and PET-X. **b** Zoom on the TGA curves under air(10 °C/min) of PET, BC and PET-X

Fig. 3b, the first step in the weight loss curve of PET composites gradually shifted to higher temperatures as the loading of bamboo charcoal in the composites increased. Table 2 compares the onset temperatures of 50% degradation ($T_{d50\%}$) with different amounts of bamboo charcoal in the PET composites. It reveals an increase in $T_{d50\%}$ with the amount of bamboo charcoal, and a related improvement in the thermal stability of PET.

Dispersion characteristics of PET/BC composites

Figure 4 shows SEM images of surface of PET that was blended with bamboo charcoal fillers and a compatible agent. SEM images reveal bamboo charcoal fillers in a

polymer matrix. Figure 4a, b, c, d display well-dispersed bamboo charcoal fillers in a PET matrix. The PET domains in PET-1, PET-3, PET-5 and PET-10 have a narrow size distribution, with an average particle size of 0.3~0.7 μm —evidence that milling and with a compatible agent for PET/bamboo charcoal blending is important in the dispersion of bamboo charcoal fillers in a PET matrix. However, Fig. 4(e) displays agglomerations of the compatible agent that is encapsulated in bamboo charcoal fillers in the PET matrix when the bamboo charcoal filler loading is 15 wt%. This effect is attributed to the insufficient shear stress but sufficiently long residence time to disperse the bamboo charcoal fillers, PET polymer and compatible agent.

Besides observing the surface morphology, performing a filter test is also effective in elucidating the dispersion of the bamboo charcoal fillers in PET matrix. Figure 5 displays results of the filter test on PET-X, with diluted 1% bamboo charcoal in PET chips at 285 °C. The initial (P_i) and final (P_f) pressures of the PET-X composites are obtained. The pressure of PET-1 rose from 40 bar to 43 bar; that of PET-3 rose from 44 bar to 48 bar; that of PET-5 rose from 45 bar to 48 bar; that of PET-10 rose from 44 bar to 46 bar, and that of PET-15 rose from 44 bar to 46 bar. All of the delta pressure values ($\Delta P = P_f - P_i$) are less than 5 bar. In general, a favorable delta pressure value for melt-spinning is less than 10 bars. A higher delta pressure indicates higher pack pressure when the fibers are spun. A low delta pressure value is associated with effective coupling and uniform dispersion of the bamboo charcoal particles in the PET matrix.

Flame retardancy

A cone calorimeter is one of the most effective bench-scale devices for determining the flammability properties of materials. The heat release rate (HRR), and in particular

Table 2 Thermogravimetric analysis of PET and PET-X

Sample code	in nitrogen		in air	
	residual at 600 °C		residual at 600 °C	
	$T_{d50\%}$	(%)	$T_{d50\%}$	(%)
Pristine PET	436.4	11.44	423.6	0.25
PET-1	432.7	15.95	426.1	0.26
PET-3	423.1	17.42	426.7	0.29
PET-5	432.6	18.07	427.0	0.50
PET-10	432.8	21.50	430.4	0.54
PET-15	435.9	27.11	433.0	0.68
BC	—	93.46	480.0	2.77

Fig. 4 SEM images of PET-X
a PET-1 **b** PET-3 **c** PET-5 **d**
PET-10 e PET-15

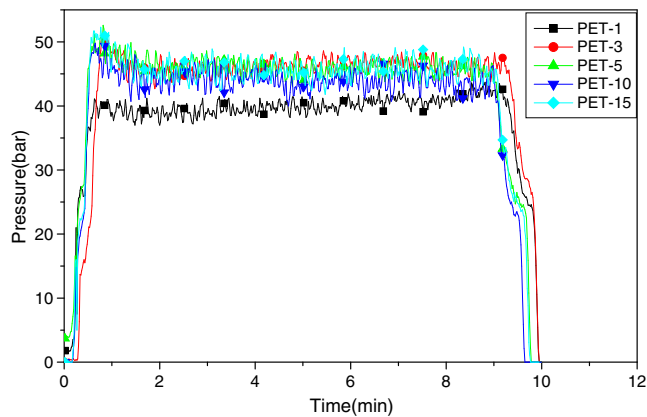
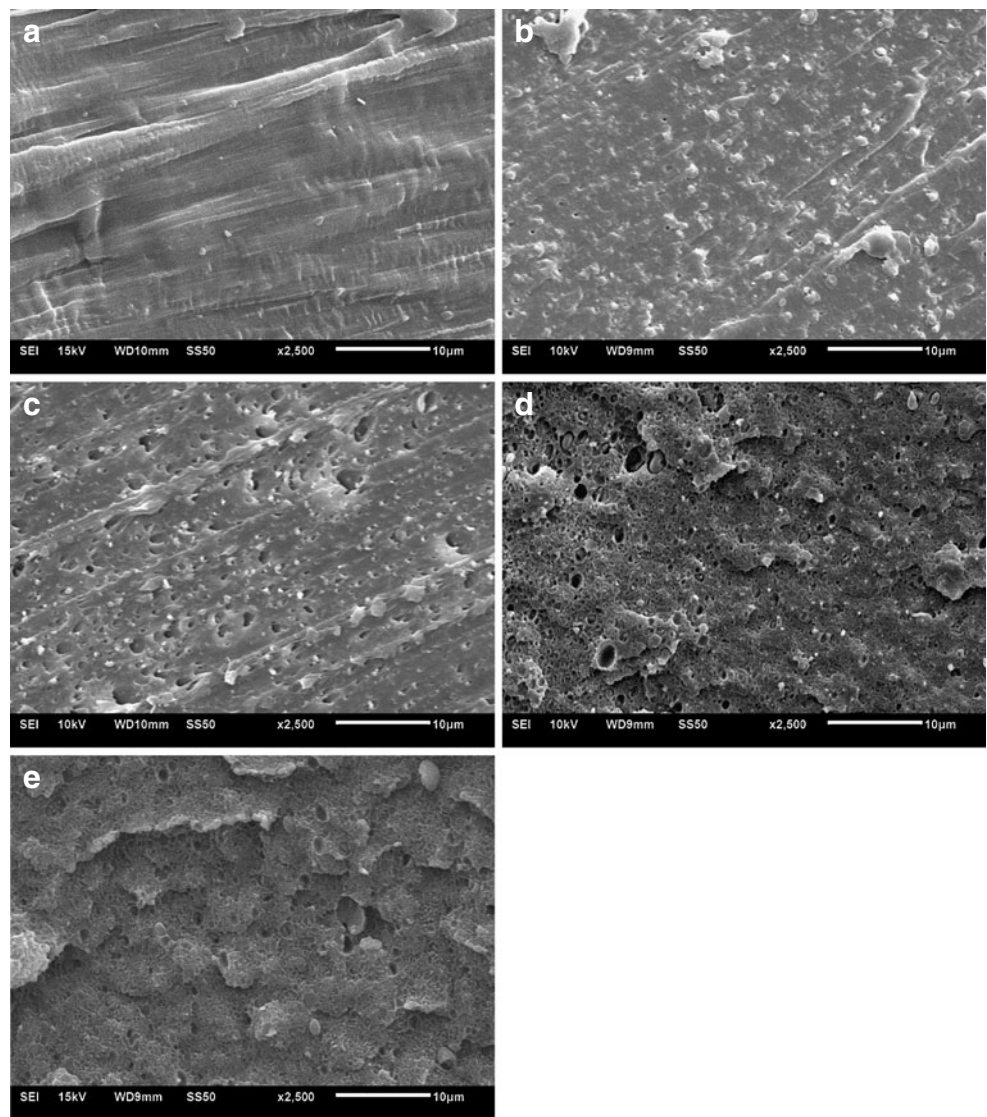


Fig. 5 Filter test result of PET-X dilute to 1% bamboo charcoal with PET chips at 285 °C

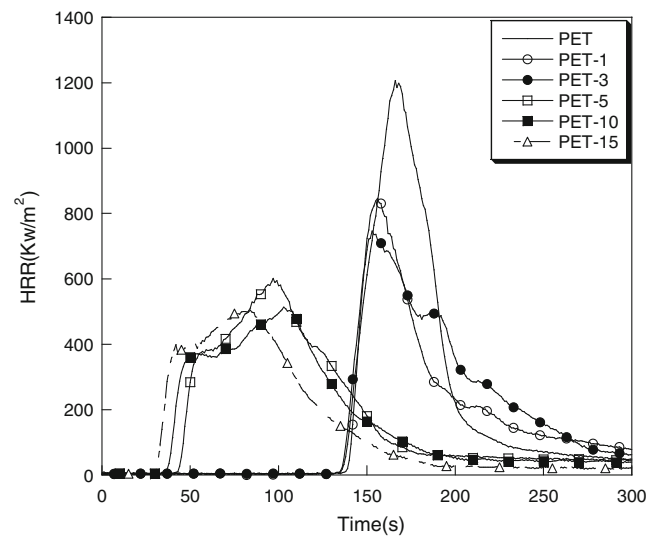


Fig. 6 Heat release rate (HRR) plots for PET and PET-X

Table 3 Cone calorimeter data for PET and PET-X (50 kW/m²)

Sample code	TTI. [sec.]	Peak HRR [kW/m ²]	FPI	Ave.SEA (m ² /kg)	SP (kW/kg)	Peak Ext Coef [m ⁻¹]
Pristine PET	144.0	1207.0	0.119	8.382	10117	8.59
PET-1	137.0	846.4	0.162	6.178	5229	6.83
PET-3	141.4	738.6	0.191	5.276	3937	6.87
PET-5	46.77	601.5	0.078	12.86	7735	6.09
PET-10	39.23	513.3	0.076	13.085	6717	4.88
PET-15	32.54	504.1	0.064	15.49	7810	4.22

the peak HRR, has been found to be the most important parameter in evaluating fire safety [11].

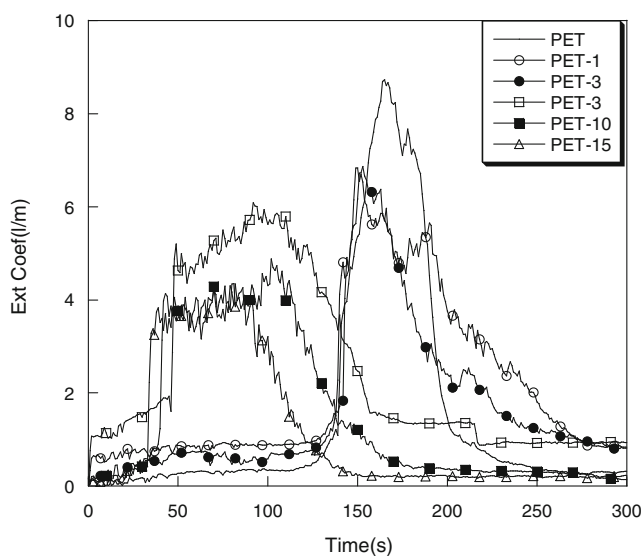
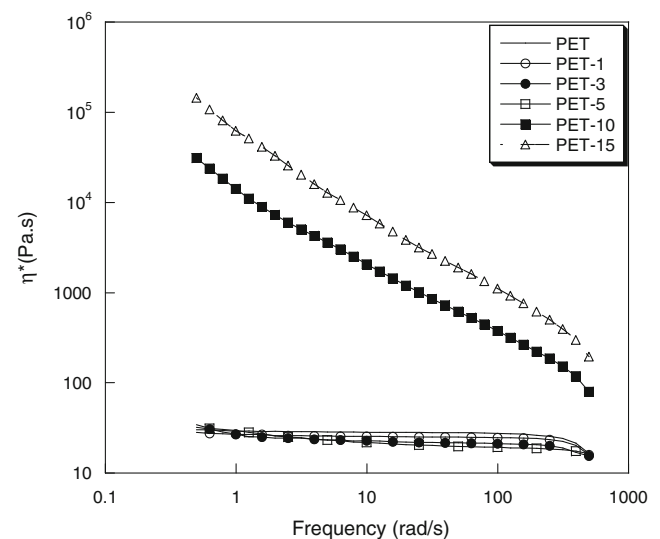
Figure 6 displays HRR data of PET and its composites (PET-X), obtained from a cone calorimetry test. Table 3 presents the cone calorimeter data for pristine PET and PET-X. Clearly, peak HRR of PET-X was lower than that of pristine PET. The PHRR of PET-X declined as the amount of bamboo charcoal increased. The peak HRRs of PET-X (with X=1, 3, 5, 10, 15 wt% of bamboo charcoal) were 30%, 39%, 50%, 57% and 58% lower than that of pristine PET, respectively.

Pristine PET needed 137 s to ignite at a heat flux of 50KW/m² and the times to ignition (TTI) of PET-X (X=1, 3, 5, 10 and 15 wt% of bamboo charcoal) were 140.9, 144.0, 46.8, 39.2 and 32.5 s, respectively. The TTIs of PET-1 and PET-3 were only slightly higher than those of non-filled PET. However, as the proportion of bamboo charcoal increased from 5 to 15 wt%, the PET-X exhibited a sharp decrease in ignition time. Increasing the amount of bamboo charcoal into PET composite simultaneously increased its compatible agent content; this agent was decomposed to volatile combustibles in the early stage of the experiment

and the decomposition contributed significantly to the reduction of ignition time.

Figure 7 displays smoke extinction coefficient plots of PET and its composites, obtained from the reduction of transmission of light from a helium-neon laser source by smoke. The peak extinction coefficients of PET and PET-X in Table 3 are lower than that of pristine PET and decreased as the bamboo charcoal content increased. We believe that this observation is related to submicron-pores in the bamboo charcoal, which has numerous submicron pores, which effectively trap soot particles and reduce the extinction coefficient.

A combination of combustion parameters reportedly provides information on the behavior of material in a real fire. For example, the fire performance index (FPI), which is the ratio between the TTI and the peak HRR, is commonly adopted to characterize the flame retardancy of materials [12–15]. The FPI is considered to be the best individual indicator of overall fire hazard. It relates to the “time to flashover” and specifies the time available to escape a full-scale fire. A material with a high FPI value is considered a better flame-retardant material. Table 3

**Fig. 7** Extinction coefficient (Ext. Coef) plots for PET and PET-X**Fig. 8** Complex viscosity plots for PET and PET-X at 285 °C

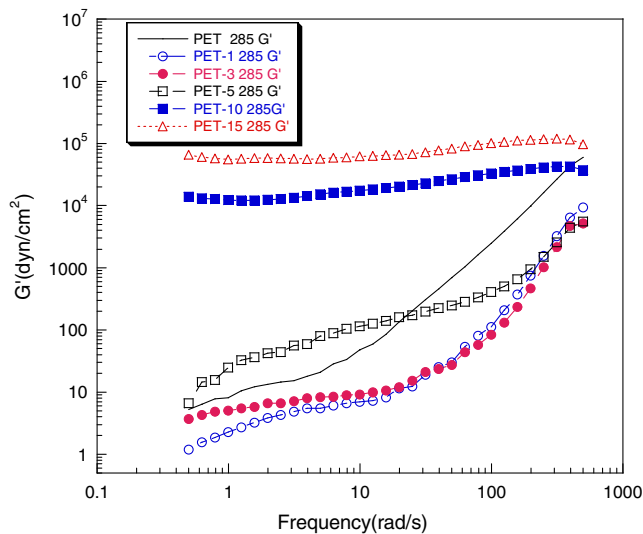


Fig. 9 Storage modulus plot for PET and PET-X at 285 °C

presents the effect of bamboo charcoal additive on the fire performance index (FPI) of pristine PET composites. Bamboo charcoal yielded optimal performance at 3 wt%, and further addition thereof worsened performance.

The smoke parameter (SP), which is the product of the average specific extinction area and the peak rate of heat release, is thought to give a more realistic indication of smoke hazard in a real fire situation [14–19]. Table 3 presents smoke parameter (SP) data for pristine PET and PET-X. These data reveal that bamboo charcoal is a very effective smoke suppressant in PET, with optimal performance again at 3 wt%.

Rheological properties

Because rheological data on molten PET/BC composites is important to the spinning process in the production of composite filaments, rheological tests were conducted at 285 °C. Figure 8 plots the variation of complex viscosity (η^*) of pristine PET and PET-X with bamboo charcoal content at 285 °C. Notably, pristine PET and PET-X with a bamboo charcoal loading of under 5 wt% exhibit Newtonian fluid behavior over most of the examined frequency range, and the magnitude of complex viscosity of PET composites decreases a little as the bamboo charcoal loading increases. However, when the loading is increased to 10 wt% and above, a high degree of relationship between shear thinning and complex viscosity is observed, the extent of which increases with the bamboo charcoal loading.

Figure 9 plots the storage modulus of PET and PET-X versus frequency. PET-5 (with 5 wt% bamboo charcoal loading) was the first in the series of composites to have a storage modulus that exceeded that of pristine PET at a frequency of less than 20 rad/s. For the PET composites that

had a bamboo charcoal loading of over 5 wt%, the storage modulus increased with the loading, and was almost constant over the frequency range of interest. The above rheological results suggest that PET-X with a bamboo charcoal loading of above 5 wt% forms some physical associations, which result in a solid-like structure.

The yield stress behavior for pristine PET and PET-X is determined from the Casson plot in Fig. 10:

$$G''^{1/2} = G_y'^{1/2} + K\omega^{1/2}$$

where G_y' denotes the yield stress and K is a constant. Pristine PET and PET-1 give a zero yield stress. Other composites have a non-zero positive value. In particular, with loading of 5 wt% or greater, the yield stress increased with bamboo charcoal content, suggesting that a content bamboo charcoal filler content that exceeds a critical value can significantly increase the heterogeneity of the composite, resulting in interconnections among the bamboo charcoal fillers. This result is consistent with the results of the aforementioned dynamic rheological tests.

Conclusion

Incorporating bamboo charcoal fillers into PET greatly improves its volume electric resistance, but the coefficient of thermal conductivity is slightly increased. This incorporation of bamboo charcoal fillers also increases the onset temperature of 50% degradation ($T_{d50\%}$) in a thermo-oxidative degradation test. The flammability properties of PET/BC composites found herein revealed that 3 wt% bamboo charcoal loading in PET gave the best flame retardancy and the most effective smoke suppress-

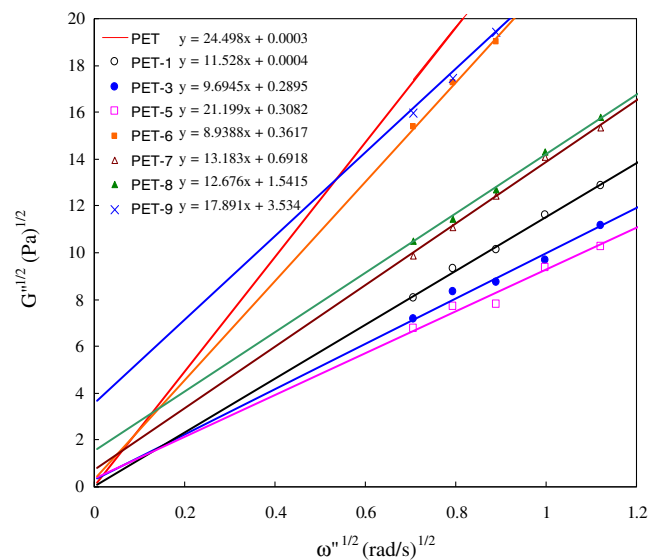


Fig. 10 Casson plot for PET and PET-X

sion. Rheological investigations of dynamic viscosity, modulus and yield stress suggested that the addition of more than a critical amount of bamboo charcoal particles significantly increases in viscosity by the formation of interconnections among the bamboo charcoal particles in the PET composites. Since high bamboo charcoal loading produced a high degree of shear thinning in the composites, their viscosity at high frequencies is close to that of pristine PET. SEM images and the filter test indicate effective coupling and uniform dispersion of various loads of bamboo charcoal in PET composite.

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