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Physical Properties of Polyolefin / Bamboo Charcoal Composites

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Abstract

The physical properties of two kinds of polyolefin / bamboo charcoal composites, based upon polypropylene (PP) and low density polyethylene (LDPE), were studied for varying levels of charcoal inclusion between 0 and 20 phr. A Brabender mixer and two-roll mill were used for the mixing process of both polyolefin and bamboo charcoal composites, followed by compression moulding of the homogeneous mixtures to form the composite materials. The tensile strength and Young's modulus were both found to increase, whilst the elongation at break decreased, in a dose-dependent manner with increasing bamboo charcoal content in the composite materials. The tensile strength of PP / bamboo charcoal composites was higher than that of the original PP, but the tensile strength of LDPE / bamboo charcoal composites was slightly lower than that of LDPE. In addition, the water absorption of both polyolefin / bamboo charcoal composite series were significantly higher than that of either original polyolefin. Finally, the electrical resistance of both polyolefin / bamboo charcoal composites decreased compared to that of pure PP and LDPE.

Key words : Polyolefin, Bamboo charcoal, Composite, Polypropylene, Polyethylene

Introduction

Polyolefins are some of the most widely used types of commercial polymers. The most important polyolefins include polyethylene (polyethylene, PE) and polypropylene (PP). PE is produced by polymerizing the olefin ethylene, whilst PP is made from the olefin propylene. Moreover, polyethylene is classified into several different categories based principally on its density and branching since the extent and type of branching, the crystal structure and the molecular weight all strongly affect the mechanical properties of PE. Of these, low density polyethylene (LDPE), defined by a density range of 0.910–0.940 g/cm^3, has a high degree of short and long chain branching. The inability of the chains to pack into a crystal structure, and the reduced instantaneous-dipole induced-dipole attraction and intermolecular forces result in a lower tensile strength and increased ductility suitable for both thick film rigid containers and thin film applications such as plastic bags and film wrap.

Typically polyolefin products are manufactured by extrusion blow moulding, injection moulding, compressing moulding or film extrusion. Polyolefins and especially PE and PP have been widely used in food packaging, clothing, automotive parts, consumer products and industrial appliances. The large numbers of end use applications for polyolefins are often possible because of their durability, excellent chemical resistance, low density, recycling ability and relatively low cost. However, polyolefin chemistry has some intrinsic properties, e.g. lack of optical transparency, hydrophobicity, static generation leading to dust attraction and very poor biodegradability. These problems may be overcome by incorporation of either organic or inorganic fillers such as carbon black, natural fiber, starch, bamboo charcoal or rice husk.

Raw bamboo charcoal is made from bamboo branches, shoots and roots by pyrolysis (carbonizing) under high temperatures, typically being processed in a high-performance clay furnace oven heated to about 1000ºC, which produces bamboo charcoal of the highest quality.

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The resultant bamboo charcoal has innumerable pores in its structure making it an excellent medium for absorbing volatile chemicals (odors), controlling temperature, voiding moisture (e.g. air conditioning), inhibiting the growth of bacteria and fungi, preventing static electricity buildup which otherwise causes static shocks in dry conditions, and also has the ability to absorb far infrared energy from the environment and emit it to help cell activation for promoting blood circulation.[1] Bamboo charcoal has many applications in both conventional and hi-tech industries.[2-3] It can be used in medicines, cosmetics, food processing, health-related products, deodorants and composites. Most of the 1000 odd species of bamboo are fast growing and can be harvested and replanted with little damage to the sensitive forest ecosystems and thus bamboos, including the prized moso Bamboo (*Phyllostachys heterocycla pubescens*), within limitations are a renewable and sustainable environmentally sound product.

Many previous studies have shown that the addition of proper filler (either organic or inorganic fillers) is an effective strategy for achieving improved morphology and mechanical properties in polymer composites. In recent years, intensive fillers added in the polymer have been carbon black and clay. Many research articles have studied PP / clay nanocomposites. Nam, *et al*. prepared the intercalated nanocomposites of PP / clay by using maleic anhydride modified PP (PP-MA) and organophilic clay via melt extrusion process.[4] Mingliang and Demin prepared the organically modified clay (organoclay) by treating Na-montmorillonite with alkylammonium ions through a solid state method. The addition of organoclay did not affect the crystal structure of PP. But impact strength and thermal decomposition temperature of PP / organoclay nanocomposites were higher than those of neat PP when the organoclay content was below 7 wt%.[5] Yui, *et al*. studied the influence of density polyethylene (HDPE), carbon black structure and PP viscosity on morphology and electrical conductivity of injection-molded HDPE / PP / CB composites. The study found that the electrical resistivity of these mixtures decreased with the increase of HDPE content and increased with increasing the viscosity of the PP matrix. The morphological changes were correlated to the variation of electrical conductivity.[6] Lou, *et al*. studied the effect of bamboo charcoal on the mechanical properties of polyester (PET) / polypropylene (PP) blend with bamboo charcoal. The tensile strength and impact strength of the PET / PP_{ext} (extrusion grade PP) composites were better than those of the PET / PP_{inj} (injection grade PP) composites with 10% and 20% of polyester composition.[7]

Some previous research articles studied the effect of bamboo charcoal addition in the polymer composites. Bamboo charcoal has innumerable pores in its structure making it an excellent medium for preventing static electricity buildup and absorbing volatile chemicals. These two advantages of bamboo charcoal could enhance the water absorption and electrical conductivity of the polyolefin. Therefore, this work is undertaken to investigate the effect of bamboo charcoal loading on the physical properties, water absorption and volume resistivity of polyolefin / bamboo charcoal composites.

Material and Experimental Procedures

Materials

Commercial polypropylene (PP) and low-density polyethylene (LDPE) were used as the matrix of the composites. PP with a density of 0.90 g/cm^3 and a melt flow rate of 2.1 dg/min was supplied by HMC Polymers Company Limited. LDPE having a density of 0.92 g/cm^3 and a melt flow rate of 2.0 dg/min was supplied by Thai Polyethylene Co., LTD. Bamboo charcoal used as filler was purchased from Charcoal Home Co., LTD. Prior to use the bamboo charcoal was sieved through a 325-mesh sieve filter to attain a small, and less heterogeneous, particle size preparation. Bamboo charcoal particle size was determined by using Mastersizer 2000. According to the tested results, the average particle size of bamboo charcoal was 18.52 micron and the specific surface area of bamboo charcoal was 0.523 m^2 / g.

Methods

Polyolefin / Bamboo Charcoal Composite Preparation

Bamboo charcoal was compounded with PP or LDPE in order to obtain polyolefin / bamboo charcoal composites, which contain 5-20% (phr) of bamboo charcoal at 5% intervals (i.e. 0, 5, 10, 15 and 20 phr). PP / bamboo charcoal and LDPE / bamboo charcoal composites were prepared by melt mixing of the compounds in a mixing

chamber of a Brabender W30EHT for 10 min at 170ºC or 140ºC, respectively. Polyolefin composites were re-mixed by using a two-roll mill (LAB TECH) for another 10 min at 180ºC for PP/ bamboo charcoal and at 150ºC for LDPE / bamboo charcoal. After the mixing process, composite samples were prepared in the form of a square with dimensions of 6" x 6" and 1 mm thickness by compression moulding. The compression condition for the formation of PP/bamboo charcoal composites was a processing temperature of 180ºC and a pressure of 1300 psi for 8 min, followed by cooling at ambient conditions for 10 min, whilst that for LDPE / bamboo charcoal was as above except the processing temperature and pressure were 150ºC and 1200 psi, respectively.

Mechanical Properties

The tensile strength at break, Young's modulus and elongation at break of the polyolefin / bamboo charcoal composites were determined using a Universal Testing Machine (LLOYD LR 100K) according to ASTM D 638, with a gauge length of 25 mm, a crosshead speed of 50 mm/min and a load cell of 1,000 N. Wallace test equipment was used to cut the standard specimen for testing.

Water Absorption

The water absorption of polyolefin / bamboo charcoal composites was evaluated according to ASTM D 570-95. Specimens of 2 x 1.5 cm and 1 mm thickness were cut and dried in the oven at 60ºC for 24 hours, and placed in a desiccator for 10 minutes before weighing and then immersed totally into distilled water in a water-bath at ambient conditions for the indicated duration. At the end of each indicated immersion time, the specimens were removed, patted dry with a lint dry cloth and weighed immediately to determine the wet weight of specimen. Water absorption is expressed as the percentage increase in weight relative to the pre-immersed dry sample. The results of the mechanical properties and water absorption tests were obtained by averaging the values of six specimens.

Volume Resistivity

The volume resistivity of polyolefin / bamboo charcoal composites was determined according to ASTM D 257 by using a Resistivity Adapter of Keithley 6105, a High Voltage Supply of Keithley 247 and an Electrometer of Keithley 617. The specimens were placed at 23ºC and 50 % RH for 48 hours before testing.

Scanning Electron Microscopy Observation

Scanning electron microscopy (SEM) (JEOL JSM-6400) was employed to investigate the fracture surface of polyolefin / bamboo charcoal composites. The specimens were immersed in the liquid nitrogen and then fractured. The samples taken from the fractured parts were coated with gold for a few minutes before SEM observation at a magnification of 10,000 times.

Results and Discussion

The Influence of Bamboo Charcoal on the Mechanical Properties of Polyolefin / Bamboo Charcoal Composites

The effect of bamboo charcoal incorporation with either LDPE or PP on the tensile strength, Young's modulus and elongation at break of the resultant LDPE / bamboo charcoal and PP / bamboo charcoal composites are summarized in Figures 1, 2 and 3, respectively.

The tensile strength of PP / bamboo charcoal composites increased slightly with increasing bamboo charcoal content up to 20 phr (the highest tested dose), at which point the resultant composite tensile strength was ~ 15 % higher than pure PP. By contrast, bamboo charcoal incorporation into LDPE did not significantly affect the tensile strength of the LDPE / bamboo charcoal composite, although the tensile strength of all the LDPE / bamboo charcoal composites were slightly lower than that of virgin LDPE. It is concluded that bamboo charcoal presented interfacial adhesion with PP and could add into the PP matrix and reinforce the strength of the PP / bamboo charcoal composite. For LDPE / bamboo charcoal composites, no reinforcement was obtained by the addition of bamboo charcoal in the LDPE matrix, although the bamboo charcoal could also add into the LDPE matrix and had interfacial adhesion with LDPE as well. This may be because the chemical structure of LDPE has a high degree of short and long chain branching. When bamboo charcoal is added into the LDPE matrix may interfere with the entanglement of both short and long chain branches of LDPE and also cause a

lower intermolecular force, which together would lead to a lower tensile strength.

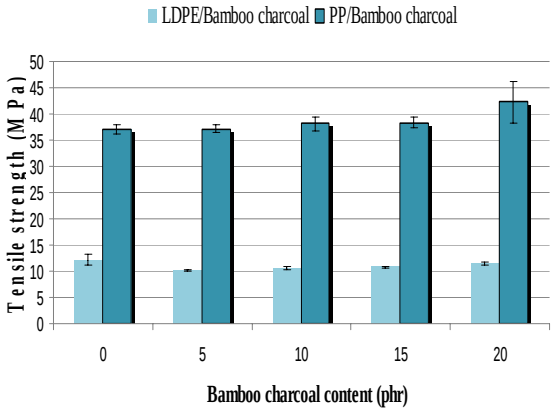


Figure 1. The tensile strength of polyolefin-charcoal composites with different bamboo charcoal contents.

Young's modulus is frequently used as a marker to evaluate the rigidity of polymeric materials, and is used as such here. Young's modulus of LDPE / bamboo charcoal and PP / bamboo charcoal composites increased in a dose-dependent manner with increasing bamboo charcoal contents. Although pure PP displayed a significantly greater Young's modulus than pure LDPE, the degree of increased Young's modulus induced by the addition of charcoal was broadly similar for both LDPE and PP composites, reaching about ~ 75-80% increase at 20 phr bamboo charcoal. This may be because the bamboo charcoal is comprised of very fine particles and can easily penetrate into the amorphous structures of LDPE and PP and provide a better rigidity for both polyolefin / bamboo charcoal composites. Since the data revealed no evidence of approaching an asymptote, the incorporation of bamboo charcoal at greater than 20 phr into the LDPE and PP matrices potentially could result in even further increases in the tensile strength and Young's modulus and merits further investigation. However, it was not evaluated in this study because the equipment available did not mix bamboo charcoal contents at more than 20 phr with PP or LDPE well enough to ensure homogeneity prior to compression. Heterogeneously mixed composites would impair the mechanical properties leading to erroneous values for the composite materials.

Young's modulus is a measure of the ability of a material to withstand changes in length, and indeed the elongation at break of both polyolefin / bamboo charcoal composites decreased rapidly in a dose-dependent manner with increasing levels of bamboo charcoal content in the composites. This may be because the bamboo charcoal, once incorporated with LDPE or PP, agglomerates and reduces the extensibility of the matrix in the composites. The resistance created by the bamboo charcoal particles would reduce the deformability of the PP or LDPE macromolecules.

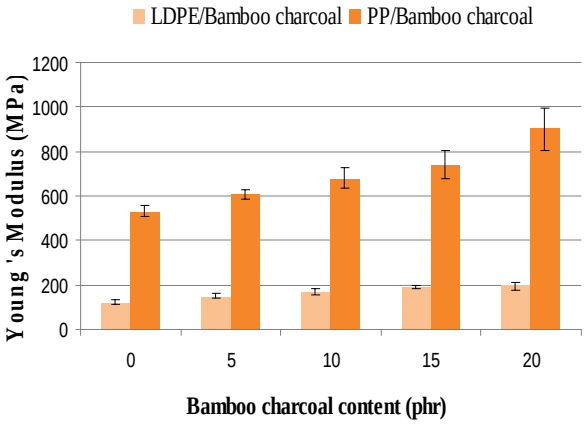


Figure 2. Young's modulus of polyolefin-charcoal composites with different bamboo charcoal contents.

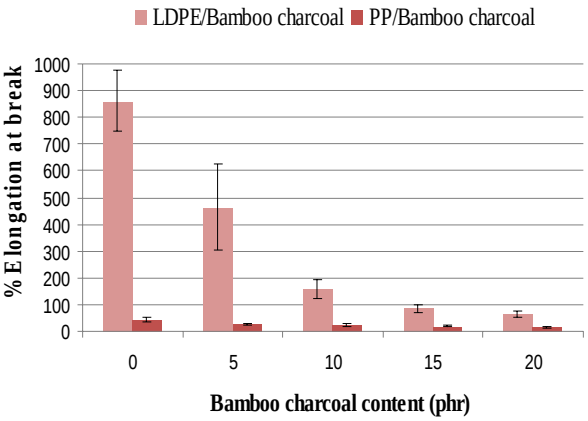


Figure 3. The elongation at break of polyolefin-charcoal composites with different bamboo charcoal contents.

Electrical Conductivity of Polyolefin / Bamboo Charcoal Composites

The influence of bamboo charcoal content at 10 and 20 phr on the DC electrical resistivity of LDPE / charcoal and PP / charcoal composites is summarized in Table 1. The electrical resistivity of both PP / bamboo charcoal and LDPE / bamboo charcoal composites decreased with increasing

bamboo charcoal contents, but this was more marked for PP than for LDPE (~ 85 and 30% reduction at 20 phr, respectively). The electrical resistivity of both polyolefin / bamboo charcoal composites seemed to reduce substantially. But these values of electrical resistivity of polyolefin / bamboo charcoal were still in the range of insulators. Normally, the electrical resistivity of pure metals extends from approximately 1.5 x 10^{-8} ohm-meter for silver, the best conductor, to 135 x 10^{-8} for manganese, the poorest pure metallic conductor. Insulators have electrical resistivity within the approximate range of 10^{8} to 10^{16} ohm-meters. This is assumed to be because the amount of bamboo charcoal content applied in this study might be insufficient to form conductive networks in the LDPE and PP composite matrices. In addition, the innumerable pores of bamboo charcoal may interrupt the conductive networks.

Table 1. The volume resistivity of polyolefin / bamboo charcoal composites

Tested Sample	Thickness (mm)	Volume Resistivity (Ω-cm) × 10^{16}
Virgin PP	98.6 ± 1.0	42.3 ± 2.7
PP/bamboo charcoal (10 phr)	103.2 ± 1.1	15.0 ± 1.0
PP/bamboo charcoal (20 phr)	103.7 ± 0.7	6.39 ± 0.67
Virgin LDPE	106.8 ± 1.5	6.52 ± 0.19
LDPE/bamboo charcoal (10 phr)	108.8 ± 1.3	6.26 ± 0.35
LDPE/bamboo charcoal (20 phr)	111.2 ± 1.4	4.61 ± 0.13

Water Absorption of Polyolefin / Bamboo Charcoal Composites

The influence of bamboo charcoal content on the water absorption of LDPE / bamboo charcoal and PP / bamboo charcoal composites is summarized in Figures 4 and 5, respectively. The water absorption of both polyolefin / bamboo charcoal composites increased continuously week by week and also showed a marked dose-dependent effect with increasing water absorption at each time point with increasing charcoal levels in the composites. Normally, LDPE and PP do not have good water absorption (< 0.02%). Bamboo charcoal was not considered as a hydrophilic material, but the significantly increased water absorption of both polyolefin / bamboo charcoal composites was likely to be attributed to the many pores and gaps in the bamboo charcoal structure.

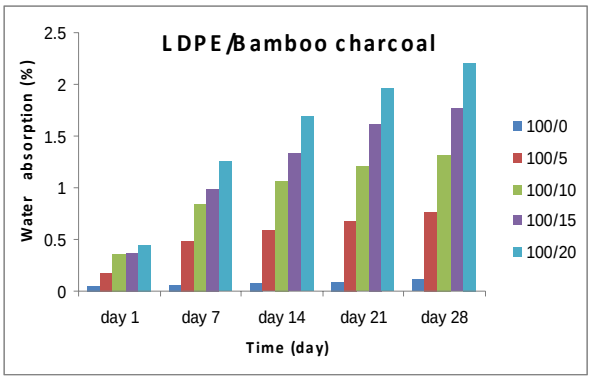


Figure 4. Water absorption of LDPE / bamboo charcoal composites with different bamboo charcoal contents.

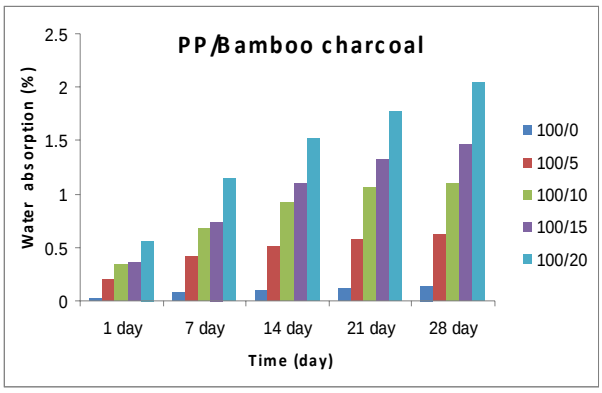


Figure 5. Water absorption of PP / bamboo charcoal composites with different bamboo charcoal contents.

SEM Observation of the Surface of LDPE/ Bamboo Charcoal and PP/Bamboo Charcoal Composites

A SEM micrograph of the bamboo charcoal particles is shown in Figure 6. The bamboo charcoal appeared to display a somewhat heterogeneous appearance with particles of different sizes and irregular shapes. Typically, many fine particles and pores were visible in the structure but with smaller particles agglomerated around larger particles with different sizes and irregular shapes. This heterogeneous structure and especially the large number of pores present in the bamboo charcoal could affect its ability to alter the composite water absorption, electrical conductivity and the strength of materials. In contrast, the surface features of LDPE or PP look relatively homogeneous and similar to each other, as seen from SEM micrographs (Figure 7). SEM micrographs of LDPE / bamboo charcoal composites and PP / bamboo charcoal composites, with different contents of bamboo charcoal, are shown in Figures 8 and 9, respectively.

For both polyolefin / bamboo charcoal composites, the bamboo charcoal granules appeared to have added into the polyolefin matrix, but were distributed much more evenly in the LDPE matrix than in the PP matrix. Presumably, this is because LDPE is a much softer material than PP. The amount of bamboo charcoal granules distributed within the LDPE matrix increased with increasing bamboo charcoal content. Bamboo charcoal distributed more evenly in the polyolefin matrix could provide better properties of Young's modulus and tensile strength of the composite materials. Polyolefin / bamboo charcoal composites contained bamboo charcoal content at 20 phr had better tensile strength and Young's modulus than those of polyolefin / bamboo charcoal composites containing bamboo charcoal content at 15 phr. This may be attributed to the fact that the good distribution pattern of bamboo charcoal in polymer matrix could enhance the physical properties of composite materials.

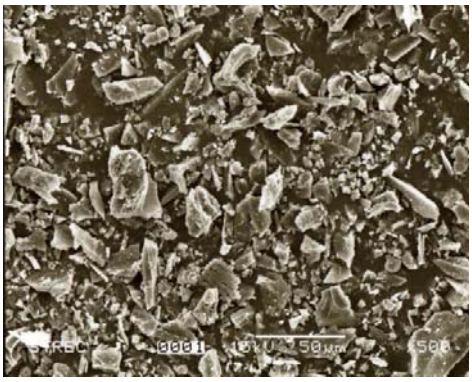
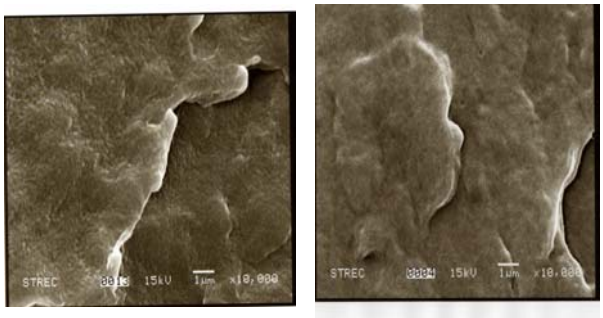
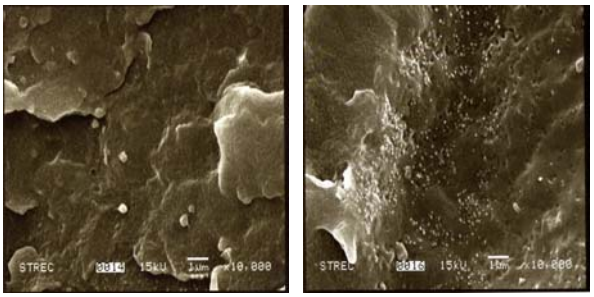


Figure 6. SEM micrograph (x500) of bamboo charcoal

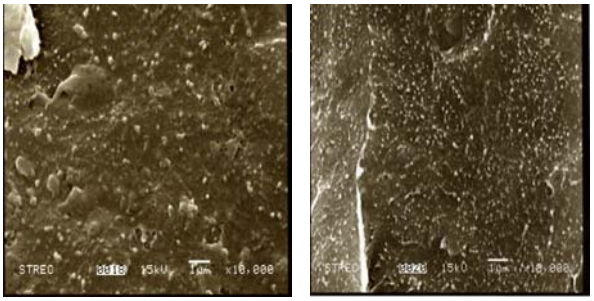


LDPE PP

Figure 7. SEM micrographs (x10000) of LDPE and PP

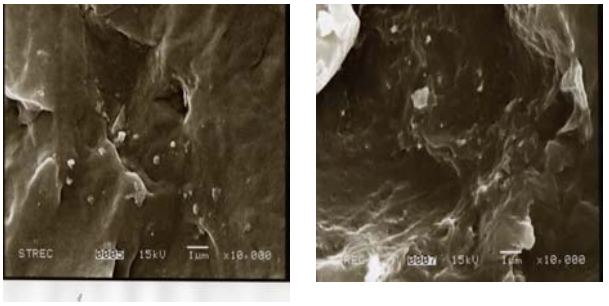


(a) (b)

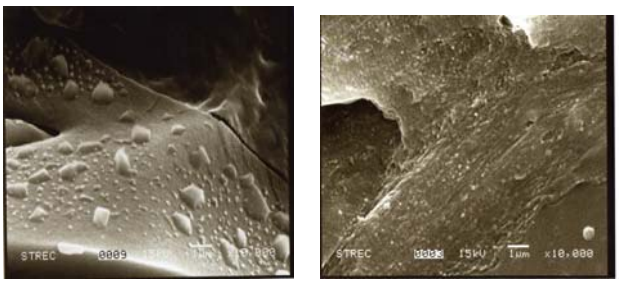


(c) (d)

Figure 8. SEM micrographs (x10000) of LDPE / bamboo charcoal composites with a bamboo charcoal content of (a) 5 phr (b) 10 phr (c) 15 phr and (d) 20 phr



(a) (b)



(c) (d)

Figure 9. SEM micrographs (x10000) of PP / bamboo charcoal composites with a bamboo charcoal content of (a) 5 phr (b) 10 phr (c) 15 phr and (d) 20 phr

Conclusion

Thermoplastic composites were made from blending either LDPE or PP with bamboo charcoal at 0 to 20 phr by melt mixing and then compression moulding. The mechanical properties, water absorption and electrical conductivity of both resultant series of polyolefin / bamboo charcoal composites were investigated. The incorporation of bamboo charcoal into the PP matrix enhanced the tensile strength and Young's modulus whilst decreasing the elongation at break in a dose-dependent manner. The tensile strength of LDPE / bamboo charcoal composites was less than that of virgin LDPE. Young's modulus and elongation at break of LDPE/ bamboo charcoal composites showed the same broad trends as observed in PP / bamboo charcoal composites. The water absorption of both polyolefin/ bamboo charcoal composites was significantly greater than that of the original PP or LDPE polyolefin. The electrical resistance of both polyolefin/ bamboo charcoal composites decreased with increasing charcoal content compared with that of pure PP and LDPE.

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