Low Percolation Threshold and High Conductivity in Carbon Black Filled Polyethylene and Polypropylene Composites

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ABSTRACT: High electrically conductive composites have been manufactured using twin and single screw extruders from carbon black with polyolefin. High density, low density polyethylene, polypropylene, polyethylene/polypropylene copolymer, and maleic anhydrite grafted polypropylene have been compounded with three carbon blacks (CBs), i.e., Black Pearl, Printex, and Ketjen, respectively. The lowest percolation threshold (0.8 vol %) for conductive composite was obtained using Ketjen CB blended with high density polyethylene (HD3690, MFI = 36 g/10 min). Polypropylene composites also achieved low percolation thresholds of 1.5 vol % when compounded with Printex or Ketjen CB. Decreasing melt viscosity of polymer matrix resulted in decreasing resistivity of composites. Ketjen CB showed the best conductive behavior for both polyethylene and polypropylene composites. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 115: 3527–3534, 2010

Key words: carbon black; conductive composite; polyethylene; polypropylene; electrical resistance

INTRODUCTION

Electrically conductive polymer composites have a wide application range in industries, such as antistatic materials, self-regulating heaters, over-current and over temperature protection devices, and electromagnetic radiation shielding.[1,2] According to the standards of package material classification from electronic industry association, the conductive materials have a surface resistivity of less than 1.0 × 10^5 Ω/sq, dissipative materials have a surface resistivity from 1.0 × 10^5 to 1.0 × 10^{12} Ω/sq and insulative materials have a surface resistivity above 1.0 × 10^{12} Ω/sq.[1] To avoid the damage from electrostatic discharge, the surface resistivity of materials must be in the range of 1.0 × 10^6 to 1.0 × 10^9 Ω/sq. However, the surface resistivities of most thermoplastics are in the range from 1.0 × 10^{16} to 1.0 × 10^{18} Ω/sq. A number of methods have been used to increase surface conductivity of polymers. Conductive coating is one of the conventional methods.[3–5] Although surface coating can increase conductivity of polymer materials initially, the conductivity of materials decreased with time due to oxidation and the wearing out of the surface layer.[6]

Thermoplastic polymer can be easily compounded with conductive fillers, such as carbon black (CB), carbon fiber, metallic powder, graphite flake, and glass bean or glass fiber coated with metal to make conductive polymer composites.[7–9] The conductive property of composites depends on polymer matrix and conductive fillers, such as shape, volume percentage, and microstructure. Polyethylene (PE) and polypropylene (PP) are low cost and easy fabricated polymers. Currently, some of the articles have reported the conductivity and mechanical properties of CB/PE composites.[10–14] Either articles focused on increasing the conductivity of materials using high carbon black contents (more than 10 wt %) filled polymer, or focused on reducing the percolation threshold of CB/polyolefin composites, using a blend with two immiscible polymers to compound with CB.[3,15–17] The percolation threshold value obtained was 3.6 wt % in HDPE/EVA polymer blends.[17] The morphology of carbon black in polyethylene composite was studied using X-ray scattering method.[18] The effect of coupling agent of maleic anhydride grafted ethylene-propylene copolymer was studied using CB filled HDPE.[19] The results showed that at high CB contents such as 15, 20, 30 wt %, addition of 5 wt % maleic anhydride grafted ethylene-propylene copolymer increased the conductivity of composites.

Currently, the percolation threshold value for CB/polyolefin is too high (about 5 wt %), which causes difficulty in processing, and decreases the mechanical properties, especially the impact toughness of materials. The pollution of carbon black powder is also a big problem for the environment and the health of the operator. It is important to develop

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new conductive composites which have good mechanical properties and requires less carbon black filler to meet the percolation threshold.

This article compared the conductivity of composites made from two processing methods and got CB/polyolefin composite with very low percolation threshold using single screw extruder. Different factors for conductivity of materials were studied, such as polymer matrix, processing methods, structure of carbon black in polymer matrix. The microstructures of composites were analyzed using SEM.

EXPERIMENTAL

Materials

High density polyethylene (HD0490, HD2090, HD3690), low density polyethylene (LD6215), polypropylene (PPN2033, PPV1780, PPW1780), powder polypropylene (PPU1080), copolymer of polyethylene and polypropylene (PPV2735) were supplied from Qenos Company (Australia). Maleic anhydrite grafted polypropylene (MAPP) was purchased from DuPont (MD100D, Australia). Three kinds of carbon blacks were used, i.e., black pearls 2000 (Cabot, Australia), Printex XE 2B (Degussa, Germany), and Ketjen EC 600JD (Lion Cooperation, Japan). Vapor grown carbon fiber (VGCF, PR24-LHT, USA) was supplied from Pyrograf Products.

Processing

Polymer and carbon black were compounded using a single screw extruder (Single Screw Compounding Line). The temperature used for compounding was 175°C and rotation speed of the screw was set at 180 rotations per minute (RPM). The extruded composite was cooled with a water bath, and then chopped with a blender. As a referent material, polypropylene and CB was compounded using co-rotated twin screws extruder with high shear force screw configuration (HAAKE). The sample for conductivity test was made using hot press. About 10 g material, dried priory at 70°C for 12 h, was put in a Teflon coated round mold with a diameter of 100 mm and depth of 0.5 mm. The temperature was kept at 175°C for 10 min for CB/PE and 190°C for CB/PP composites. After that cooling water was let into the mold until temperature dropped to below 60°C. A round film sample with thickness of 0.5 mm was obtained for the test of resistivity.

Characterization

The electrical surface resistivity of composite was measured according to different resistivity levels. For high resistant ($<1 \times 10^6$ Ω/sq) composites, the surface resistivity was measured using the four point method with a Keithley Electrometer (Model 6517A), which was connected to a concentric (guarded ring) and fixture (Model 8009). If the resistant of composite was lower than 1×10^6 Ω/sq, the two probes technique was used. A pair of brass bars 20 mm in length was used as electrodes and the distance between two electrodes was 20 mm. The electrodes were pressed against the sample to ensure better contact. The surface resistance was displayed on a digital multimeter.

The microstructures of composite were analyzed using a scanning electronic microscope (Leica 360FE) at a low voltage (2 KV). The sample was coated with carbon.

RESULTS AND DISCUSSION

Percolation threshold

The behavior of conductivity of composites depended on the content, shape and structure of conductive filler, the interface between filler and polymer, and morphology of composites. For carbon black filled polyolefin composite, the conductivity of composites increased with CB content. However, it is not a simple linear additive characteristic. When volume fraction φ of filler was below the critical value φ_c (so called percolation threshold), the conductivity of composite gradually increased with the content of CB. Once the content reached the percolation threshold, there was a rapid increase in conductivity due to the formation of a net of conductive paths. After certain point the conductive curve reaches a plateau as further additions of conductive paths do not have a significant effect on the conductivity. A theoretical approach for the change in conductivity (σ) of conductor-insulator composite beyond the threshold can be expressed as follows

$$\sigma \propto (\varphi - \varphi_c)^t$$

Where φ is the volume fraction; t is the critical exponent. For each composite system φ_c and t have different values. Figure 1 gives an example of the relationship between conductivity and the content of CB using Ketjen carbon black filled polyethylene (HDPE3690).

The percolation threshold of Ketjen CB/HDPE3690 was about 0.8 vol % (1.5 wt %), which was significantly less than the theoretically predicted threshold of 16.4 vol % and current literature data of 3.3 vol %.[4] When Printex and Black Pearls 2000 CB were used in polyethylene, the percolation threshold of composites was 1.0 vol % (2 wt %) and 1.5 vol % (3 wt %). For CB/PP composites consisting of

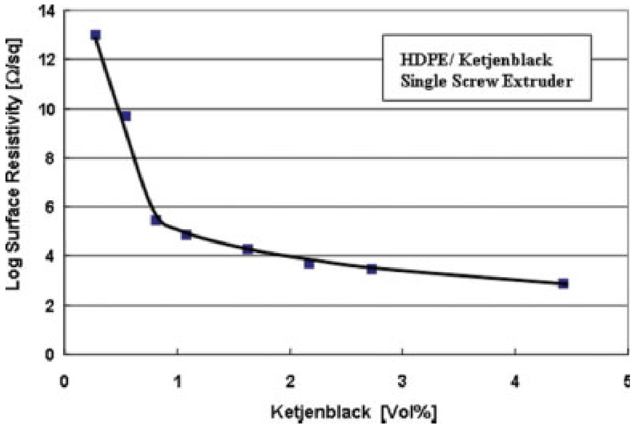


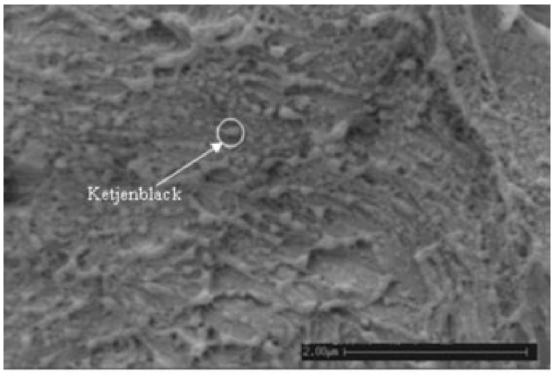
Figure 1 Relationship between resistivity of CB/HDPE composite and volume fraction of CB. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

Ketjen, Printex, and black pearls 2000 CB with PPV1780, the percolation threshold of composites was 1.5, 1.5, and 2.0 vol % (3, 3, and 4 wt %), respectively. Figure 2 shows the conductive net structure in the composite consisting of Ketjen CB/HDPE3690.

Effect of processing method

Different processing method leads to different morphology of CB in polymer matrix. In most filler/polymer composites, the ideal morphology is for the filler to be dispersed at nanosize in the polymer matrix. However, in conductive composites, the conductive fillers have to be connected or very close to each other to form conductive paths, as only this kind of structure allows electrons to be transferred from one particle to another particle.

To study the effect of processing method on the conductivity of composites, polypropylene was compounded with carbon black pearls 2000 using single and twin screws extruders. The conductivity of CB/PP composite in all range of CB content was higher when the composite was made by single screw extruder as compared to that made with twin screws extruder (Fig. 3).



HDPE3690/Ketjenblack 0.8 Vol%

Figure 2 Conductive net structure of Ketjen carbon black filled polyethylene (HD3690).

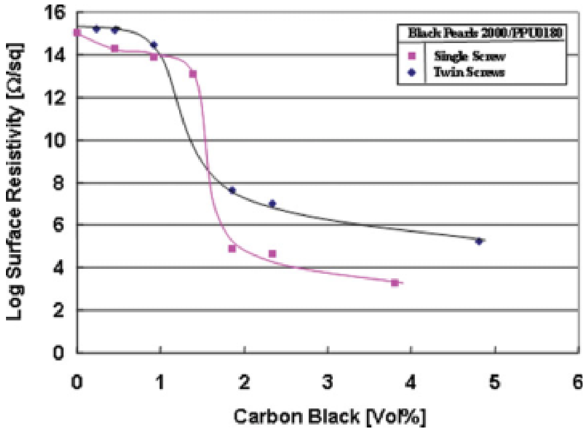


Figure 3 Effects of different processing methods on the conductivity of CB/PP composite. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

To further study the effects of processing methods on the conductivity of materials, VGCF was compounded with PP using single and twin screws extruder at a filler content of 2.5 vol % (5 wt %). The resistivity of VGCF/PP composite made by twin screws extruder is clearly higher than that made by single screw extruder (Fig. 4).

The morphology of carbon black filled polypropylene made from single and twin screws extruder were analyzed using SEM. In the CB/PP composite made using the twin screws extruder, carbon black particles were dispersed in polymer matrix [Fig. 5(a)]. The carbon black particle became covered by polypropylene molecules, which obstructed the flow of electrons from one particle to another and hence increased the resistivity of materials. In contrast, CB/PP composite made by single screw extruder

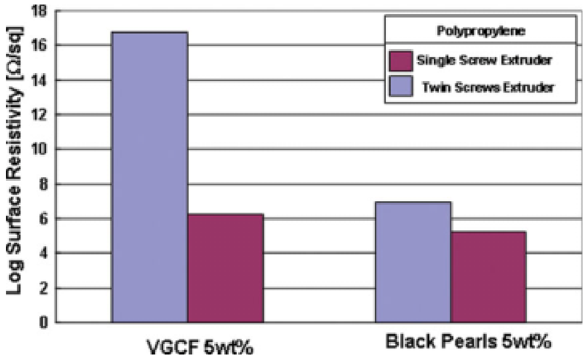
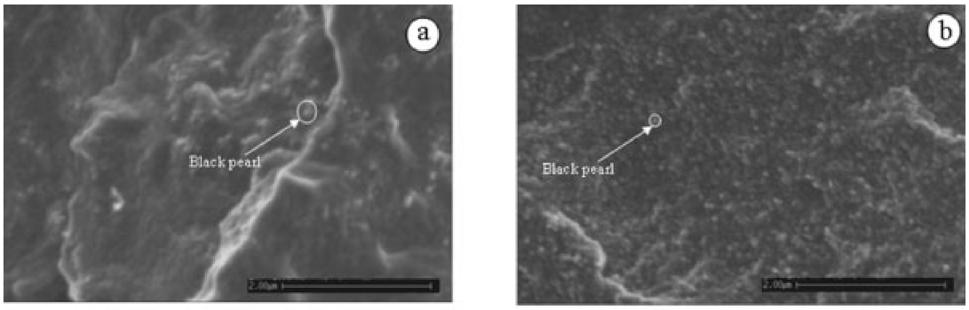
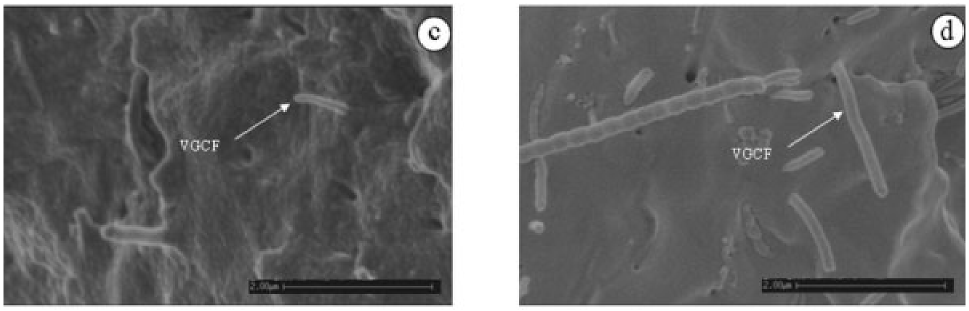


Figure 4 Resistivity of CB/PP and VGCF/PP composites at the filler loading 5 wt % using different processing methods. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]



Twin Screws Extruder PPU/Black Pearls 5wt%

Single Screw Extruder PPU/Black Pearls 5wt%



Twin Screws Extruder PPU/VGCF 5wt%

Single Screw Extruder PPU/VGCF 5wt%

Figure 5 Morphology of CB/PP and VGCF/PP composites made by different processing methods.

showed a grape-like structure, thus CB particles were well connected allowing electrons to flow freely [Fig. 5(b)]. Therefore, the single screw extruder is more suitable for making conductive composite than twin screw extruder.

The morphology of VGCF/PP made by twin screws extruder showed that the fiber length were much shorter than that made by a single screw extruder [Fig. 5(c,d)]. This is due to the twin screws extruder having a stronger shear force, which broke the VGCF. In contrast, since the single screw extruder has a low shear force, VGCF were longer in the composite resulting in more overlaps and thereby enabling better conductivity.

Effect of the melt viscosity of polymer on the conductivity

Three high density polyethylene, i.e., HDPE0490 (MFI = 4 g/10 min), HDPE2090 (MFI = 20 g/10 min), and HDPE3690 (MFI = 36 g/10 min) were compounded with CB (Black pearl 2000) using single screw extruder. CB/HDPE3690 showed the lowest resistivity and lowest percolation threshold value (1.5 vol %). The lower the melt viscosity of polymer matrix was, the lower the surface resistivity of its composite [Fig. 6(a)].

Same as high density polyethylene, polypropylene, i.e., PPN2033 (MFI = 2 g/10 min), PPV1780 (MFI = 22 g/10 min), PPU0180 (MFI = 27 g/10 min), and

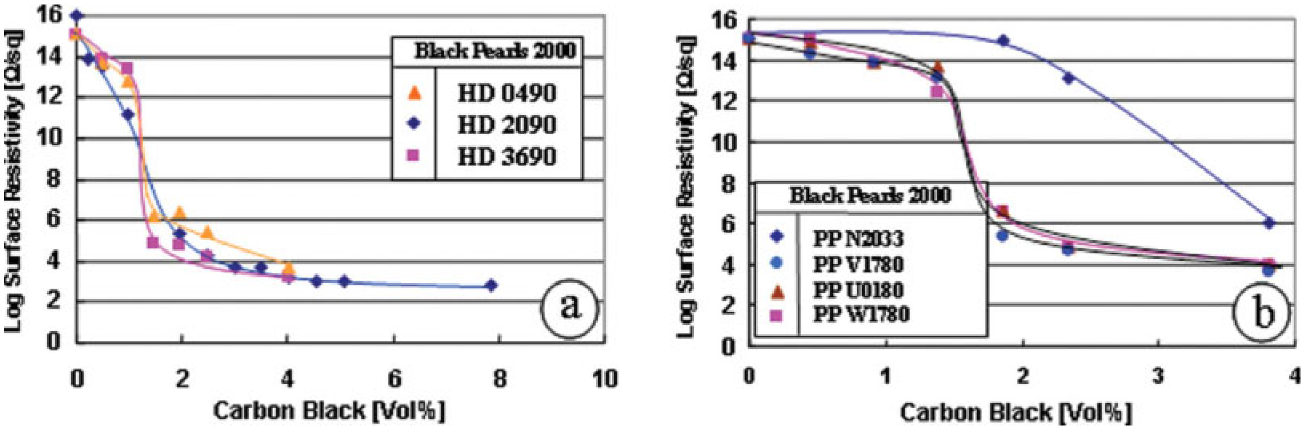
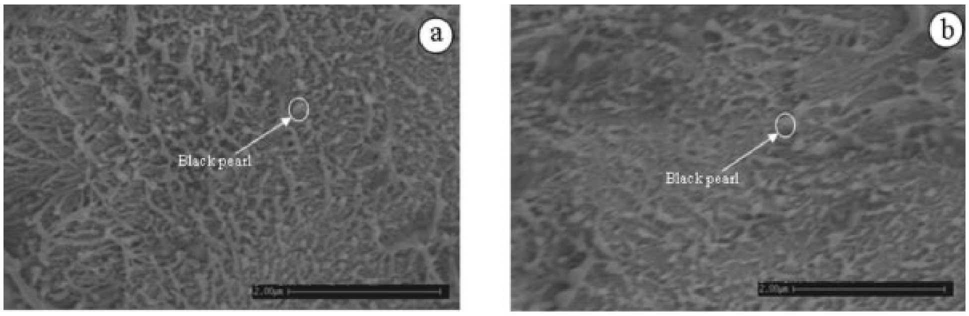
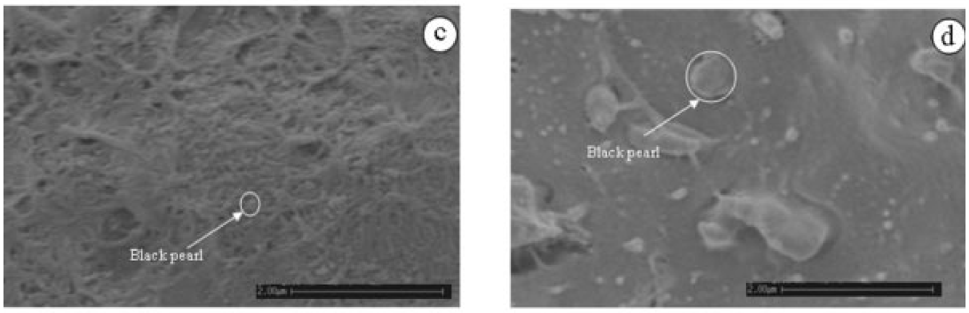


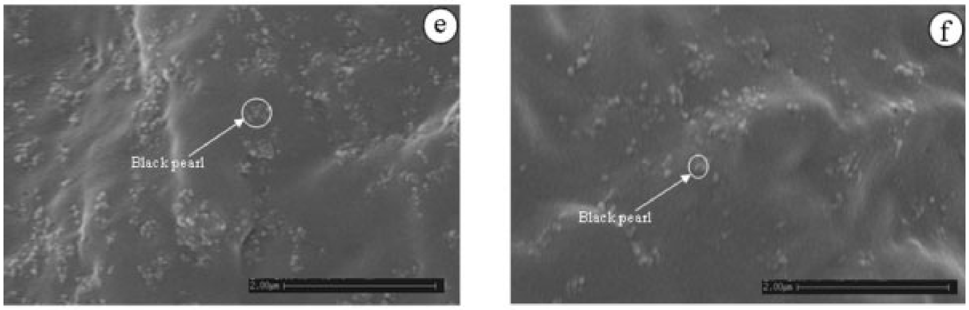
Figure 6 Resistivity of CB filled PE and PP with different melt viscosities. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]



HDPE0490/Black Pearls (MFI=4) 3wt%   HDPE2090/Black Pearls (MFI=20) 3wt%



HDPE3690/Black Pearls (MFI=36) 3wt%   PPN2033/Black Pearls (MFI=2) 4wt%



PPV1780/Black Pearls (MFI=22) 4wt%   PPW1780/Black Pearls (MFI=48) 4wt%

Figure 7 Microstructure of CB in polymers with different melt viscosities.

PPW1780 (MFI = 48 g/10 min) were each compounded with CB (Black pearl 2000) using single screw extruder. CB/PPW1780 composite showed the lowest resistivity in CB/PP group [Fig. 6(b)].

The microstructures of CB in different melt viscosity polymer matrices were studied using SEM. For high melt viscosity polyethylene (HD0490) composite, CB particles were separated at 3 wt % content [Fig. 7(a)]. When melt viscosity of HDPE decreased (HDPE2090), the distance between CB particles decreased [Fig. 7(b)]. When HDPE3690 was used, CB particles formed a net structure in the polymer matrix at a content of 3 wt % CB [Fig. 7(c)].

In polypropylene matrix group, CB showed a very inhomogeneous distribution in the high melt viscosity PPN2033 (MFI = 2.0) matrix, which resulted in very high resistivity of composite [Fig. 7(d)]. As the melt viscosity of polypropylene decreased, the particles of CB broke down to smaller size and dispersed homogenously in PPV1780 (MFI = 22) and PPW1780 (MFI48) matrix [Fig. 7(e,f)].

It can be supposed that low melt viscosity polymer penetrated into carbon black agglomerated structure causing the agglomerated structure to break into fine CB particles. On the other hand, it would be difficult or impossible for high melt viscosity polymer (PPN2033) to penetrate into CB agglomerated structure, thus it remains unbroken.

Effects of different polymer matrices

The molecular structure of polymer is an important factor on the conductivity of composite. Polyethylene has lower resistivity than polypropylene at low content of CB (Fig. 8), since polyethylene is a linear polymer, which easily penetrates into carbon black agglomerated particles.

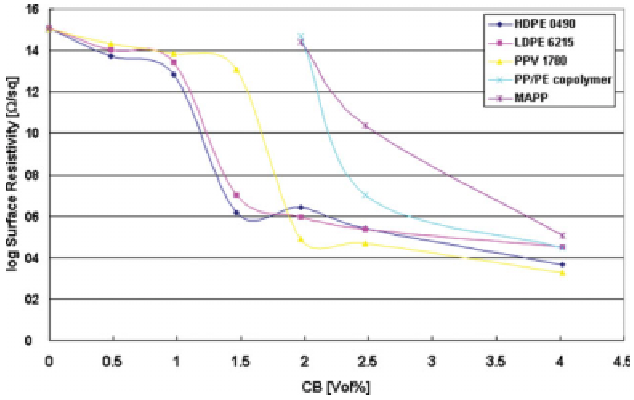


Figure 8 Effects of different polymer matrices on conductivity of composites. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

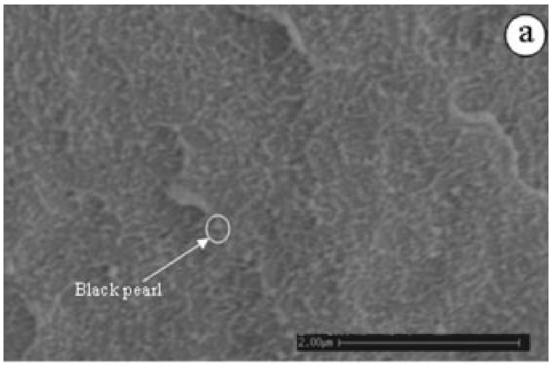
For the polyethylene group, low density polyethylene (LDPE) had higher resistivity than high density polyethylene (HDPE), since it is more difficult for polymer to penetrate into the agglomerated CD particles when there are more branches. The conductive net did not form at a CB content of 3 wt % for CB/LDPE [Fig. 9(a)]. In contrast, HDPE penetrated more easily into the agglomerated CD particles due to the linear structure and was able to form a conductive net at a carbon black content of 3 wt % [Fig. 7(c)].

For CB/PP system, neat PPV1780 revealed the lowest resistivity, followed by PE/PP copolymer, and malic graft polypropylene (Fig. 8). The SEM image showed that CB formed conductive net in PPV1780 matrix at a content of 4 wt % CB [Fig. 7(e)]. In comparison with neat PP, polypropylene/polyethylene copolymer had high resistivity although the melt viscosity was the same for both polymers. The particle size of CB in PE/PP copolymer was much bigger than that in PPV1780 [Fig. 9(b)]. Maleic anhydride grafted polypropylene had the highest resistivity (Fig. 8), even though the size of CB was very small [Fig. 9(c)]. It can be supposed that maleic anhydride grafted polypropylene had strong bonding with CB,[19] causing CB to be covered with polymer. In addition, the melt viscosity of MAPP (MFI = 8 g/10 min) was much higher than that of neat PP (MFI = 22 g/10 min). High melt viscosity of polymer had low conductivity of composite similar to that of CB/HDPE composites discussed earlier.

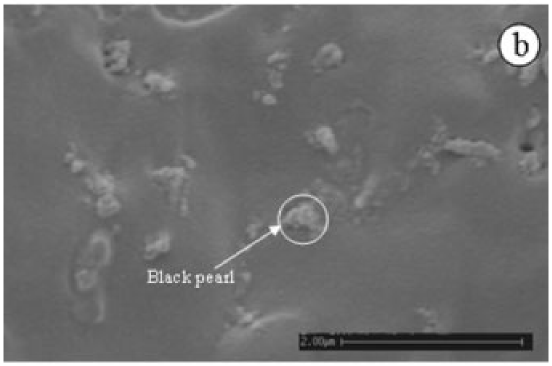
Effect of different CB

Three CBs, i.e., black pearls 2000 (Cabot), Printex XE 2B (Degussa), and Ketjen EC 600JD (Lion Cooperation) have been compounded with HDPE 3690 and PPV1780. The resistivity of Ketjen CB showed the lowest resistivity at low CB content for both polyethylene and polypropylene [Fig. 10(a,b)]. The percolation threshold of CB/HD3690 composites was 0.8 vol %, 1.0 vol %, and 1.5 vol % for Ketjen, Printex, and Black pearls 2000, respectively. Similar results were obtained in CB/PP system. The resistivity of Ketjen CB/PP composites was the lowest, followed by Printex, and then black pearls 2000.

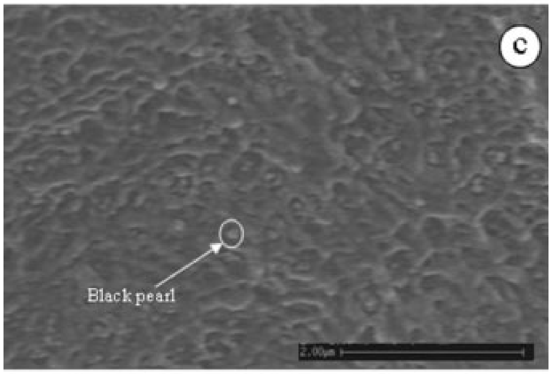
The fractured surface of different carbon blacks blended with polyethylene (HD3690, 2 wt %) and polypropylene (PPV1780, 3 wt %) were analyzed. Carbon black pearls 2000 have isolated particles in



LDPE6215/Black Pearl 3wt%



PP-copolymer/Black Pearl 4wt%



MA-PP/Black Pearl 4wt%

Figure 9 Microstructures of carbon black in different polymer matrices.

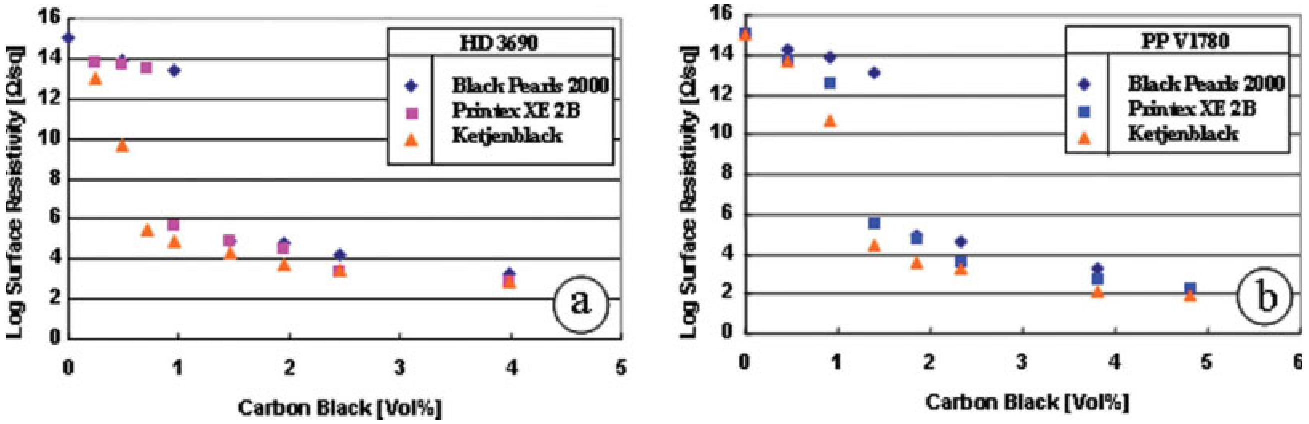
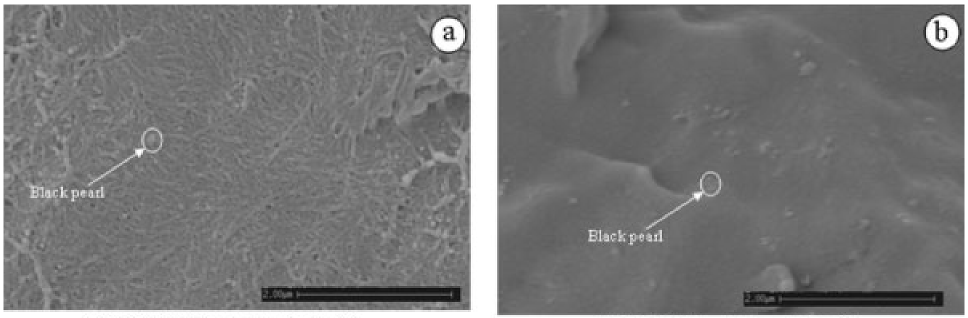


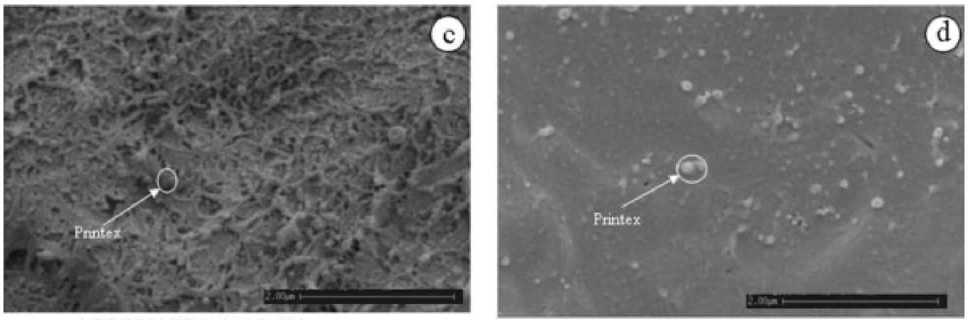
Figure 10 Resistivity of different carbon blacks filled PE and PP composites. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

both polyethylene [Fig. 11(a)] and polypropylene matrices [Fig. 11(b)]. Printex CB could form a conductive net in the polyethylene matrix [Fig. 11(c)], but not in the polypropylene matrix [3 wt %, Fig. 11(d)]. Ketjen carbon black showed the smallest particle size and connected with each other to form



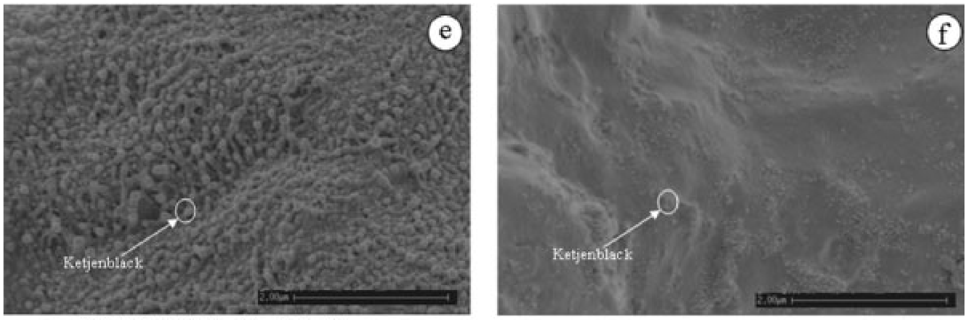
HDPE3690/Black Pearls 2wt%

PPV1780/Black Pearls 3wt%



HDPE3690/Printex 2wt%

PPV1780/Printex 3wt%



HDPE3690/Ketjenblack 2wt%

PPV1780/Ketjenblack 3wt%

Figure 11 Microstructure of different carbon black filled PE and PP composites.

conductive nets in both PE [Fig. 11(e)] and PP matrices [Fig. 11(f)].

As different microstructures and surface conditions of each carbon black resulted in different morphology of CB/PE and CB/PP composites, their resisitivity were also different.

CONCLUSIONS

To develop a conductive material with low percolation threshold, carbon black filled polyethylene and polypropylene composites were made using single or twin screws extruder. Single screws extruder with a lower shearing force was more suitable than twin screws extruder in making conductive composites. The lowest percolation threshold for composite was obtained when high density polyethylene (HD3690) was filled with carbon black (Ketjen) at 0.8 vol % (1.5 wt %). It was found that the resistivity of composites decreased with melt viscosity of polymer matrix. Also, the resistivity of linear polymer composites (HDPE) was lower than that of branched polymer (LDPE) composites. Ketjen carbon black showed the best conductive properties followed by Printex, then black pearls 2000. Although satisfactory conductive properties have been achieved for polymer composites, further investigation needs to be undertaken in relation to their mechanical properties.

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