

ORIGINAL ARTICLE

Effect of the processing of injection-molded, carbon black-filled polymer composites on resistivity

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To improve the application of carbon black (CB)-filled polymer composites, we investigated the relationship between the processing parameters, microstructure and electrical properties of injection moldings made from the material. Standard tensile specimens were fabricated under different injection pressures and packing pressures. Up to five layers were removed from the surfaces of the molded specimens to observe the microstructure at different positions within the moldings. Microstructures were observed with a scanning electron microscope, and electrical properties were measured at room temperature with a standard two-terminal direct current (DC) resistor. The results showed that CB particles form the best conductive path at high packing pressures combined with high injection pressures. If the packing pressure is low, the resistivity in the skin zone when loaded by high injection pressures is less than when loaded by low injection pressures, but resistivity increases in the sub-skin zone. We found that the sub-skin zone is a high-resistivity area that can be expanded under the action of higher injection pressures along with lower packing pressures. In contrast to an injection-molded single polymer, an injection-molded, CB-filled polymer composite develops a highly oriented microstructure in the core zone rather than in the skin or sub-skin zones because of the migration of CB particles.

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INTRODUCTION

Polymers are often endowed with some outstanding properties when mixed with different fillers. Nanotechnology-stimulated research attempts to create multifunctional composites by integrating nanoparticles into polymer matrices. Nanoscale carbon black (CB) particles, a type of filler, have practical applications in manufacturing nanoparticle reinforced polymer composites because of their low cost and good moldability. In past decades, many researchers have focused on the electrical properties of CB-filled polymer composites.^{1–3} For a given composite, its electrical conductivity is determined not only by the CB structure and concentration but also by the specific polymer matrix used and the morphology generated during processing.^{4–7} There is extensive research on the conductive characteristics of polymer-containing CB particles with different morphologies^{8–10} and the effect of the dispersion state of CB particles in the matrices on the electrical conductivity.^{11,12} When CB particles fill a polymer matrix, it is beneficial to conductivity when the CB particles are located in the amorphous phase or in the interface between two phases. Both the conductive pathway of CB particles in the phase and the continuity of the phase in the composites are basic requirements for maintaining a conductive network through the composite.^{13–15}

When a given CB-filled polymer composite is injected into a molding chamber, the difference in conductivity levels may be

observed by the segregation of CB particles during flow-induced orientation into axial channels.⁸ It is known that injection-molded materials always possess a characteristic skin-core microstructure that exhibits a stronger orientation at the sub-skin zone and a relatively uniform microstructure at the core zone. The microstructure of injection-molded, CB-filled polymer composites is more complex because CB particles migrate from the high shear stress region to the low shear stress region. The migrating velocity, which leads to changes in the microstructure and electrical properties, varies with processing conditions. The morphology of the polymer matrix and the distribution of CB particles are significantly deformed by the high-pressure-driven molding flows, especially in the area near the surface of the molded specimens.^{16–17}

However, apart from the migration of CB, the effect of self-agglomeration of CB particles varies with processing conditions. Therefore, the final distribution of CB in the matrix depends on the overall action of these two factors. Currently, it is not completely understood how processing conditions affect the mobility of CB particles and their distribution in the matrices at the skin, sub-skin and core zones of the moldings. To obtain improved electrical properties of the moldings, it is necessary to investigate how the conductivities of these three zones vary with different processing parameters. In this study, we focused our attention on the distribution of CB particles

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in the polymer matrix at different molding depths for moldings prepared under different processing conditions. The objective was to gain a better understanding of two issues. One relates to the effect of injection molding conditions on the distribution of CB particles and the skin-core microstructural characteristics of the moldings. The other issue is the relationship between microstructure, processing conditions and conductivity of the moldings, which we explore here to determine practical methods to control the conductivity of polymer composites filled by CB particles.

EXPERIMENTAL PROCEDURE

Materials

The CB particles used in the experiments were made by the Huangang Chemical Factory in Zibo, China. The resistivity was $0.45 \Omega \text{ cm}$, and the diameter of the CB particles ranged from 28 to 32 nm. The nitrogen Brunauer-Emmett-Teller (BET) surface area was $\sim 1080 \text{ m}^2 \text{ g}^{-1}$. The polypropylene (PP) used was obtained in pelletized form from the Sinopec Group (Nanjing, China). The melting point of the PP used was 165°C and its melt flow index was 12 g per 10 min.

Fabrication of composite pellets

CB particles were mixed with PP in a ME100LA mixer at a temperature of 190°C , and the concentration of CB particles was 25 wt%. The mixing time was 20 min, and the speed of the mixing blades was 200 r.p.m. Before mixing, the CB particles were chemically modified, which formed an active agent on the surface of the particles. The particles were then dried in a vacuum oven to improve their wettability with PP. Pellets were made using an SHJ35 twin-screw plastic pelleter.

Injection molding samples

Standard plastic tensile samples, shown in Figure 1, were injected with composite pellets. The injection pressure and packing pressure were changed to investigate the effect of processing parameters on the microstructure and conductivity of the samples. For all samples, the heating temperature of the charge barrel and the cooling time of moldings were kept constant. The temperature of the mold was 25°C for all experiments. The device used to control temperature during experiments was shown in Figure 2.

Microstructure analysis

The rectangular sample was cut into the shape of a standard tensile specimen, as shown in Figure 1. Next, milling was used to remove five layers from the top surface of the molding samples. The thickness removed with each layer was 0.1, 0.2, 0.4, 0.6 and 0.8, respectively. We defined the first and the second layers as the skin zone, the third and the fourth as the sub-skin zone and the last layer as the core zone, as shown in Figure 3. The size of the sample was $10 \times 10 \text{ mm}^2$. A Quanta FEG 250 Scanning Electron Microscope (FEI Company, Hillsboro, OR, USA) was used to observe the distribution of CB particles at the top of each layer in the PP matrix, as shown in Figure 3.

Measurement of resistivity

The volume resistivity in the thickness direction of each layer was measured at room temperature using a standard two-terminal DC resistor. The sample was $10 \times 10 \text{ mm}^2$ and was affixed to a slide using polyimide tape. Silver paste was used to ensure good contact between the sample's surface and the copper electrodes. The resistivity of three samples cut from each layer was measured, and the reported resistivity for each layer was a mean value of the three measurements. Volume resistivity (ρ) was calculated as follows,

$$\rho = RS/t \quad (1)$$

where R was volume resistance, S was the area and t was the thickness of the sample.

The first step was to measure the resistivity of pellets formed by extrusion. Then, the resistivity of each layer was measured to investigate the effect of processing on the microstructure and electrical properties of injection-molded, CB particle-filled PP.

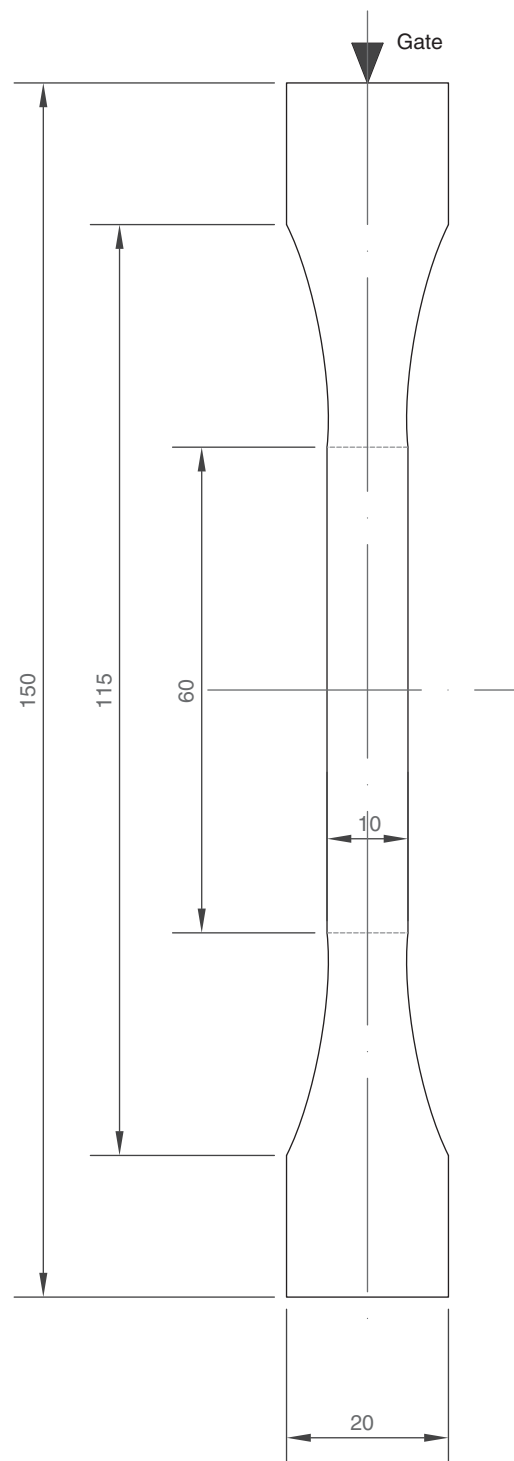


Figure 1 The size and shape of specimens used in the experiments. A full color version of this figure is available at *Polymer Journal* online.

RESULTS AND DISCUSSION

The skin-core microstructure for an injection molding has been studied by many researchers. It is known that the microstructure at the skin and sub-skin zones is always oriented in the flow direction of the polymer melt, and the microstructure at the core is more uniform because the shearing stress in the core area is much smaller than at the surface.

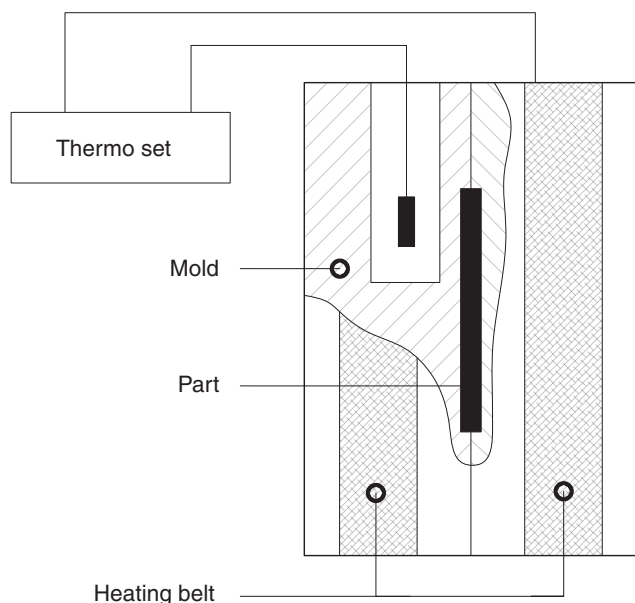


Figure 2 Schematic map of temperature control device on mold during the injection process. With this device, the mold was kept at the same temperature in order to investigate the effects of processing pressures on the microstructure and properties.

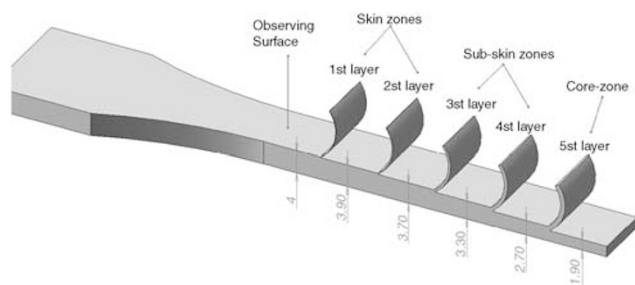
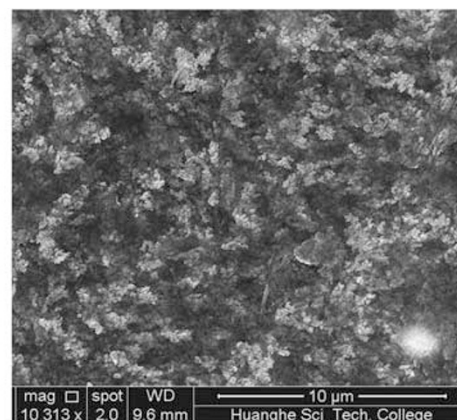
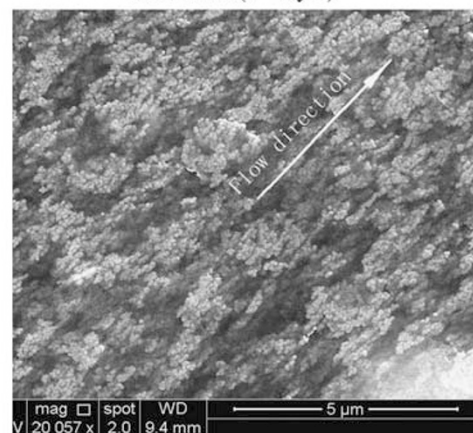


Figure 3 Schematic map to define skin, sub-skin and core zones of the molding, which were defined by measured electrical properties. The first and second layers exhibited similar values of resistivity, which was defined as the skin zone. Other zones were defined in the same manner. The skin zone is a highly resistive zone, the sub-skin zone has moderate resistivity and the core zone has low resistivity. A full color version of this figure is available at *Polymer Journal* online.

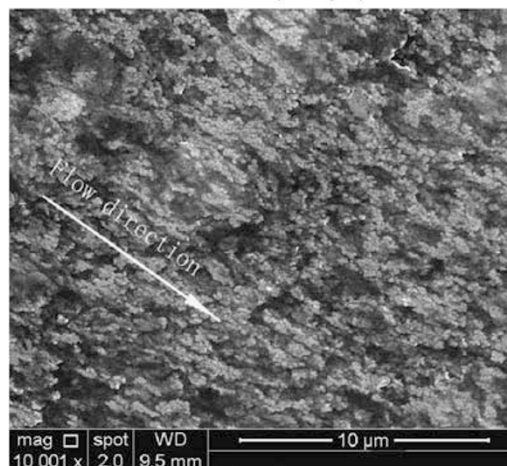
For tested CB particle-filled PP composites, we found that the orientation of CB particles in the matrix, shown in Figure 4, differed from that of injection-molded PP, especially in the core zone, where CB particles exhibited a highly oriented distribution and formed continuous conductive paths. During processing, CB particles moved in two directions. The particles moved in the flow direction of the melt and from the skin zone with high shearing stress to the core with low shearing stress. The results, shown in Figure 4, indicated that CB particles moved from the skin zone to the core. As a result, the skin zone was depleted of CB particles, which accumulated in the core zone because of self-agglomeration. The results also showed that a non-orientated distribution of CB particles formed in the skin zone because rapid cooling of the melt near the mold wall resulted in its solidification before orientation could occur. In the second layer of the skin zone, the resistance to migration of CB particles was less than in other zones because of oriented molecular tension. Hence, CB



Skin zone (2nd layer)



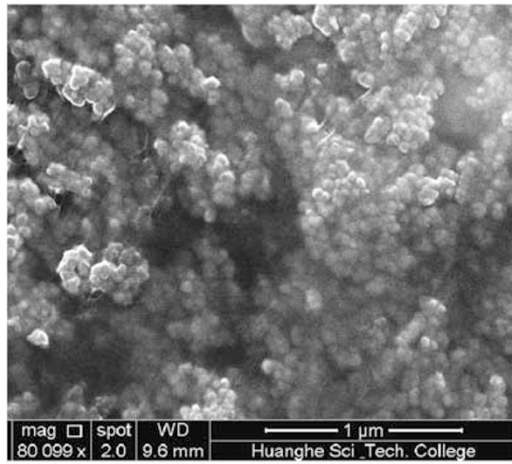
Sub-skin zone(3rd layer)



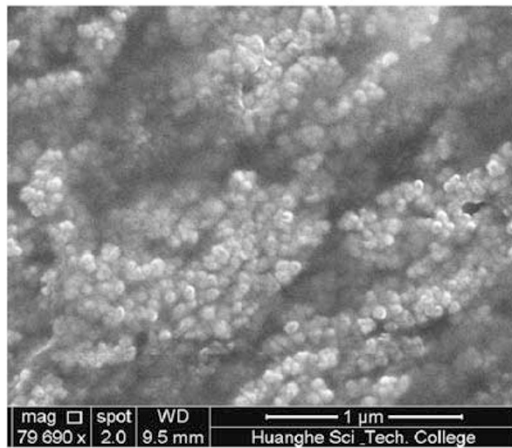
Core zone

Figure 4 The microstructures of different layers at injection pressure of 70 MPa and packing pressure of 50 MPa. The white particles denote CB particles; and the black, the matrix.

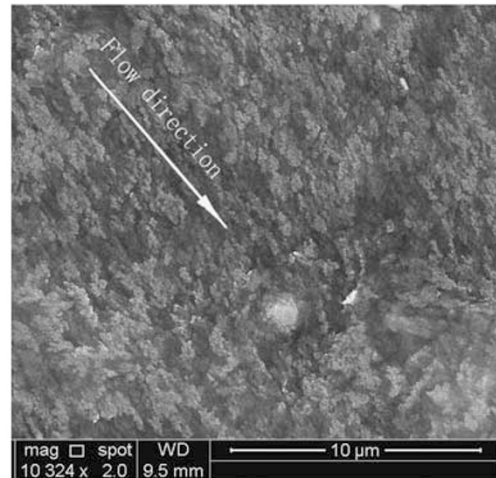
particles easily migrated from the skin zone to the core zone, which resulted in the formation of a highly conductive cluster in the core zone where the resistivity was less than in the skin zone. The results also proved that modified CB particles might self-agglomerate into highly anisotropic structures during processing because the immiscible particle core and grafted polymer surface attempted to phase separate but were constrained by chain connectivity.¹⁸ The cluster morphology



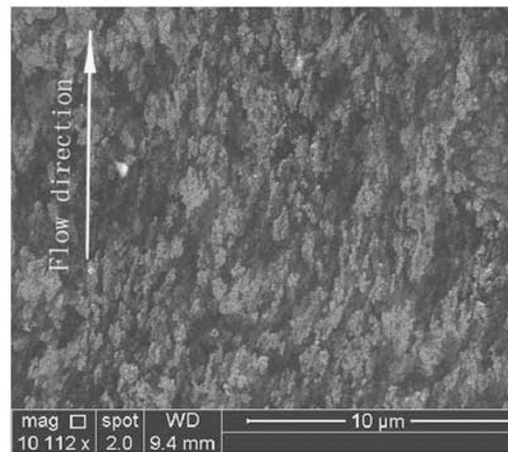
Skin zone (2nd layer)



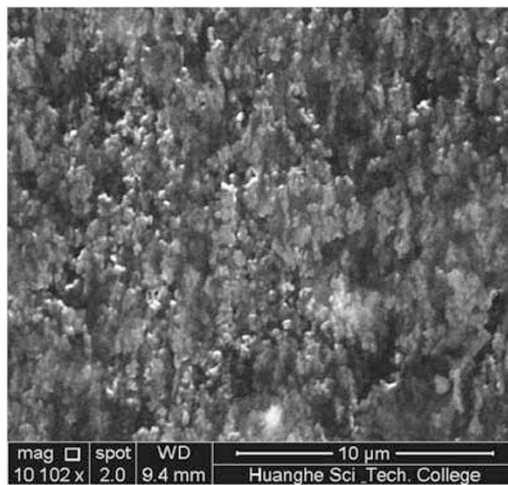
Sub-skin zone(3rd layer)



Skin zone (2nd layer)



Sub-skin zone(3rd layer)



Core zone

Figure 5 Morphology of CB particles at skin and sub-skin zones at injection pressure of 70 MPa and packing pressure of 50 MPa. The skin zone exhibited a different agglomeration of CB particles than the sub-skin zone because of a shearing effect.

of CB particles in different zones was observed with high magnification, as shown in Figure 5. It was shown that CB particles in the skin zone agglomerated into nearly spherical clusters and formed distinctly oriented morphologies in the sub-skin zone.

To investigate the effect of injection pressure on the microstructure and resistivity of the molding, another group of specimens was injected at a higher injection pressure of 110 MPa. The packing pressure was kept at 50 MPa. The microstructures of the different layers were shown in Figure 6.

As shown in Figure 7, because the flow velocity of the melt in the chamber increased along with the injection pressure, the migration of CB particles from the skin zone to the core zone was inhibited. This led to an increase in CB particles in the skin zone and better dispersion than the sample fabricated at an injection pressure of 70 MPa and a packing pressure of 50 MPa. Accordingly, the resistivity in the skin zone under these conditions was less than at low injection pressure. It could be speculated that the flow shear stress dominates the movement of CB particles in this zone at high injection pressure.

Because CB particles moved rapidly in the flow direction at higher injection pressures, the number of CB particles in the matrix decreased

Figure 6 Comparison of the microstructure of different layers at injection pressure of 110 MPa and packing pressure of 50 MPa. The effect of injection pressure on the distribution of CB particles in the matrix and the electrical property of the different zones are also shown.

in the sub-skin zone and core zone, which was verified by their measured densities. As a result, the resistivity of the sub-skin zone increased, but the resistivity decreased in the core zone, where a good

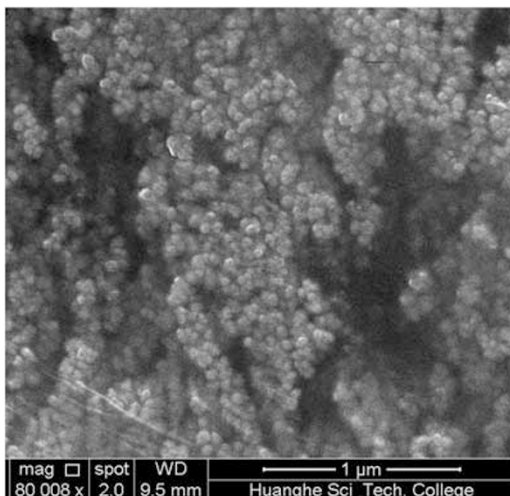


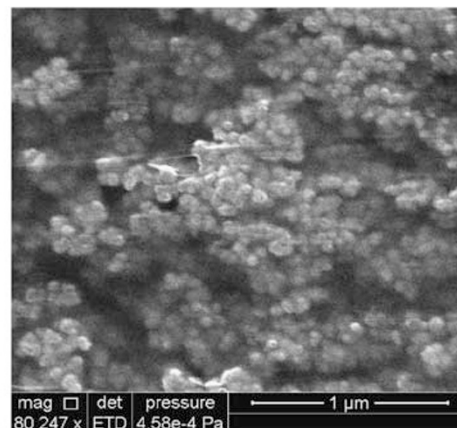
Figure 7 The agglomeration of CB particles in the skin layer under the higher injection pressure of 110 MPa and a packing pressure of 50 MPa.

conductive path was formed. Similar conclusions were obtained by repeating the experiments. The results might be relevant to post-filling during the packing process. Post-filling might increase the number of CB particles and improved their distribution in non-solidified zones. Because dispersed CB particles were capable of self-agglomeration, forming a clustered structure, a higher injection pressure was not always beneficial for decreasing the resistivity of the moldings when packing pressure was low. At high injection pressure, the thickness of the sub-skin zone with high resistivity was an important factor affecting the conductivity of the molding. It would be necessary to investigate further the effect of the thickness of different zones on the conductivity of the molding. The results also revealed that the number of CB particles in the PP matrix decreased with the decrease in packing pressure, especially in the sub-skin and core zones as shown in Figure 8. The resistivity of the molding had a noticeable increase at lower packing pressure. Because each layer experienced a different cooling rate and action of flow shear stress, the distribution and orientation of CB particles at different layers varied with processing conditions. As shown in Figure 8, the separation between CB particle clusters at both low injection pressure and packing pressure was larger than at high injection pressure and packing pressure, which led to an increase in the resistivity of the molding. These results indicated that the electrical properties of injection-molded CB particle-filled polymer might be controlled with processing conditions and might be predicted from the resistivity of each zone.

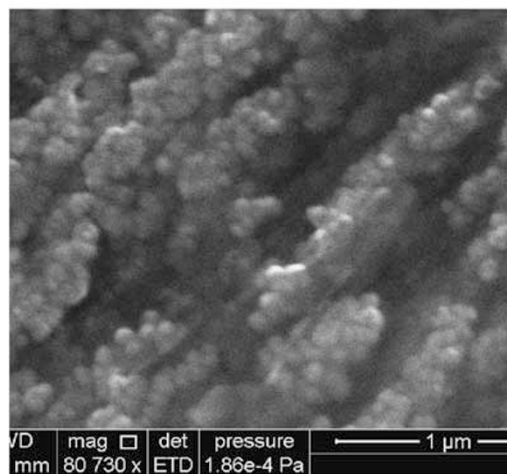
The resistivity of each layer under different processing conditions is shown in Table 1. The accuracy of each measurement was $\pm 1.5\%$. The results show that the resistivity of the skin zone was larger than that of other zones. For the skin zone, under the action of constant packing pressure, resistivity was reduced from 62 to 74% as injection pressure was increased from 70 to 110 MPa. If the injection pressure was held constant, the resistivity in the skin zone would decrease from 13 to 66% as the packing pressure was increased from 10 to 50 MPa.

At high injection pressure, the resistivity of the sub-skin zone was larger than for other zones. The results show that improvements in the electrical properties of the molding could be achieved with high injection pressure in conjunction with high packing pressure.

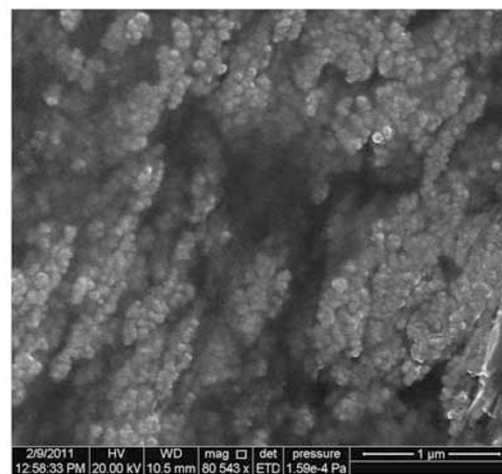
Based on the experimental results, the relationship between processing conditions and the resistivity of the different layers is shown in



Skin-zone(2nd layer)



Sub-skin zone(3rd layer)



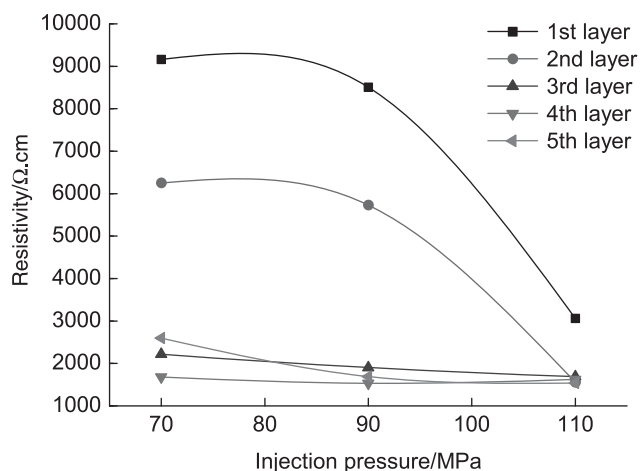
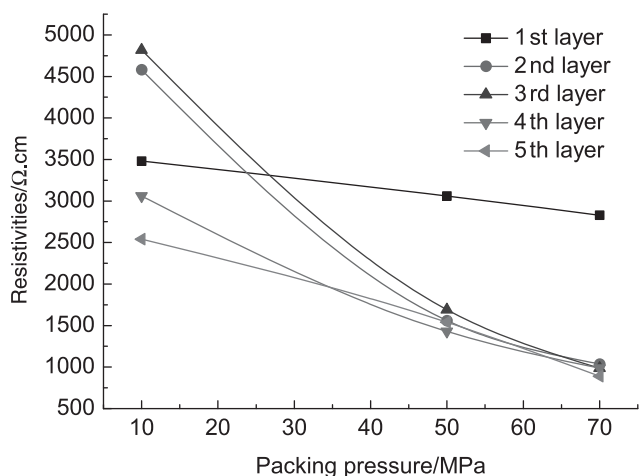
Core zone

Figure 8 The microstructure of different layers at injection pressure of 70 MPa and packing pressure of 10 MPa. The effect of packing pressure on the distribution of CB particles in the matrix and the electrical property of different zones at low packing pressure are shown. A band without CB particles was observed.

Figures 9 and 10. PP is a crystalline plastic. Because plastic is not a good thermal conductor, the cooling rate in the core zone is always slow, which leads to high crystallinity of the PP. Hence, apart from the

Table 1 Resistivity of each layer (10 Ω cm)

| Injection pressure (MPa) | Packing pressure (MPa) | Skin zone | | Sub-skin zone | | Core |
|--------------------------|------------------------|-----------|------|---------------|------|------|
| | | 1st | 2nd | 3rd | 4th | 5th |
| 70 | 10 | 1329 | 1184 | 1250 | 1218 | 401 |
| 70 | 50 | 916 | 625 | 222 | 168 | 260 |
| 110 | 10 | 348 | 458 | 482 | 465 | 254 |
| 110 | 50 | 306 | 156 | 169 | 162 | 154 |


Figure 9 The effect of injection pressure on the resistivity of each layer (packing pressure=50 MPa). A full color version of this figure is available at *Polymer Journal* online.

Figure 10 The effect of packing pressure on the resistivity of each layer (injection pressure=110 MPa). A full color version of this figure is available at *Polymer Journal* online.

action of low injection pressure combined with low packing pressure, the resistivity in the core zone was generally the smallest of all zones because CB particles were easily localized into the interface of different phases of the polymer.¹⁹ It is advantageous to conductivity that the CB particles are localized at the interface of different structures to act as conducting paths.²⁰ In the theory of crystallizing dynamics, dispersed

CB particles could act as nucleating additives and become nucleation centers leading to crystal growth in the process of crystallization, which took place during the cooling of a molten polymer sample. Changing the conductive path of an injection-molded CB particles/PP composite is more complex because the material experiences an inhomogeneous shear flow within a very short-time during processing.

At higher packing pressure, the resistivity of the skin zone was rapidly decreased with the increase of injection pressure. A comparison of the results at high packing pressure with those at low packing pressure showed that injection pressure had less influence on resistivity at the core than in other zones at low pressure.

The results revealed that high injection pressure combined with high packing pressure was advantageous to improving the electrical properties of the moldings. However, at lower packing pressure, the number of CB particles in the sub-skin zone underwent an obvious decrease, forming a band where the conductive path was not continuous, which would hinder conductivity. The conductivity of an injection-molded CB particles/polymer composite could be controlled by selecting processing conditions that would vary the thickness of different zones and vary the conductivity of the molding.

CONCLUSIONS

No skin-core microstructure was observed for an injection-molded CB particle/PP composite for which an oriented microstructure was formed not only at the sub-skin but also at the core. In three zones, the injection pressure and packing pressure had a different effect on the resistivity. The best processing condition for obtaining good electrical properties may be at high injection pressure combined with high packing pressure. High injection pressure alone will not improve the electrical property of the molding because of the discontinuous band of CB particles formed in the sub-skin zone and in the core zone. The number of CB particles in the matrix would decrease in the sub-skin and the core at high injection pressure combined with low packing pressure. High packing pressure would be beneficial for forming a good conductive path in the matrix and improving the electrical property of the molding if injection pressure is held constant.

CONFLICT OF INTEREST

The authors declare no conflict of interest.

ACKNOWLEDGEMENTS

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