

Morphology and Properties of Conductive Carbon/Polyolefins Composite

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ABSTRACT

Conductive polymer composite materials are fabricated by mixing high density polyethylene or polypropylene with conductive fillers. To overcome the deterioration in mechanical properties of carbon-polymer composites with high carbon loading, ethylene-propylene rubber is blended into the composites. The electrical and mechanical properties of the composite materials are studied. Because blending of polymeric phase with conductive particles influences the morphology which in turn affects the performance of the final composite, the morphology and microstructure of the blends and that of the composites are examined as well.

Key Words: conductivity, polyolefin, carbon black, composites, blends

INTRODUCTION

Conductive polymeric materials have attracted much attention in recent years due to the needs arising from their high electrical properties and electrochemical stability. The electrical resistance of most polymers is very high and conductivity probably results from the presence of ionic impurities. For a given composite polymer type, electrical conductivity is determined in most cases by the amount, type and shape of conductive fillers. Conductivity in such composites is due to the formation of a continuous network of filler particles through the polymer matrix [1]. Among the various combinations, carbon black/polymer composites have received more attention than others, as they are cheap, chemically resistant and easy to make

and process. In a previous paper [2] it was reported that conductive plastic materials with volume resistivity as low as $0.2 \Omega \cdot \text{cm}$ can be fabricated from mixtures of carbon black and graphite fibres. In the present paper the morphology and the microstructure of the composite are studied.

EXPERIMENTAL

Preparation of Composites

The following materials were used in the preparation of the composites:

Polymers: polypropylene (PP, propatene LZM60, ICI Chemical Co., Australia), high density polyethylene (HDPE, Hostalcn, Hoechst Ltd., Australia), ethylene-propylene rubber (EPR

Vistalon 404, Exxon Chemicals, Australia).

Conductive fillers: carbon black (Vulcan XC-72, Cabot Corp., USA), graphite powder (Lonza KS-2.5, Lonza Inc., USA) and graphite fibre (Kureha C-203s, 3mm, Kureha C-206s, 6mm, Kureha Co. Ltd., Japan, and FMI 3200 micron fibres, 6mm, Fibres Materials Inc., Maine, USA).

Metal: 100 mesh (150 micron) of brass mesh (Swiss Screen Pty. Ltd., Australia).

Preparation Procedure

Each grade of plastic was pre-mixed in a "Haake 600" internal mixer with the elastomer for 5 minutes followed by 10 minutes mixing with conductive powder. Graphite fibre was then added slowly for 20 minutes. The mixture was compression moulded with 250 kg/cm² pressure at 200 °C for at least 30 minutes. The composite sheet was placed inside the mould and the mould was heated up to 200 °C for 20 minutes. The mould was then cooled down rapidly.

Electrical and Mechanical Properties Measurements

ASTM D 991 (four-probe method) and ASTM D 638 (with Instron M1115) were employed for evaluating the electrical and mechanical properties of the conductive composite materials respectively. To evaluate the area resistance of the composites, the "two-plate" method was employed (as described in a previous publication [1]), which involved placing a copper plate above and below the composite sheet to be tested. These copper plates were compressed to a pressure of 50 g/cm². A DC current was then applied to the composite test sample through the copper plates. Potential drop values were measured on a digital Hewlett Packard (3465B) multimeter which was connected to the other two corners of the copper plates. Plotting the potential drop in Volts versus the current density in A.cm⁻² from the value of the slope, the resistance of the composite could be determined with units of Ω.cm².

SEM, FESEM, DSC and TGA Studies

To evaluate the surface microstructure of the

selected samples, morphologies of the blends and composites were characterized with a Cambridge 360 scanning electron microscope and a S-900 Hitachi field emission electron microscope.

Samples were cut at a temperature of around -150 °C in liquid nitrogen and the rubber particles were extracted for 5 minutes in boiling n-heptane vapour. The surface was then covered with a thin gold and chromium layer for SEM and FESEM, respectively. DSC and TGA studies were carried out with a Du Pont Instrument 910 differential scanning calorimeter and a Du Pont Instrument 951 thermogravimetric analyzer respectively.

RESULTS AND DISCUSSION

The Effect of Carbon Black Content

In previous publication [3] it was reported that the trend in conductivity with addition of conductive carbon black to the polymer is a non-linear relationship and it was observed that initially for up to 5 wt% carbon black the composite is not sensitive to loading but it is still as insulating as the polymer. In the present work, further investigation was carried out to obtain a better understanding of this behaviour. As can be seen from Figure 1 the carbon black particles (white spots) do not actually touch each other in this sample and the connections are via the polymeric matrix (gray portions). It has been suggested that [4] for transferring electrons through the polymer, there should be a distance of less than 10 nm between the particles. As seen in the sample of Figure 1 however, the average distance is close to 24 nm for 5% carbon loading. As the level of the carbon black additive increases, however, the inter-connection of carbon particles occurs (Figure 2) and at a critical level of conductive filler, a sharp fall of resistivity occurs with the conductivity increasing very rapidly. At this point, particles of filler come into intimate contact with each other resulting in formation of a continuous conductive network. This percolation level can be placed in the region of about 10 wt% carbon black. After

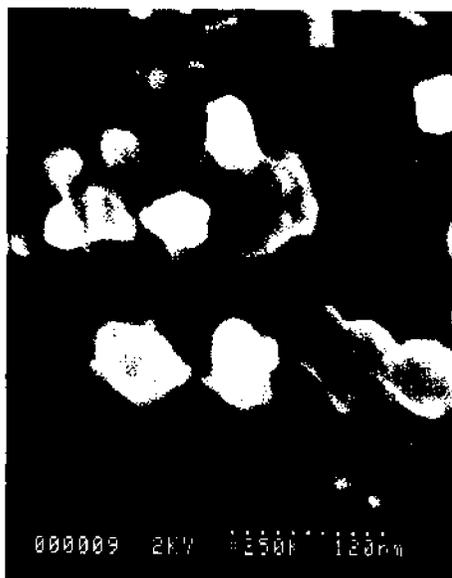


Figure 1. Electron micrograph of carbon black particles in the polypropylene matrix (95% PP + 5% carbon Black).

the first conductive network is formed, the conductivity of the mixtures again shows an increase with the growing filler content which can be rationalized in terms of an improved quality of the conductive network.

Thus it has been confirmed that, for the underloaded case, the carbon black particles are isolated to such an extent that electrical resistance is high while after a critical loading (more than 10%), carbon black particles form structures which provide an electrical network through the sample.

Further experiments showed that even lower resistivity could be obtained by increasing the conductive fillers. However, samples with more than 30% carbon black (overloading region) were difficult to mix since the resultant compound was in the form of a powder that would not flow. As seen in Figure 3 the melt flow rate of the composite was strongly dependent on filler concentration and the flowability was ensued above 20% conductive filler. The rapid decrease in



Figure 2. Electron micrograph of carbon black particles in the polypropylene matrix (90% PP + 10% carbon Black).

fluidity of the carbon black and polyolefin mixtures is attributed to their strong interaction [5].

The Influence of Graphite Fibre

The preliminary experiments showed that addition of the optimum amount of graphite fibre to the polymer/carbon black mixture results in higher conductivity and better mechanical properties [6]. The increased conductivity was attributed to a network-like structure formed by the graphite fibres and the carbon particles [3]. Further experiments have shown that the electrical conductivity of the composites varies significantly as a function of the ratio of the graphite fibre to carbon black. Figure 4 shows that a significant increase in conductivity obtained when the graphite fibre content was increased up to 20 wt% of the composite and reducing the ratio of graphite fibre to carbon black increases the volume resistivity of the PP composites (the total loading of conductive fillers was 40%, and only the ratio of

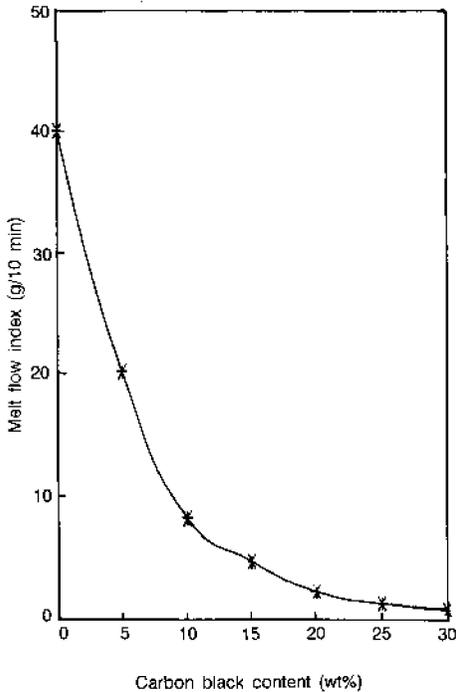


Figure 3. The influence of carbon black on the melt flow behaviour of the carbonblack/PP composite.

graphite fibre to carbon black was varied). On the other hand, increasing the graphite fibre/carbon black ratio above 1, again increases the volume resistivity of the composite. Thus it can be realized that the optimum combination of carbon black particles and graphite fibre results in a more effective contact and leads to a decrease in electrical resistivity.

The effect of graphite fibre type on the conductivity of the composite was also evaluated. Three types of graphite fibres, i.e. Kureha C-203s, Kureha C-206s and FMI 3200 micron fibres were used. As can be seen from Table 1, with the same loading of graphite fibres, Kureha fibres resulted in higher electrical conductivity. This experiment indicates that the properties of graphite fibres vary considerably from one source to the other. This might be due to the differences in the processing

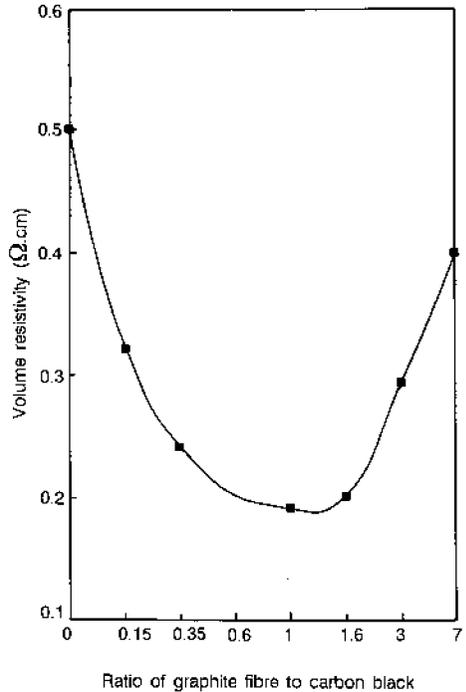


Figure 4. Effect of graphite fibre/carbon black ratio on volume resistivity of the PP composite.

methods and precursors used in manufacturing the various fibres which result in the different surface microstructure of the fibres. This would lead to a different degree of interaction with oxygen which in turn would affect the electrical properties of the fibres [7,8]. As can be seen from Table 1, the

Table 1. Influence of graphite fibre types and length on volume resistivity of composite (60% PP + 40% carbon black and graphite fibre).

Graphite fibre type	Length of fibre (mm)	Volume resistivity (Ω .cm)	
		10%GF	20%GF
FMI	6.0	0.92	0.51
	6.0	0.25	0.19
Kureha	3.0	0.43	0.24

Table 2. The influence of graphite fibre on volume and area resistivity of compound (60% PP + 40% conductive fillers).

Conductive filler	Sample thickness (mm)	$\Delta V/I$ (Ω)	Volume resistivity ($\Omega \cdot \text{cm}$)(mould plane)	Calculated area* resistivity ($\Omega \cdot \text{cm}^2$)	Measured area* resistivity ($\Omega \cdot \text{cm}^2$) (perpendicular plane)
20% CB + 20% GF	1.5	0.32	0.19	44.2	120.1
40% CB	2.0	0.62	0.50	86.2	85.0

* Area of sample = 138 cm^2

conductivity of the composite is also dependent on the length of fibre. The conductivity of the composite containing 6 mm fibres is higher than the composite with 3 mm fibres.

Table 2 shows that for samples with graphite fibre, the measured area resistivity is considerably greater than that calculated from the sample thickness and volume resistivity value. These results indicate that in the absence of graphite fibres, although volume resistivity of the composite dramatically increases, but area resistivity decreases. This shows that while carbon black particles are more efficient than graphite fibres in increasing conductivity of the composite in the perpendicular direction of the sheet, but the latter are more effective in increasing the conductivity parallel to the plane of the moulded composite sheets. This would be related to the high aspect ratio of the fibres. Aspect ratio is defined as the ratio of the length of a particle to its thickness which is typically around 1 and 20 for spherical black particles and fibres respectively. Thus the shape of the individual particle has a great influence on the conductivity of the composite. Furthermore, as seen in Figure 5, this can be also attributed to orientation of fibres during the compression moulding of the composite [1].

Effect of Polymeric Substrate Structure

As can be seen from Table 3, for the same conducting filler content, PP showed higher electrical conductivity than HDPE. The difference between the conductivity of the above mentioned polymers may be attributed to the microstructure of the polymer and properties such as viscosity,

crystallinity, interaction of polymer with carbon black and its wetting by the polymer. Poor wetting results in segregated filler distributions leading to fewer connections and lower electrical conductivity. Whether the filler for the polymer is a powder or fibrous, the contact between it and the polymer must be intimate and capable of remaining so even when the material is subjected to deformation [9]. As seen in Figure 6 poor wetting of filler by the polymer can result in formation of a gap between the graphite fibres and polymeric matrix which was observed in HDPE composites. On the other hand, in the case of PP, as seen in Figure 7, the graphite fibres are tightly held in the matrix, without any

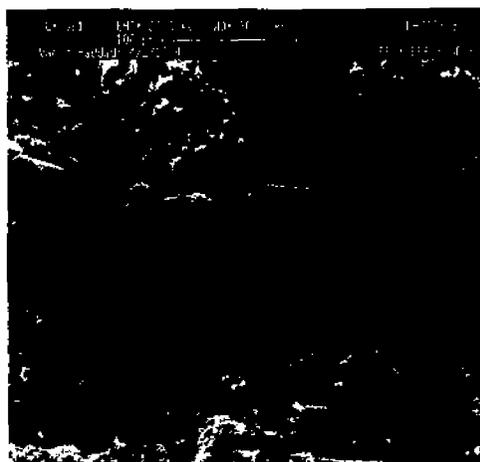


Figure 5. SEM cross-section micrograph of the orientation of graphite fibres during compression moulding of PP composite.

Table 3. Effect of plastic types on volume resistivity of composite (60% plastic + 20% carbon black + 20% graphite fibres).

Plastic type	Sample thickness (mm)	Volume resistivity ($\Omega \cdot \text{cm}$)
PP	1.17	0.19
HDPE	1.23	0.23

gaps due to differences in contraction of matrix and the fibre.

Further experiments showed that even lower resistivity can be obtained by increasing the conductive fillers. Increasing the proportion of carbon black however, resulted in a deterioration in the mechanical properties of the composite, i.e. both tensile strength and elongation decreased. To overcome this problem, a blend of plastic and rubber was used to improve the mechanical



(a)



(b)

**Figure 6.** SEM cross-section micrograph of formation of gap between graphite fibre and polymer (bar=3.35 μm).**Figure 7.** (a) SEM (bar = 1.34 μm) and (b) FESEM cross-section micrographs of carbon black/polypropylene composite bonding to the graphite fibre at various magnifications

Table 4. Mechanical properties of composites (40% plastic + 20% EPM rubber + 20% carbon black + 20% graphite fibres).

Plastic	% Elongation at break	Tensile strength (MPa)	Modulus of elasticity (GPa)
HDPE	2.0	10.0	0.5
PP	3.0	11.7	0.4

properties at high carbon loading [2]. A range of rubbers was blended with the plastic and it was found that EPM rubber to be the best rubber for this modification [1]. EPM rubber was thus employed in the present study to overcome this drawback.

Blends of PP or PE with EPR or different types of EPDM are of commercial interest. Homopolymers polypropylene and polyethylene have a tensile strength of 35 and 28 MPa respectively, and EP elastomer only about 8.3 MPa. Therefore, the primary determining factor of tensile strength is the amount of homopolymer in the blend. Addition of small to moderate amounts of EPDM or EPR to HDPE or PP dilute the small amorphous disperse phase, without fully affecting overall properties of the crystalline continuous matrix. Thus at high PP or HDPE content most properties tend to remain near those of the PP or HDPE. Table 4 shows the mechanical properties of the HDPE and PP composites modified with EPM rubber.

The addition of graphite fibre produced an opposite effect to that of the rubber on the yield stress and strain, decreasing the elongation at break significantly as illustrated in Figure 8 for a 40 wt% PP + 20 wt% EPR blend with 40 wt% conductive filler. Incorporation of carbon black into such a graphite fibre/rubber/polyolefin system, produced a combination of properties with more complicated behaviour. In fact, it should be noted that the interface between the polymer blend and the filler particles is crucial in determining the properties of the composite because at the interface the stress is transferred from the polymer to the filler and has a reinforcement role in the

composite as well.

It is generally accepted that the interaction between carbon black and rubber is both chemical and physical [10]. The distribution of carbon black in these blends was considered highly significant in the present study, since it has already been demonstrated that it can greatly influence the physical properties such as hysteresis and extrusion shrinkage [11]. In order to establish the distribution of the conductive filler in the blends under study, the rubber phase was etched by boiling n-heptane for 5 minutes. If there were equal partitioning of the conductive filler between the plastic and rubber phases, in the case of a mixture of 40 wt% plastic, 20 wt% rubber and 40 wt% conductive filler, a maximum up to 13 to 14 wt% conductive filler would be placed in the rubbery phase. Etching the rubber phase in a sample with the above mentioned composition revealed, however, that around 19 wt% conductive filler was distributed in the rubbery phase of the composite. It can thus be

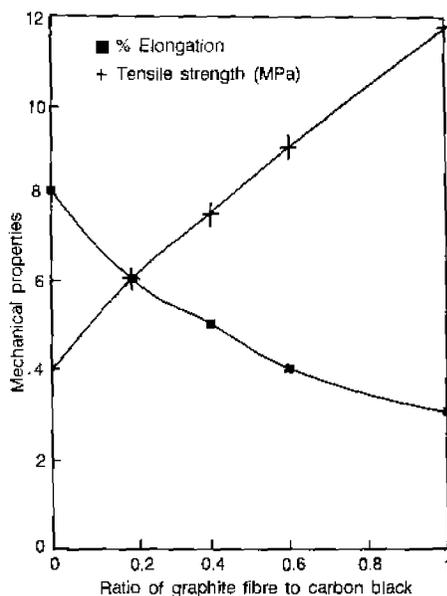


Figure 8. Effect of graphite fibre to carbon black ratio on mechanical properties of composite (40% PP + 20% EPR + 40% conductive particles).

concluded that conductive fillers will partition unequally between the polymeric phases and are concentrated more in the elastomeric phase than in the plastic matrix. According to two-phase conduction theory the reason for this behaviour lies in the interaction of several parameters which result from rubber characteristics such as surface tension and wettability of the rubber for conductive particles leading to a different contact area of the conducting fillers and affecting the electrical conductivity of the composite [12,13].

From a comparison of Figures 9(a) and 9(b) it can be realized that the conductive fillers are coated by the rubber phase (the rubber phase of the composite was slightly etched (1 minute) by boiling n-heptane). This coating of the conductive fillers by the insulating rubber phase may be one of the reasons for the higher resistivity of rubber/plastic/carbon black composite compared with the plastic/carbon black composite. Furthermore, the higher concentration of carbon black in the etched rubber phase may also be related to this phenomenon.

Although increasing the rubber content increases the impact properties of the composite, but it decreases the conductivity of the composite as seen in Table 5 for the PP/EPR blends. As it was mentioned previously, conductive fillers are concentrated more in the elastomeric phase than in the plastic matrix, and these results reveal that the role effect of rubber is very complicated.

In order to establish the effect of carbon black in the structure of the blend, the percentage crystallinity for a range of PP/EPR/carbon black composites was calculated by using the following equation [14]:

$$\% \text{Crystallinity} = \frac{\Delta H_f^{\text{observed}}}{\Delta H_f^0} \times 100$$

where $\Delta H_f^{\text{observed}}$ = heat of fusion of the sample and ΔH_f^0 = heat of fusion of 100% crystalline PP homopolymer.

A value of ΔH_f^0 of 209 J.g⁻¹ for 100% crystalline PP homopolymer was used for calculating the percentage of crystallinity [15].

Figure 10 shows a decrease in degree of



(a)



(b)

Figure 9. FESEM cross-section micrograph of EPR modified carbon/PP composite, (a) before and (b) after slight rubber etching.

Table 5. The influence of rubber content on volume resistivity of compound.

PP (wt%)	EPR 404 (wt%)	Carbon black (wt%)	Graphite fibre (wt%)	Volume resistivity ($\Omega \cdot \text{cm}$)
40	20	20	20	0.21
30	30	20	20	0.32
20	40	20	20	0.75

crystallinity with an increase in carbon black concentration. This phenomenon is explained by lower crystallization in the boundary layer [5]. Because carbon black is microcrystalline, it may act as a nucleating agent, affecting the size of the PP spherulites. In addition, the existence of only one peak at the melting point of the DSC curve of this carbon/PP/EPR composite indicates that the composite is homogeneous (Figure 11).

Morphology

In general, there are several conflicting theories on

these polyolefinic blends. Although Gisbergen et al. [16] reported that the blends are incompatible, Utracki suggested that the blends are compatible but immiscible [17]. On the other hand, Bartczak and coworkers believe that PP is partially miscible in EPR [18]. From literature sources on incompatible systems, it seems that their morphology is determined predominantly by the rheological factors of the components.

In the present study, the surface and cross-section topographies of the EPR/modified conductive PP composite were investigated by use of scanning and field emission scanning electron microscopies. For blends modified by black filler as black loadings were raised above 20 wt% no important information could be deduced from the optical-light microscopy. The morphologies of the blends are shown in Figures 12-13. It should be remembered that the morphology of the matrix itself is very complex, consisting of the amorphous and crystalline regions with complex supermolecular organization such as spherulites. A

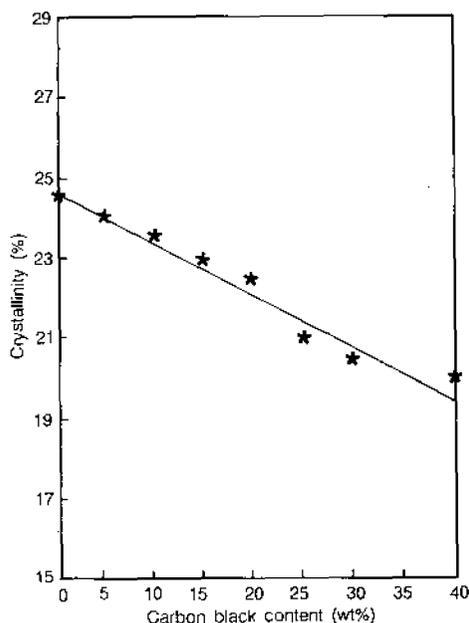


Figure 10. The influence of carbon black concentration on the degree of crystallinity of polypropylene.

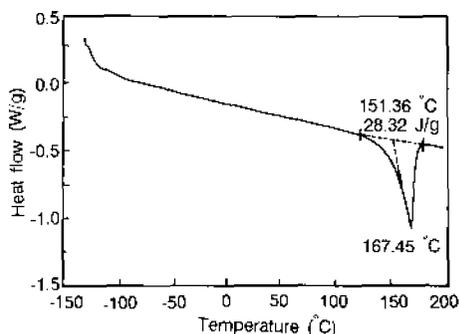


Figure 11. DSC analysis of EPR modified carbon/polypropylene composite.

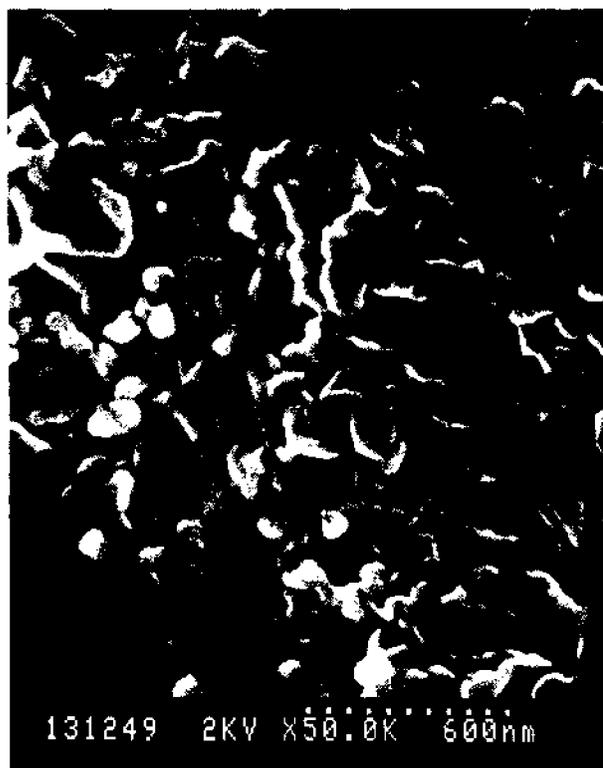


Figure 12. FESEM cross-section micrograph of carbon/PP composite.

micrograph of a binary blend of EPM copolymer and polypropylene is shown in Figure 12. The dispersion of rubber in the polyolefin matrix seems to be quite homogeneous and fine.

After etching the rubber by boiling n-heptane, a continuous structure of PP is observed in the cross-section of the sample seen in Figure 13 (the etching method was described in the previous paper [1]). For pure PP no material could be etched out by boiling n-heptane even after 20 minutes and measuring the weight loss of the composite confirmed that after 5 minutes, the rubber phase was completely removed. The white portions of the micrograph are polypropylene, and the dark voids (with average size of $3.0 \mu\text{m}$) are the areas where the EPM resided prior to extraction via the solvent. The polypropylene is clearly a continuous phase resembling an open-celled sponge with micron-sized porosity.

From the morphological studies of these materials, the existence of a high resistance polymeric skin was observed on the surface of the

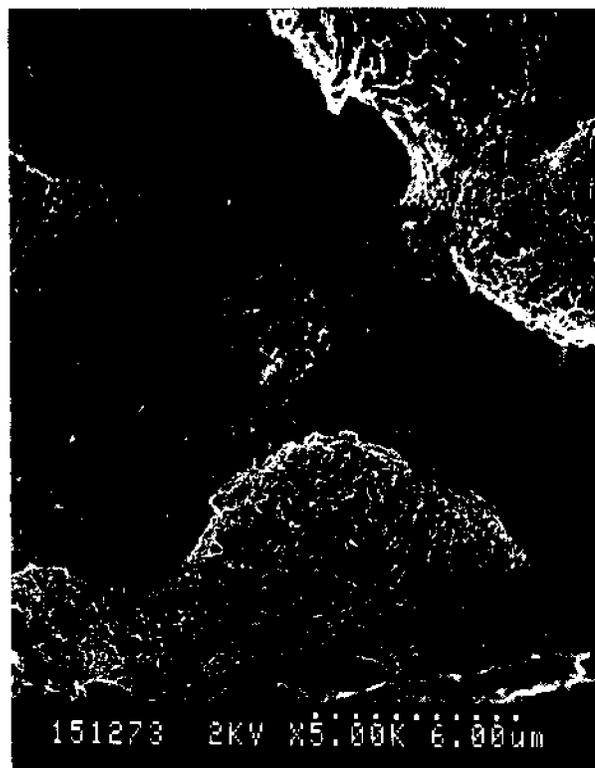


Figure 13. FESEM cross-section micrograph of EPR modified carbon/PP composite after rubber etching.

composite sheets. From Figure 14, something like a skin-core morphology can be seen where the composite has a smooth polymeric surface (with an average thickness of about 240 nm) with less carbon black particles. For further investigation thermal gravimetry analysis of the surface layer was studied using a TGA analyzer. As a quantitative technique TGA can be used to determine the composition of additives based on their volatility or degradation. Polymer matrix can be removed at high temperatures (i.e., 350–450 °C) and at high temperatures only inorganic fillers remain as residue. The use of N_2 atmosphere also could prevent the oxidization of the carbon filler. Figure 15 shows that the thermal destruction of the composite (polymeric fraction) begins about 320 °C and brings about an abrupt weight loss, down to practically 5.41% which indicates the amount of filler. In other words, although 30% carbon black was mixed with the polyolefin blend, only 5.41% filler remains in the surface layer of the composite.



Figure 14. FESEM cross-section micrograph of carbon/PP composite.

Thus it can be concluded that in order to reduce the contact resistance between the composite substrate and a current collector, the metal must penetrate into the bulk of the composite where there are more conductive particles and consequently, the electrical conductivity of the electrode can increase. A metal mesh would thus be more appropriate than a metal sheet for making electrical contact to this type of material.

CONCLUSION

The present investigation has revealed that up to 5 wt% carbon black, the carbon/polymer composite material is not very sensitive to loading and is still as insulating as the polymer. As the level of the carbon black increases, however, at a critical level (around 10 wt%) a sharp fall in resistivity occurs and the conductivity increases very rapidly. On the other hand, composites with more than 35 wt% carbon black are very brittle and with

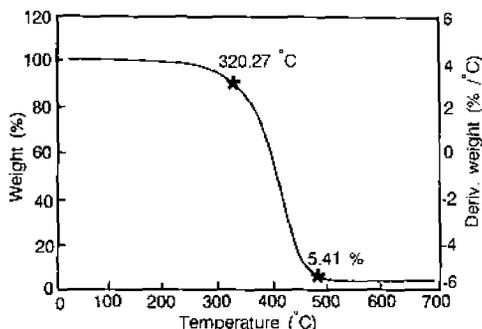


Figure 15. Thermal gravimetry analysis of surface layer of EPR modified carbon/PP composite.

more than 40 wt% carbon black are difficult to mix since the resultant compound is in the form of a powder that would not flow. A rubber blended polyolefin composite is thus developed to overcome the problem of poor mechanical properties at high carbon loading.

SEM studies revealed 2 phases in the rubber toughened polyolefins in terms of a continuous phase consisting of plastic, and a semidiscontinuous phase consisting of rubber. The conductive filler is shown to be strongly bound in the polymeric systems and partition unequally between the phases. In addition in blends of rubber/polyolefin materials, the carbon black is bonded to the elastomeric phase with less filler residing in the plastic phase. However, depending on processing conditions, the characteristics of the composite vary considerably.

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REFERENCES

1. Haddadi-Asl V., Kazacos M. and Skyllas-Kazacos M., *J. Appl. Polym. Sci.*, **57**, 1455, 1995.
2. Zhong S., Skyllas-Kazacos M., Kazacos M. and Haddadi-Asl V., *International Patent*, WO 94/06164, 1994.
3. Haddadi-Asl V., Kazacos M. and Skyllas-Kazacos M., *J. Appl. Electrochem.*, **25**, 29, 1995.
4. Scarisbrick R. M., *J. Appl. Phys.*, **6**, 2098, 1973.
5. Petrovic Z. S., Martinovic B., Divjakovic V. and Budinski-Simendic J., *J. Appl. Polym. Sci.*, **49**, 1659, 1993.
6. Haddadi-Asl V., Kazacos M. and Skyllas-Kazacos M., *Proceeding of the Ninth Australian Electrochemistry Conference*, Wollongong, New South Wales, Australia, 64, Feb.1994.
7. Thrower P. A., *The Electrochemistry of Carbon*, Electrochem. Soc., Pennington, NJ, USA, 40, 1983.
8. Gulden T. C., Jenkins R. G., Otake Y. and Scaroni A. W., *Proceeding of the Workshop on the Electrochemistry of Carbon*, Cleveland, Ohio, The Electrochem. Soc., Proceedings **84-5**, 61, August, 1983.
9. Wright W. M. and Woodhan, G. W., *Conductive Polymers and Plastics*, Margolis J. M. (Ed.), Chapman & Hall, 119, 1989.
10. Kraus G., *Reinforcement in Elastomer*, Wiley, New York, 1965.
11. Sincar A. K., Lamond T. G. and Penter P. E., *Rubber Chem. Technol.*, **47** 48, 1974.
12. Bueche F., *J. Appl. Phys.*, **43**, 4837, 1972.
13. Bueche F., *J. Appl. Phys.*, **44**, 532, 1973.
14. Choudhary V., Varma H. S., and Varma I. K., *Polymer*, **32**, 14, 2534, 1991.
15. Greco R., Martuscelli E., Ragosta G. and Yin J., *J. Mater. Sci.*, **19**, 1690, 1988.
16. Gisbergen J. G. M., Meijer H. E. H. and Lemstra P. J., *Polymer*, **30**, 2153, 1989.
17. Utracki L. A., *Polymer Alloys and Blends, Thermodynamics and Rheology*, Hanser, Munich, 1989.
18. Bartczak Z., Galeski A., Martuscelli E. and Janik H., *Polymer*, **26**, 1843, 1985.