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Electrical and Mechanical Properties Of Conducive Carbon Black/ Polyolefin Composites Mixed With Carbon Fiber

by

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ABSTRACT

The electrical conductivity of polymers can be increased by the addition of conductive fillers, including forms of carbon fibers and carbon black . The resulting composites can be used in applications where metals have typically been the materials of choice. The advantages of using these materials include lighter weight, resistance to corrosion, and the ability to be readily adapted to the needs of a specific application.

One of the most significant applications for conductive polymer composites are conductive carbon-polymer composite electrodes. As many properties such as conductivity, mechanical integrity, low permeability, electrochemical activity and stability in the electrolytes are required of materials to be used as electrodes, so " material selection" plays a crucial role in fabricating these materials.

In this work it was found that high density polyethylene (HDPE) / ethylene-propylene-diene monomer (EPDM) blend ratio (70/30) has lower percolation threshold and volume resistivity than individually carbon black filled HDPE and EPDM due to "double percolation" effect. Carbon fibers were also added to the polymer-carbon black mixtures to enhance the conductivity and mechanical Properties. The electrical conductivity of composites with different ratios of carbon black (CB) content to carbon fiber (CF) content was studied. The CB content is the main factor to determine the resistivity of the composites filled with CB and CF.

Mechanical properties, including tensile strength, elongation at break and impact strength of the conductive composites were evaluated.

The results showed that incorporation of CB and CF in the composites will enhance tensile strength, but decrease elongation at break and impact strength of the composites. In mechanical properties, CF content has a greater effect than CB content. From the comparison of the resistivity and mechanical properties of the composites filled with CB and CF with that of the composites filled with CB only, it is concluded that using CF as a substitute for part of the CB in CB-filled composites can enhance electrical and mechanical properties.

INTRODUCTION

Carbonaceous fillers are regularly employed in the production of polymer composites to enhance electrical conductivity and mechanical properties, as well as to maintain light weight and corrosion resistance. Conductive carbonaceous fillers of current commercial relevance include carbon black (CB), graphite(G) and carbon fiber(CF), which differ greatly in both structure and form.

Conductive polymer composites are used in a wide variety of industrial application such as battery and fuel cell elcetrodes, antistatic media and corrosion-resistant materials. Consider, for example, the utility of CB particles, which have been routinely added to polyethylene (PE) and other polymers over the past quarter century for four main purpose: improved electrical conductivity, mechanical properties ,color and UV stability [7,8]. For a given polymer composite, the electrical conductivity is determined in most cases by the amount and type of the conductive additives. According to the conduction theory of two phase systems, the conductivity of a composite is dependent on the type, shape and content of conductive fillers [1,2].Conductivity in such composites is due to formation of a continuous network of filler particles through the Polymer matrix[3].

An indication of the exacting requirements of an ideal filler for a conductive composite may be obtained from the following properties: high electrical conductivity, maximum improvement of the desirable physical and mechanical properties of the plastic compound, good dispersion characteristics, availability in controlled particle size, low specific gravity and density, low moisture adsorption, non-inflammability, low cost and good availability. The properties of the filler that play a significant role in determining the conductivity of the composite include the filler type, size, shape, and orientation within the matrix. Different forms of carbon generally have different microstructures and, therefore, will affect electrical conductivity in different ways.

Clingerman[4] has shown that the shape of the filler alters the conductivity. For spherical particles, smaller particles have been reported to lower the percolation threshold and for fillers with an aspect ratio(length/diameter) greater than 1, larger aspect ratios and a broader range of aspect ratios will lead to lower percolation threshold [5,6].The previous works have addressed polymer composites containing a single filler, mostly CB. This is due to the cost, small particle size (high surface area) and aggregate behavior of CB, the latter two of which are responsible for the relatively low loading levels needed to achieve desired conductivities. Therefore, in this study, we used carbon black as a conductive filler in HDPE matrix. One of the most exciting developments in the design of a composite with low percolation threshold concentration (PTC) involves the use of immisible polymer blends in which the conductive particles selectively reside in one of the polymer phases or along the interface [9,10].Over the past decade, several studies have investigated polymer blends filled with CB [11,12].As far as we are aware, Asai and his coworkers[13] have reported the first use of a polyethylene blend as the matrix of a conductive polymer composite. Their analysis of an immisible blend composed of high density polyethylene (HDPE) and polypropylene (PP) clearly demonstrates that CB particles predominantly locate in the HDPE phase of the blend. Morever, localization of CB in the HDPE phase induces a much lower PTC than that exhibited by either of the constituent polymers [14].So, in this study we used HDPE blended with ethylene propylene diene monomer(EPDM) as the matrix to enhance the electrical properties and also to improve impact strength and elongation at break. Tensile strength of the composites will be reduced by adding the EPDM rubber to the composite and in the other hand, it is difficult to prepare well-dispersed polymer/CB composites containing more than 30wt% CB with simple mixing techniques. To overcome these limitations we prepared composites with mixtures of CB and CF using conventional mixing and molding processes. In these samples, the CF provides charge transport over large distances, whereas the CB particles serve to improve interaggregates and interfiber contact. Composites with different ratios of HDPE/DPDM blend containing mixtures of CB and CF have been prepared. The electrical conductivity and mechanical properties of these conductive polymer composites have been examined as functions of rubber content, filler type, composition and content ratio.

EXPERIMENTAL

Materials

The following materials were used in the preparation of the composites: High density polyethylene (HDPE 5218 EA, Arak Petrochemical Co.), Ethylene-propylene diene monomer(Vistalon 7500), Carbon black (CB, printex XE2-B, Degussa-Huls Co.) and pitch-based chopped carbon fiber (Tensile strength :600 Ksi , Elong. (%) :1.76 , Size level (%) :1.3 , Density (g/cc) : 1.75 , Resistivity (Ohm.cm) :$1.5 * 10^{-3}$, Toho Co.,Japan).

Preparation

The HDPE, EPDM and fillers spread in a 100r100 mm^2 metal picture frame mold with a thickness of 2 mm. The mold was placed in a hydraulic press and heated to $190^{\cdot c}$ .A pressure of 230 kg/cm^2 was applied and held for 3 min. to completely melt the matrix. The mold was then cooled by circulating cold water through the platens.

Characterization

The electrical resistivity of the molded films was measured at ambient temperature according to ASTM D-991 using the four-point probe technique. The median value for the three measurements was reported as the volume resistivity. Tensile strength and elongation at break were measured according to ASTM D-638 with jaw seperation speed of 50 mm/min. and impact strength of the samples was measured according to ASTM D-256(Izod type specimens) using a U-F Impact tester.

RESULTS AND DISCUSSION

Electrical Resistivity

Conductive filler effect

To evaluate the filler effect on the resistivity of the composites, two procedures were employed including:

A)Evaluation of the composites resistivity in constant total conductive filler content. B)Evaluation of the composites resistivity when a filler content is fixed and another one is changed. The first measurements were carried out for total filler contents of 20 wt%, 30wt% and 40 wt% .The results are shown in Tables 1,2 and 3.

For more accurate comparison between the resistivity values of different mixtures, the results of the tables have been plotted in a unique graph and is shown in Figure 1.

The results in the tables show that in a constant filler content combination of the conductive fillers induces a much lower volume resistivity than that exhibited by either of the constituent fillers. Addition of CF to HDPE/EPDM/CB composites increases the electrical conductivity due to the bridging of uninterrupted length of the conductive paths and the strength of the percolated filler network and, hence, the level of conductivity.This synergistic effect have been reported in many other studies[4,15,16]. As shown in Figure1 with increasing the total filler content the resistivity of the composite will be reduced . The general theory to explain the conduction mechanism of fibers or particle-filled polymer composites is the“ theory of conductive paths”[17,18] , which suggests that it is the existence of conductive paths (fibers or partice contacts) that results in the conductivity of the composites. With increasing of the content of the fibers or the particles, conductive paths among the fibers or the particles increase, and the avarage distance between the fibers or the particles becomes smaller; thus, the resistivity of the composites decreases. An other feature evident in Figure 1 is that for the same filler content, the greater CB proportion in the fillers, the lower is the resistivity of the composites, whichever total filler content was investigated. But if the content of the CB is filled, a conductive network has been formed in the composites; then, increasing the content of CB can only slightly increase the conductive paths. The other way to evaluate the fillers effect on the composite resistivity, is investigation of the effect of increasing each filler while an other filler content retains constant. Table 4 shows the resistivity values of composites with CB content when CF content is fixed on 5wt%. Table 5 shows the variation of the resistivity of the composites with CF content when CB content is fixed on 5 wt%.

Therefore, for the composites mixed with CB and CF, it can be concluded that if one of the filler contents (CB or CF) is fixed, increase of the content of the other can directly lead to a decrease of the resistivity of the composites. A comparison of the resistivity levels and the slope of the curves in figure 2 indicates that the effect of the rsistivity of the composites with CB content if CF content is fixed is greater than that with CF content if CB content is fixed.

From all the discussions above, it can be concluded that the main factor to determine the conductivity of the HDPE/EPDM composites mixed with CB and CF is the content of CB. These results are not unexpected, as this particular material was chosen specifically because of its ability to impart electrical conductivity to a matrix material. This is mainly due to small size and high surface area of the carbon black particles. Clingerman[4] has also investigated the conductivities of CB,CF and graphite filled nylon 6.6 and polycarbonate composites and reported that whichever matrix is used the CB has the higher effect and makes a larger change in electrical conductivity among other fillers.

Effect of EPDM Rubber

To evaluate the effect of EPDM content on HDPE/EPDM/CB composites , different mixtures of HDPE and EPDM with 5 wt% CB were prepared and the resistivity results are shown in table 6.

According to the data in Table 6, the resistivitis measured from these composites are sensitive to blend composition. Increasing the EPDM content in the blend will lead to the decrease in volume resistivity and after reaching to a specified content then resistivity increases as the concentration of EPDM is increased further .

In accordance with the results of chan et al. [19], the higher viscosity of EPDM is anticipated to promote filler localization at the HDPE-EPDM interface, whereas the lower viscosity of HDPE may help to connect CB channels throughout the entire composite volume. Thus, a combination of the distinctly different melt-flow properties of these polymers may synergistically achive higher Conductivity than that of the constituent polymers. In one article by sumita etal. dispersion of carbon black and electrical conductivity of polymer blends were discussed. There are two Types of heterogeneous distribution of carbon black in filled Polymer blends. One is predominantly distributed in one phase of the blend, and the other is distributed concentratedly at the interface of two polymers. If carbon black is distributed at the interface, the envelope formation of CB particles around the dispersed phase makes the conductive paths more effective than the single matrix.

On the other hand, if carbon black is distributed in one phase of the blend, the electrical conductivity of CB filled polymer blends is determined by two factors. One is the concentration of CB in the filler rich phase, and the other is the structural continuity of this phase.

Several different polymer blends composed of HDPE filled with CF have also been examined by Zhang et al. [21,22]. Their results reveal that composite conductivity depends on the occurrence of double percolation, which refers to the percolation of CF in the HDPE phase and continuity of the HDPE phase in the blends.

Therefore the reduction in composite resistivity with respect to increasing EPDM concentration is attributed to the selective localization of CB particles in the amorphous phase of HDPE matrix and double percolation phenomenon. The schematic view of the blend morphology is illustrated for three different blend compositions at constant filler concentration in Figure 3.

In blends with a low EPDM content [Fig.3(a)], EPDM-rich regions are dispersed within a continuous HDPE-rich matrix. Because the melt viscosity of EPDM is higher than that of HDPE, the filler particles are expected to reside almost exclusively in the continuous HDPE-rich matrix. As the concentration of EPDM increases [Fig.3(b)], the volume of the HDPE-rich matrix available for filler particles to occupy decreases, resulting in a greater concentration of conductive elements within continuous HDPE-rich channels. Therefore much more effective conduction paths will be produced and as a result the volume resistivity will be decreased. As the composition of EPDM is increased further [Fig.3c], the filled HDPE-rich regions become increasingly discontinuous due to volume exclusion, therefore the second factor for double percolation will be excluded and results in a net increase in composite resistivity.Thongruang and his coworkers have also been reported the same results for the HDPE/UHMWPE blends filled with different carbonaceous fillers by variation in the blend compositions.[16]

Mechanical Properties

Incorporation of carbon fillers into the mixtures of HDPE and EPDM produces a combination of properties with complicated behavior. Addition of CB particles to the polymer blend, will change the material behaviour to that of a stiff or brittle material. As the amount of the CB particles increases in the matrix, the filler networks may lead to trap some portion of polymers inside themselves and this will increase the effective volume ratio of the solid particles in the composite. In the other hand, polymer- filler interaction may result in the absorption of the polymer molecular chains on the filler surface and decreases the movement of those parts of the polymer chains. As a result, the polymer viscosity and modulus and tensile strength will be increased while elongation at break and impact strength will be decreased. 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. To evaluate the mechanical properties of the composites, the same mixtures as the mixtures of conductivity tests were prepared. That is the investigation of the mechanical properties with each filler content while another one is fixed, was carried out and the results are shown in Figures 4,5,6,and 7.

As we know, impact strength of the thermoplastic materials is a criteria for their toughness. One of the most useful methods for converting brittle polymers into materials with high impact strength, is through adding some rubbers to them. But for producing a high impact strength blend three conditions have to be met including: a)The glass-rubber transition of the rubber must be below the test temperature. b)The rubber material should be dispersed inside the brittle polymer. c) There should be proper adhesion between two phases.

When EPDM rubber is added to HDPE matrix, not only it improves the electrical conductivity of the matrix polymer, but also it increases the impact strength and elongation at break of the HDPE matrix. But incorporation of the carbon fillers to the matrix has an inverse effect on it. It means that high strength particles or fibers will change the matrix behaviour into a rigid material and as a result, the impact strength of the composite will be decreased (Figures 8 and 9).

From the above figures, It can be conclude that, for the composites mixed with CB and CF , if one of the filler contents (CB or CF) is fixed , increase of the content of the other, can directly lead to an increase of the tensile strength and decrease of elongation at break and impact strength of the composites .Withal the results show that the tensile strength, elongation at break and impact strength of the composites with CF content if CB content is fixed is greater than that with CB content if CF content is fixed. Thus, the main factor to reinforce the composites mixed with CF and CB is the content of CF. This is because of the higher strength of the carbon fibers and formation of a strong structure among total volume of the composite. These results are expected because the polymer matrix can transfer the stress more easily to the carbon fibers that have aspect ratios more than 1 and carbon fibers play the reinforcement role much better.

CONCLUSION

From the discussion above, the following conclusions can be made:

The resistivity of the composites filled with CF,CB or both CF and CB decreases with increase of the filler content. For the same filler content, the greater the CB proportion in the fillers, the lower the resistivity of the composites.

Incorporation of the EPDM rubber into the composites will enhance the electrical properties up to a specified concentration of the rubber that it seems at that concentration the phase inversion is occurred. In the other hand EPDM rubber will improve the impact strength and elongation at break of the composites, and will change the composite behaviour to that of a tough material.

Tensile strength and modulus of the composites filled with CB and CF increases with increasing each of filler contents but impact strength and elongation at break will be reduced. The comparison of the mechanical properties shows that carbon fibers have a much more reinforcement role in the composites.

As composites with more than 30% carbon black are very brittle and difficult to mix, using CF as a substitute for part of CB in CB-filled composites can decrease volume resistivity by a synergistic effect along with an improvement in mechanical properties of the composite.

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CB Content (%)	CF Content (%)	Volume Resistivity (Ω.cm)
20	-	2.72
-	20	15.3
5	15	0.86
15	5	0.55

Table 1. Variation of the Resistivity of the Composites Containing 80% Polymer (HDPE/EPDM : 70/30) and 20% Conductive Filler

CB Content (%)	CF Content (%)	Volume Resistivity (Ω.cm)
-	30	1.13
5	25	0.7
10	20	0.38
15	20	0.38
15	15	0.371
20	10	0.362
25	5	0.35

Table 2. Variation of the Resistivity of the Composites Containing 70% Polymer (HDPE/EPEM: 70/30) and 30% Conductive Filler

CB Content (%)	CF Content (%)	Volume Resistivity (Ω.cm)
10	30	0.23
20	20	0.2
30	10	0.13

Table 3. Variation of the Resistivity of the Composites Containing 60% Polymer (HDPE/DPEM: 70/30) and 40% Conductive Filler

CB Content (%)	Volume Resistivity (Ω.cm)
10	2.4
15	0.55
20	0.42
25	0.35

Table 4. Variation of the Resistivity of the Composites with CB Content when CF Content is Fixed 5 wt%

CF Content (%)	Volume Resistivity (Ω .cm)
10	2.6
15	0.86
20	0.79
25	0.7

Table 5. Variation of the Resistivity of the Composites with CF Content when CB Content is Fixed 5 wt %

HDPE Content (%)	EPDM Content (%)	Volume Resistivity (Ω .cm)
90	10	6.0r10^{2}
70	30	4.2r10^{2}
42	55	3.0r10^{2}
40	60	1.6r10^{6}

Table 6.Variation of the Resistivity in HDPE/EPDM Mixtures Filled with 5wt% CB

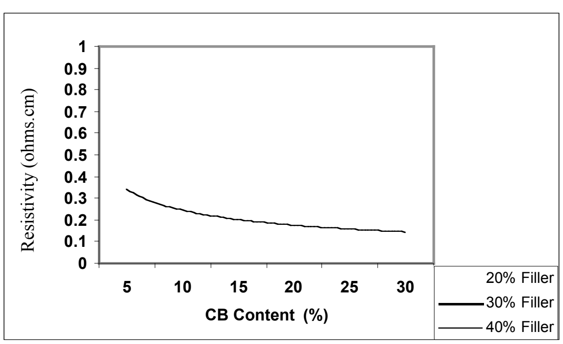

Figure 1. Effect of CB content on the volume resistivity of the HDPE/EPDM/CB/CF composites containing total filler contents of 20wt% , 30wt% and 40wt%.

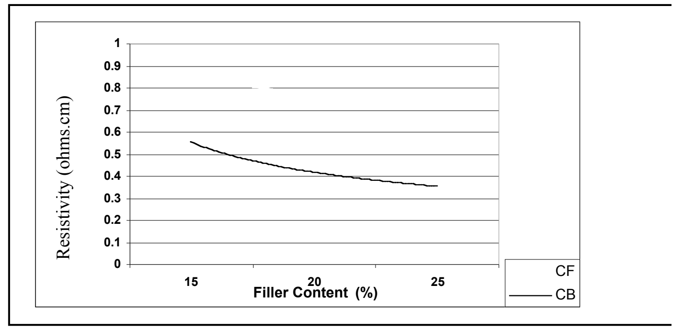

Figure 2 . Variation of the resistivity of the composites with each filler while another filler content is fixed 5wt%.

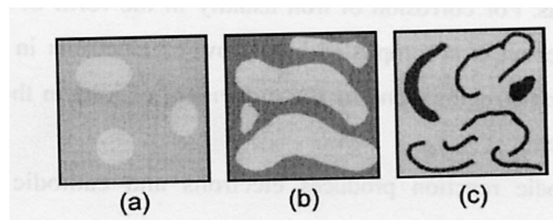

Figure 3. Illustration of volume-exclusion effect in HDPE/EPDM/CB ternary composites at a constant filler loading level.

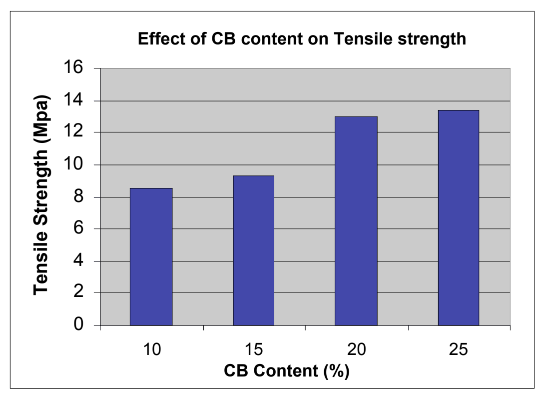

Figure 4.Variation of the tensile strength of the composites with CB content when CF content is fixed wt 5%.

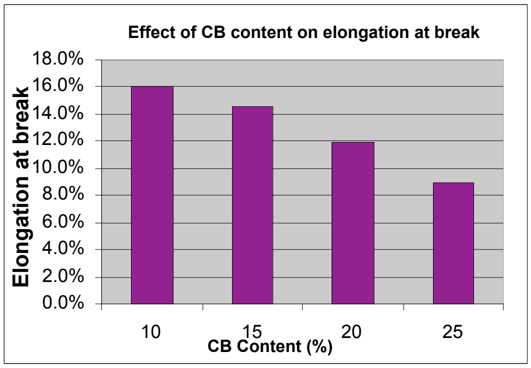

Figure 5.Variation of the elongation at break of the composites with CB content when CF content is fixed 5wt%

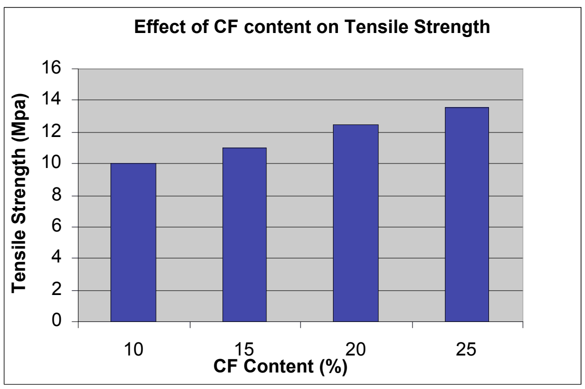

Figure 6.Variation of the tensile strength of the composites with CF content when CB content is fixed wt 5%.

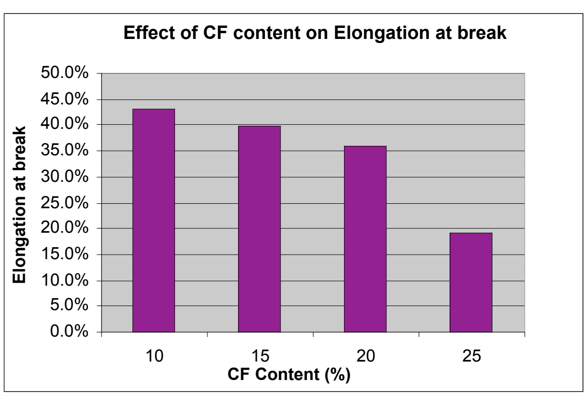

Figure 7.Variation of the elongation at break of the composites with CF content when CB content is fixed wt 5%.

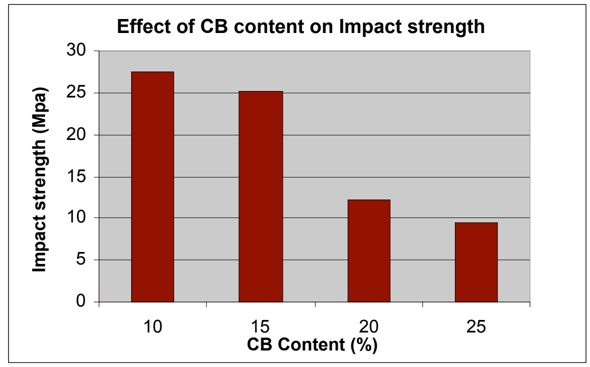

Figure 8.Variation of the impact strength of the composites with CB content when CF content is fixed wt 5%.

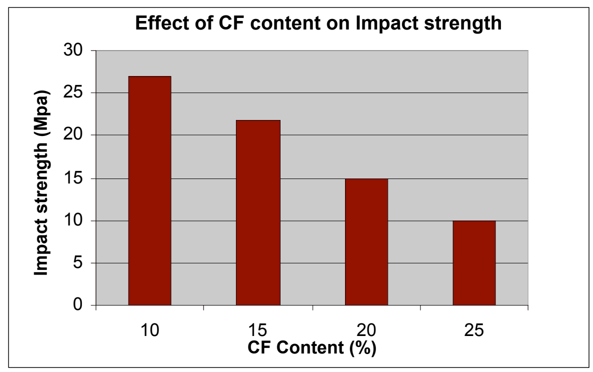

Figure 9.Variation of the impact strength of the composites with CF content when CB content is fixed 5wt%

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