
Effect of Graphite and Carbon Black Fillers on the Processability, Electrical Conductivity and Mechanical Properties of Polypropylene-based Bipolar Plates

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SUMMARY

This study investigates the hybrid effect between graphite and carbon black in a polypropylene (PP) matrix, based on optical microscopy. PP sheets filled with various types of carbon black and graphite were prepared, and the effects of fillers on the flowability, electrical conductivity and mechanical properties were investigated. The effects of three kinds of carbon black with different specific surface areas (65, 770, 1400 m²/g) on the increase of conductivity in the polypropylene (PP) matrix were compared. The best performance was observed when the carbon black with the highest specific surface was used; therefore it was used for preparing the hybrid-filled (graphite – carbon black) materials by melt blending. Optical microscopic studies proved that the carbon black exerted not only a direct but also an indirect influence on the conductivity and on the mechanical properties of the hybrid composites, as it influenced the distribution of graphite significantly. At lower graphite contents the material became more flexible because of the better dispersion of graphite, but at higher carbon black contents the stiffness increased significantly.

Keywords: Graphite; Carbon black; Electrical properties; Polypropylene; Dispersion; Bipolar plates

1. INTRODUCTION

In addition to traditional uses, polymers may find new applications by using additives, fillers and reinforcements. Such areas include the development of conductive polymers having the advantage of lower density than metals and being able to perform well in corrosive environments^{1,2}.

Conductive polymers are more and more frequently used for the preparation of bipolar plates in fuel cells³⁻⁵. Bipolar plate is one of the most important components of fuel cells, as it provides the connection between the individual cells in stacks thus ensuring the proper voltage. It supplies the anode with hydrogen and the cathode

with oxygen, while it separates the two gases and ensures the electron flow between the anode and the cathode, while it conducts the electric current formed from the membranes^{6,7}. In order to perform well and completely they have to meet certain requirements, i.e. they have to show good conductivity, proper strength and stiffness and they should be very processable⁸.

Bipolar plates weigh up to 80% of the total weight of the cell, while they represent 60% of the total costs. According to cost models, composite bipolar plates would make only 15-29% of the total fuel cell costs accompanied by a significant weight reduction⁹. Weight and cost reduction can be achieved by two

methods: materials and processing technology development. The most important challenge in materials development is to achieve the required conductivity level by adding the necessary minimum amount of the cheapest filler. The conductivity of the polymer increases significantly if the added filler forms a continuous conductive network in the matrix, this phenomenon is called percolation and it can be explained by the percolation theory. The goal is to form a possibly extensive, interconnected network in the composite. As matrix material, both thermoplastic (PP, PET - polyethylene terephthalate, PVDF - polyvinylidene fluoride, PPS - polyphenylene sulphide) and thermosetting (epoxy resin, phenolic resin, vinylester resin) polymers are used. In order to form the conductive network conductive fillers, such as natural and synthetic graphite, carbon black, carbon fibres and carbon nanotubes are used¹⁰⁻¹³.

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The most extensively used material to enhance conductivity is graphite. The conductivity of graphite depends on several factors, e.g. on the crystallinity, specific surface area, granular size and shape distribution of the material and on its origin (natural or synthetic). The conductivity of natural graphite can be higher than that of synthetic graphite, as its degree of crystallinity is usually higher, depending on the place of origin. The dispersion of the carbon based fillers in a matrix material depends on the polarity, the molecular mass of the polymer and the presence of reactive groups¹³⁻¹⁶.

Conductivity of graphite is depending not only on the crystallinity but also on the shape of its particles. According to experiments related to the shape of graphite particles, higher conductivity can be achieved by using layered graphite than with those possessing a globular shape, but a higher degree of filling and better processability can be achieved with products containing granular particles, as they have smaller specific surface area than the layered materials. The graphite content in the composite also has a significant effect on the processability; the lower the fraction of the matrix, the worse the wetting of the filler particles, resulting in lower conductivity and disintegration of the material. If using graphite and thermoplastic matrix, usually a saturation level of 70-85 wt.% is achieved^{17,18}.

The other widely used filler for conductivity increase is carbon black. Because of its higher specific surface area carbon black can be added in smaller amounts to the matrix material. The saturation level in the case of carbon blacks may vary strongly depending on the specific surface area of the material used. Based on the experiments of Mighri *et al.*, carbon blacks with increasing specific surface area can be admixed to the matrix in decreasing ratio, as the matrix can wet the filler to a lesser degree¹⁹. In general it can be said that for carbon

blacks with higher specific surface areas, lower mass percentages are sufficient to achieve the percolation threshold²⁰. However, the use of carbon black as filler not only decreases the electrical resistivity, but affects also the mechanical properties: it may increase the Shore hardness and flexural strength as well as the flexural modulus, but it may also deteriorate the impact strength^{15,16,21}.

The separate use of graphite and carbon black as a filler is not sufficient to increase the conductivity significantly. The resistivity of composites can be reduced with higher efficiency if using combined fillers. Hybrid systems contain a significant amount (40-70 wt.%) of graphite, while they usually contain 5-10 wt.% carbon black. The advantage of hybrid systems is that the smaller carbon black particles may fill the "holes" between larger graphite particles, so a continuous conductive network is formed in the composite (higher conductivity values can be achieved); thus the percolation threshold is reached at lower degree of filling^{11,22}.

Besides the type of the filler, the degree of filling at the percolation threshold is also affected by the type of the matrix material. PP is a promising material as matrix regarding the processability and the cost, but its main chain does not contain polar groups; thus proper adhesion cannot be ensured between the filler and the matrix²³.

The effects of conductive fillers on the conductivity and mechanical properties of polymers have been studied by several workers, but the morphology of these materials has not really been researched. The aim of the present study was to provide a general explanation of the effects of graphite and carbon black filling

on the properties of polypropylene, based on morphological investigations, processability, electrical conductivity and mechanical properties, as these determine mostly the applicability of the conductive composite developed.

2. MATERIALS AND METHODS

2.1 Materials

Tipplen H949A polypropylene (TVK, Hungary) with an MFR value of 45 g/10 min was used as a matrix material in the experiments.

The graphite powder used to increase the conductivity (Carbosint Ltd., Hungary) was a crystalline natural graphite with a specific surface of 6 m²/g, and with an average particle diameter of 20 µm.

For the three types of carbon black used ENSACO 2501 G (65CB) had 65 m²/g specific surface, ENSACO 350 G (CB770) 770 m²/g, and Ketjenblack EC-600 JD (CB1400) 1400 m²/g. The first two grades were the product of Timcal Graphite & Carbon Incorporation, while the third was from AkzoNobel.

The densities of the materials used are summarized in **Table 1**.

The various compositions were mixed by using a Brabender internal mixer at 230 °C for 15 min at 20 rpm. From the melt-mixed materials, 2 mm thick plates were hot pressed at 230 °C and 150 bar using a Collin P200E hot press.

Compositions developed for the study of the conductivity increasing effects of various carbon blacks with different specific surface areas are shown in **Table 2**.

Table 1. Densities of the materials used

	PP	Graphite	CB65	CB770	CB1400
Density [g/cm ³]	0.89	2.12	1.88	1.84	1.77

Table 2. The composition of the materials prepared using carbon blacks with various specific surface areas

Notation of the series	CB65				CB770				CB1400				
PP wt. %	95.0	90.0	80.0	60.0	95.0	90.0	80.0	60.0	97.0	94.0	91.0	88.0	85.0
CB wt. %	5.0	10.0	20.0	40.0	5.0	10.0	20.0	40.0	3.0	6.0	9.0	12.0	15.0
PP vol. %	97.3	94.7	89.4	78.7	97.3	94.6	89.1	78.3	98.3	96.6	94.9	93.2	91.5
CB vol. %	2.7	5.3	10.6	21.3	2.7	5.4	10.9	21.7	1.7	3.4	5.1	6.8	8.5

Table 3. The compositions of hybrid-filled materials

Notation of the series	0 vol. % graphite						22.8 vol. % graphite						40.6 vol. % graphite					
PP w %	100.0	97.0	94.0	91.0	88.0	85.0	60.0	57.0	54.0	51.0	48.0	40.0	37.0	34.0	31.0	28.0		
Graphite w %	0.0	0.0	0.0	0.0	0.0	0.0	40.0	40.0	40.0	40.0	40.0	60.0	60.0	60.0	60.0	60.0		
CB1400 w %	0.0	3.0	6.0	9.0	12.0	15.0	0.0	3.0	6.0	9.0	12.0	0.0	3.0	6.0	9.0	12.0		
PP vol. %	100.0	98.4	96.8	95.1	93.3	91.8	78.1	75.5	72.9	70.2	67.4	61.3	57.9	54.4	50.7	46.8		
CB1400 vol. %	0.0	1.6	3.2	4.9	6.7	8.2	0.0	2.1	4.3	6.5	8.9	0.0	2.5	5.1	7.8	10.6		
Graphite vol. %	0.0	0.0	0.0	0.0	0.0	0.0	21.9	22.4	22.8	23.3	23.8	38.7	39.6	40.6	41.6	42.6		

The compositions of the hybrid-filled materials are shown in **Table 3**. As the properties are mainly determined by the volume fraction of the fillers, the amounts used are usually given in this form. In order to do so, when evaluating the trends appearing in the material groups containing 40 wt.% and 60 wt.% graphite the volume fraction of graphite was taken as constant; minor deviations were neglected. In the case of 40 wt.% graphite: 22.8 ± 0.6 vol.%; in the case of 60 wt.% graphite: 40.6 ± 1.5 vol. %).

Impact strength tests were made using a CEAST Resil Impactor Junior equipment with 2 J hammer, at room temperature.

An Olympus PMG3 type optical microscope was used for optical microscopy, data evaluation was made by analySIS Steel Factory 5.0 software.

3. RESULTS AND DISCUSSION

3.1 Comparison of Carbon Black Fillers with Different Specific Surface Areas, Based on the Conductivity Improvement

Figure 1 shows the specific volume resistivities of polymers filled with

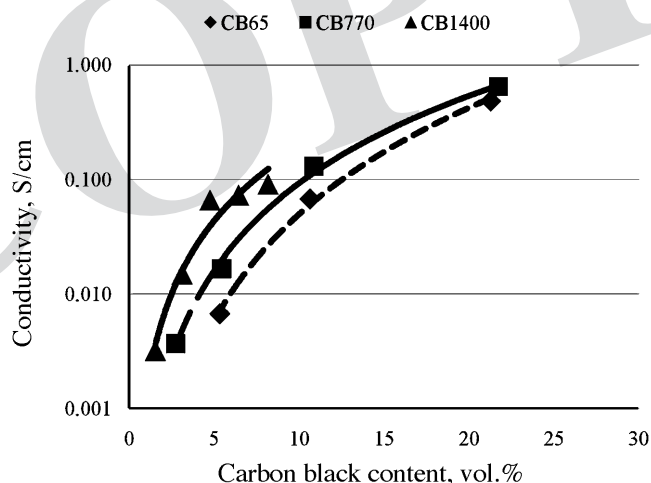
2.2 Test Methods Used

The conductivity was measured using a four probe resistivity test using an Agilent 4333B type milliohmmeter.

Flowability (MFI) was tested using a CEAST 7027.000 type capillary plastometer at 230 °C temperature, using 21.6 kg load. Melt flow rates related to the volume (MVR) were determined in the measurements.

Three point bending tests were performed on a Zwick Z020 type universal tester with 64 mm span length, at 5 mm/min deformation rate, at room temperature.

Figure 1. Changes in the conductivity of polypropylene when using carbon black fillers with different specific surface areas



various carbon blacks. The processing of the material filled with 8.5 vol.% of CB1400 carbon black was met with difficulties. It can be established that the conductivity was most effectively increased by the high specific surface area carbon blacks, CB1400 increased the conductivity of PP even at low filler loadings, and thus it was selected to prepare hybrid-filled materials.

3.2 Flowability Tests

Figure 2 shows the change of the MVR values as a function of the carbon black content for PP samples containing only CB1400 and for

the hybrid-filled samples. It can be observed that both the graphite and the carbon black content decrease the flowability of PP significantly, by more orders of magnitude. The reduction of flowability did not go parallel with the increase of the carbon black content; the largest change occurred already with the addition of a small amount of carbon black. If further carbon black was added, the decrease of flowability was approximately exponential (linear on the figure) both with 0 vol.% and 22.8 vol.% graphite contents. MVR values below 1 cm³/10 min could not be measured with the set parameters;

this limit was achieved with the 22.8 vol.% graphite containing sample at 6.5 vol.% carbon black content, with the 40.8 vol.% graphite containing sample at 2.5 vol.% carbon black content.

3.3 Optical Microscopic Studies

Using optical microscopy the distribution of graphite in the PP matrix was compared for samples with different carbon black contents (Figure 3). It can be observed that both at 20.8 vol.% and at 40.6 vol.% graphite contents, already the addition of a small amount of carbon black makes the dispersion of graphite much finer (Figures 3b and 3g). Further increase of the carbon black content results in the agglomeration of the graphite particles into larger agglomerates (Figures 3c-e and 3j).

When evaluating the micrographs, the average area of dispersed graphite particles was determined, indicating the fineness of the dispersion. Figure 4a shows that both at 22.8 vol.% and at 40.6 vol.% graphite contents, the average area of the dispersed graphite particles decreases at low carbon black loadings (below 6 vol.%), while at higher loadings an increase is observed. The higher graphite content (40.6 vol.%) results in a larger

Figure 2. Change of the flowability of hybrid samples plotted against the carbon black content

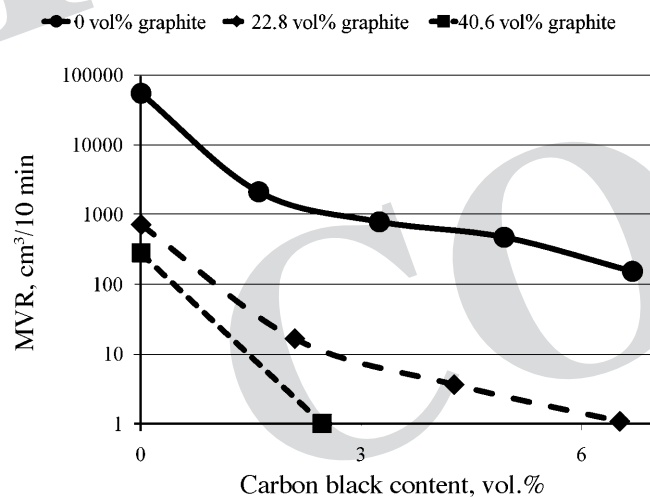
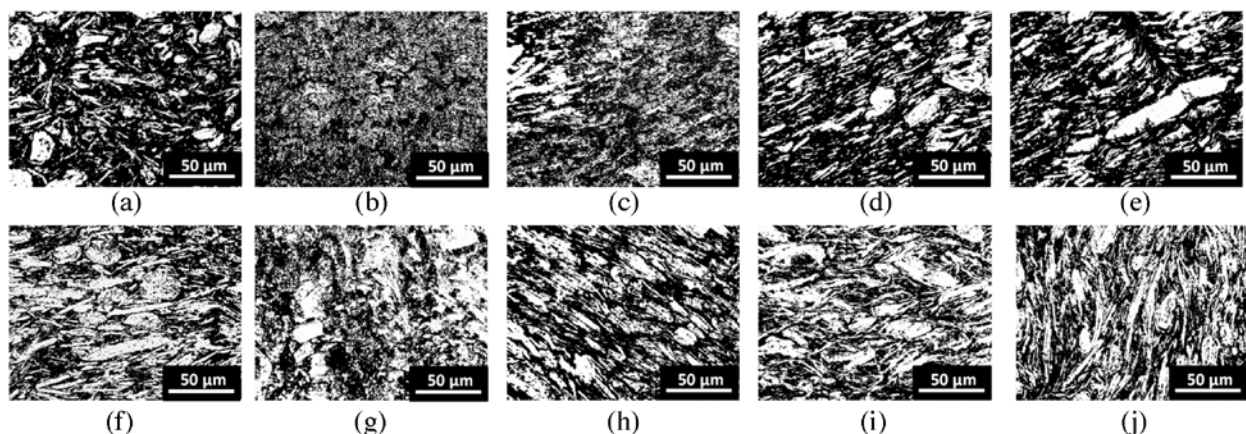


Figure 3. Digitalized optical micrographs representing the dispersion of graphite content at various carbon black contents (a) 22.8 vol.% G - 0 vol.% CB1400; (b) 22.8 vol.% G - 2.1 vol.% CB1400; (c) 22.8 vol.% G - 4.3 vol.% CB1400; (d) 22.8 vol.% G - 6.5 vol.% CB1400; (e) 22.8 vol.% G - 8.9 vol.% CB1400; (f) 40.6 vol.% G - 0 vol.% CB1400; (g) 40.6 vol.% G - 2.5 vol.% CB1400; (h) 40.6 vol.% G - 5.1 vol.% CB1400; (i) 40.6 vol.% G - 7.8 vol.% CB1400; (j) 40.6 vol.% G - 10.6 vol.% CB1400)



graphite particle area than the lower one (22.8 vol.%).

Using the evaluation software the distance between the neighbouring particles was studied for each graphite particle, and the average of these values is plotted in **Figure 4b** for 22.8 vol.% graphite content. At 2.1 vol.% and 4.3 vol.% carbon black contents the 1.7 μm average distance was first reduced to 1.2 μm , then at 6.5 vol.% and 8.9 vol.% carbon black contents it increased significantly to about 2.3 μm . At 40.6 vol.% graphite content at low carbon black loading again, a reduction was observed from 8 μm to 1.4 μm , then from 5.1 vol.% carbon black content it went back to 1.8–1.9 μm , but further increase is not observed.

Changes in the graphite dispersion were presumably due to the varying viscosity reduction caused by the carbon black addition, resulting in different shearing conditions in the internal mixer.

3.4 Conductivity Studies

Figure 5 shows the specific volume conductivity of the hybrid composites plotted as a function of the carbon black content. It can be seen that the conductivity of the hybrid-filled materials is considerably higher than that of the samples containing only one kind of filler. At similar graphite content the conductivity increases in parallel with the carbon black content. This increase is less significant above 3.2 vol.% carbon black content at 0 vol.% graphite content and from 6.5 vol.% carbon black content at 22.8 vol.% graphite content. One possible reason for this is that the graphite content also influences the dispersion of the carbon black, and the more even distribution caused by the graphite content ensures higher conductivity. Another reason is the inter-particle distance between the graphite particles, which increases in the 22.8 vol.% graphite sample with higher carbon black content. In the 40.6 vol.% graphite sample, the inter-

Figure 4. (a) Changes in the average area of graphite particle as a function of the carbon black content; (b) Changes in the average inter-particle distance values between the dispersed graphite particles as a function of the carbon black content

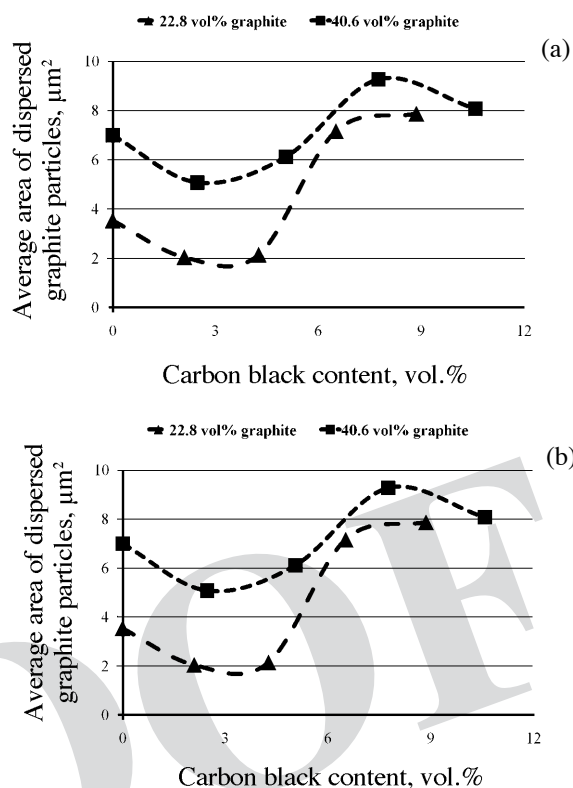
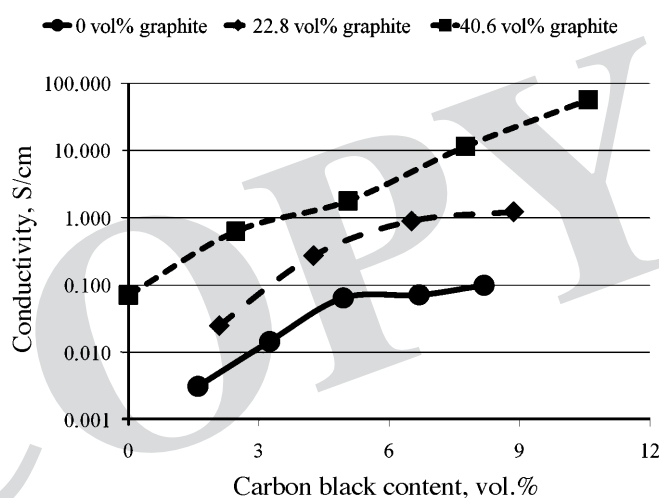


Figure 5. Changes in the conductivity of hybrid materials as a function of the carbon black content

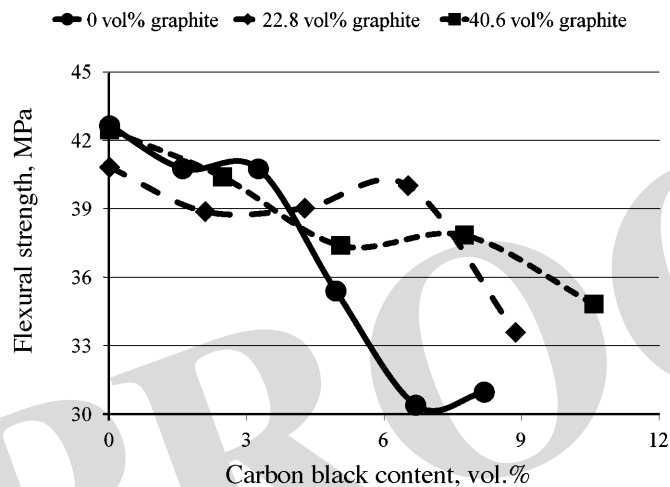
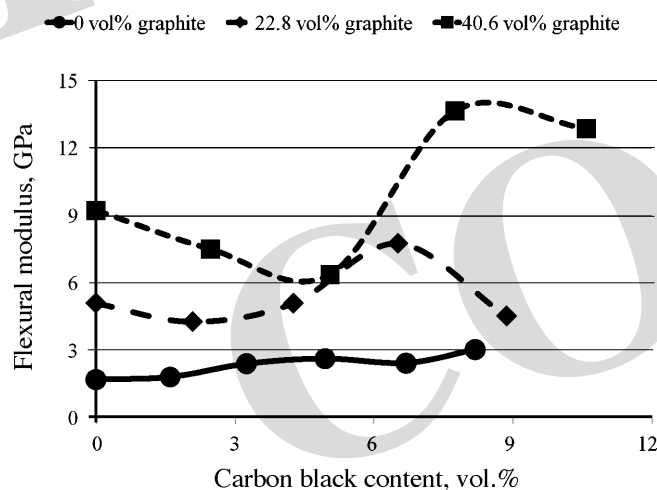
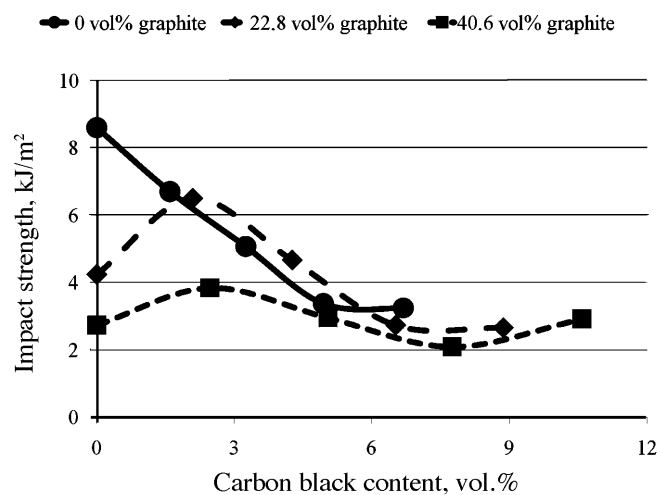


particle distance between the graphite particles does not increase significantly even at higher carbon black contents, so the conductivity increases more strongly with carbon black addition than in the previous case.

3.5 Mechanical Tests

3.5.1 Flexural Test

Figure 6 shows the changes of the flexural strength as a function of the carbon black content. The flexural

Figure 6. Flexural strength of the composites as a function of the filler content**Figure 7. Flexural modulus of the composites as a function of the filler content****Figure 8. Impact strength of the composites as a function of the filler content**

strength of the samples containing carbon black only shows slow deterioration up to 3.2 vol.% carbon black content and a faster decrease afterwards. Graphite content exerts no serious influence up to about 5 vol.% carbon black content, but above this level, it compensates for the strength reduction to a certain degree. However, as graphite itself does not reinforce the PP matrix, it can be assumed that the interaction of the fillers may explain the effect also in this case: the uniformly-dispersed carbon black reduces the strength of the material less drastically.

Figure 7 shows the flexural modulus as a function of the filler content for the same materials. Taking the modulus of the materials containing carbon black only, it can be seen that the carbon black content is less dominant in determining the stiffness. In the case of hybrid-filled materials the dependence on the size of the dispersed graphite particles is obvious: larger graphite particles increase more the stiffness of the material.

3.5.2 Charpy Impact Strength Test

Figure 8 shows the change of the impact strength values as a function of the carbon black content. It can be observed that both the graphite and the carbon black fraction and their state of dispersion strongly influence the toughness of the materials. A low level of carbon black filling improves the impact strength of the hybrid materials, but at higher filler levels this value decreases significantly. This phenomenon may be explained by the changes in the dispersion state of the graphite content; finer dispersion deteriorates the impact strength to a lesser degree.

4. CONCLUSIONS

In this work the combined effects of graphite and carbon black fillers on a PP matrix have been studied. Hybrid application of both fillers decreased the flowability of PP significantly, so the processing could only be done by hot pressing.

When increasing the electrical conductivity, the two fillers showed a synergetic effect: at higher graphite contents, the addition of carbon black improved the conductivity more efficiently.

Optical microscopic studies revealed that in the hybrid carbon black/graphite filled PP composite the carbon black content influenced the dispersion of the graphite particles, which affects not only the conductivity, but also the mechanical properties. Hybrid composites containing both fillers were more flexible at low carbon black contents than the polymers containing graphite only, as both the size of the dispersed graphite particles and the average inter-particle distance decreased. At higher carbon black content, however, the graphite particles re-agglomerated, resulting in increased stiffness and reduced impact strength.

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