

Electrical properties of hybrid carbon black/carbon fiber polypropylene composites

M. Drubetski · A. Siegmann · M. Narkis

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Abstract The electrical conductivity and morphology of injection molded polypropylene based composites containing two conductive fillers, carbon black (CB) and carbon fibers (CF) were studied. Injection moldings containing both, CB and CF, where the content of each filler was above its own percolation threshold, resulted in similar or lower values of overall composite volume resistivity compared with the resistivity of systems filled only with CB at the corresponding content. However, the resistivity of two-filler systems is always higher than the resistivity of systems filled only with CF at the corresponding content. The morphology and fiber length analysis of the injection molded composites are quite intriguing. Fiber orientation in the injection molded two-filler systems was found to be almost perpendicular to the melt flow direction, with no significant skin-core fiber orientation patterns, contrary to the typically observed fiber orientation in injection molded fiber filled composites. Moreover, the CF breakage in the presence of the CB was found more intense than when just CF is used, resulting in shorter fibers with narrower length distributions. This unexpected fiber behavior is responsible for the unexpected electrical behavior. However, the coexistence of CB and CF electrically conductive

networks, supporting each other, was confirmed, in spite of the mechanical disturbances caused by the presence of fibrillar and particulate fillers.

Introduction

The growing demand for electrically conducting plastics is the source of continued activity in the investigation and development of novel materials with desired electrical properties. The relative simplicity to convert insulating resins to conductive ones, by addition of conductive fillers, makes filled polymer systems attractive materials for this purpose.

Carbon black (CB) is one of the most widely used conductive additives [1]. The overall conductivity of a filled polymer system sharply increases, when some critical amount of CB, required for the construction of three-dimensional conductive networks, is added [2, 3]. However, a significant amount of CB is required to achieve high levels of the composite conductivity. Viscosity and mechanical properties are strongly affected by the presence of high CB contents [4, 5], representing difficulties and limitations for industrial manufacturing and applications. Attempts to reduce filler content have been made by various means such as: selection of additives with preferred shape, size and conductivity, selection of proper matrix polymers [6, 7], formation of unique matrix morphology through blending of immiscible polymers at various compositions and application of certain processing conditions leading to preferable filler distributions [8]. Studies of combining two kinds of electrically conductive fillers to

M. Drubetski · A. Siegmann (✉)
Department of Materials Engineering, Technion-Israel
Institute of Technology, Haifa 32000, Israel
e-mail: siegmann@technix.technion.ac.il

M. Narkis
Department of Chemical Engineering, Technion-Israel
Institute of Technology, Haifa 32000, Israel

affect both, the percolation threshold and conductivity level, were recently initiated. For example, systems containing CB particles or polyaniline complex and carbon fibers (CF), which promote relatively long distance charge transfer, were recently studied [9, 10]. Carbon fibers, like other conductive additives, form conductive networks within polymer matrices when added in sufficient amounts. Moreover, apart from electrical conductivity the CF, having high strength and modulus, impart also mechanical reinforcement to the composites. However, high anisotropy induced by flow conditions was reported for injected molded systems containing shot fibers, thus affecting the systems' properties [11, 12].

Combining particulate and fibrous additives, e.g., CB and CF, and thus their properties seems quite attractive. It is expected that while CF act as long distance charge transporter, CB aggregates may serve as interconnections between the fibers by forming local conductive paths. Hence, formation of co-supporting conductive networks is expected to result in composites with reduced percolation filler content, enhanced conductivity and lower anisotropy and therefore, synergistic effects are expected.

There are few reports on the electrical properties of injection molded filled polymer systems containing more than one conductive additive. A positive synergy effect was reported for systems containing polyaniline and CF in polypropylene matrix [10] and for systems containing CB, graphite and CF in Nylon 6.6 matrix [13]. Higher electrical conductivities of these multi-filler systems were observed relative to systems filled by only one of the fillers. Positive synergy for polyethylene filled with both CB and CF was reported only for highly filled compression molded samples; however, injection moldings of the same compositions exhibited rather low conductivities [9].

The objectives of the present study are to investigate the electrical properties of polypropylene based composites containing both CB and CF, attempting to determine the main factors affecting the electrical behavior and the structure of the ternary system.

Experimental

Materials

Two types of polypropylene (PP) were used as matrix polymers: high viscosity Capilene E50E and low viscosity Capilene T50E (MFI = 1.75 and MFI = 25, respectively) manufactured by Carmel Olefins (Israel). Carbon Black EC600 supplied by Akzo Nobel, Inc.

Table 1 Filler content in the investigated composites

Additive	[phr]						
	3	4	5	10	15	20	40
CB	X	X*	X				
CF			X*	X*	X	X*	X
CF (+CB-4phr)			X*	X	X	X*	
CF (+CB-3phr)			X	X	X		
GF (+CB-4phr)			X	X	X		

X*—Compression molded samples were also prepared

having density of 1800 kg/m³, BET surface area of 1250 m²/g and electrical volume resistivity of 0.01–0.1 ohm-cm.

Carbon fibers treated with epoxy, ASIF CH6HT12K S/E, produced by Asif Company (Israel), 7 μm in diameter and 6 mm in length were used to prepare conductive composites, separately and in combination with CB. Electrically insulating glass fibers (GF) supplied by Vetrotex Company (Germany), 7 μm in diameter and 6 mm in length. Table 1 summarizes the composition of investigated composites.

Sample preparation

The composite components were initially dry mixed in appropriate ratios. A co-rotating intermeshing twin screw extruder, Brabender TSC 42/6, operated at 260 °C and 50 rpm was used for compounding the mixtures. The resulting filaments were milled at room temperature and then injection molded, using an Arburg 220/150 injection molding machine equipped with a standard ASTM mold for mechanical testing samples. The barrel temperature was 280 °C in all zones, the mold temperature was 40 °C, and injection and holding pressures were about 3 MPa and 9 MPa, respectively. Glass fibers (GF) were used in combination with CB, and their composite processing conditions were the same as for the CF filled systems. Some composites were compression molded at 200 °C (as shown in Table 1).

Rheological studies of some composites (compounded only) were conducted, using an Instron capillary rheometer mounted on an Instron TT-D machine. The rheometer was equipped with a capillary 50 mm in length and 1.27 mm in diameter (L/D = 40) and operated at 280 °C and 0.5–500 mm/min, providing an approximate shear rate range of 2–3000 s⁻¹.

Measurement of electrical resistivity

The resistance measurements were carried out on the injection molded and compression molded samples.

The injection molded test samples, $65 \times 13\text{mm}^2$, were cut from the center portion of tensile dogbones (Fig. 1). The electrodes were connected to the butt-ends of the samples. Silver paint was applied to minimize contact resistance between the sample and electrodes. The compression molded test samples were cut from 3 mm thick plaques. The resistance of the compression molded samples was measured across the thickness direction. The resistance was measured using a Keithly Electrometer 6514 and the volume resistivity was calculated.

Morphology observation and fiber length characterization

The composites morphology was studied on freeze fractured surfaces, using a Joel JSM-840 SEM. Samples were fractured parallel to the injection melt flow direction.

Fiber length characterization was carried out on about 600 fibers in each sample, using a Nikon Optiphot optical microscope combined with a Sony CCD and an “Analyses” soft imaging system. The fibers were separated from the resin by hot xylene extraction. To enable the analysis, samples containing both CF and CB were then treated with fuming nitric acid at a high temperature to remove the CB particles.

Results

Based on our previous experience and on literature results, to obtain a synergistic effect, the content of each filler should be above its percolation threshold. The characteristic volume resistivity curves for the single PP/filler injection molded samples (Fig. 2) indicate that at 3phr CB and at 10phr CF the composites have turned conductive. Both curves also serve as references for comparison with the hybrid two-filler containing systems. Samples consisting of

polypropylene (T-50-E), 3phr or 4phr CB and varying contents of CF were prepared and their volume resistivities are depicted in Fig. 2. As previously mentioned, a synergy resulting in reduction of percolation filler content and composites of high conductivity is expected. However, preliminary analysis of the resistivity results is not conclusive. Comparison of the four percolation curves (Fig. 2) shows that, in spite of the lower quantity of fibers necessary to make all composites conductive at 4phr CB, the resistivity of the PP/CF/CB systems is still higher than that of the corresponding systems filled by CF only. Though the PP/CF-5phr/CB-4phr systems exhibit lower values of volume resistivity than the PP(T-50-E)/CF-5phr system and comparable to that of the PP/CB-4phr system, the lower resistivity of the two-filler system may be mainly due to the CB rather than a synergistic effect. Since the nature of interaction between the carbon black and the carbon fibers is not clear based only on resistance measurements, morphology observations, rheology and fiber length measurement have been also conducted.

Comparison of freeze fractured surfaces of injection molded samples (skin region), containing CF only and of those containing both, CF and CB show, unexpectedly, that the typical flow induced fiber orientation is dramatically disturbed in the presence of CB (Fig. 3a–c). The increasing number of white dots, representing the fibers' edges, can be observed by following Fig. 3a–c. To find out whether fiber disorientation is a unique phenomenon for the CF/CB filled composites, glass fibers (GF) were incorporated instead of CF. Interestingly, the loss of the typical, flow induced orientation is also observed in the GF/CB containing composites (Fig. 3e). Moreover, the freeze fractured surfaces of the two-filler systems exhibit no significant skin-core morphology of fiber orientation pattern, i.e., fiber orientation is quite uniform through the samples thickness, which is different from the typical skin-core structure of injection molded fiber containing composites [14].

Fig. 1 Schematic presentation of sample preparation for electrical resistance measurements

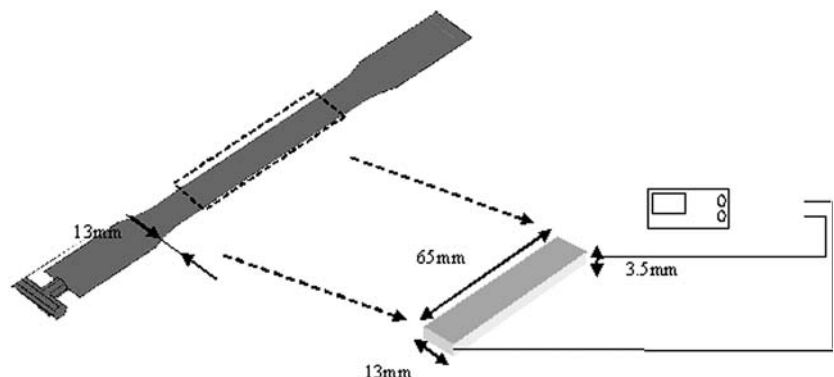
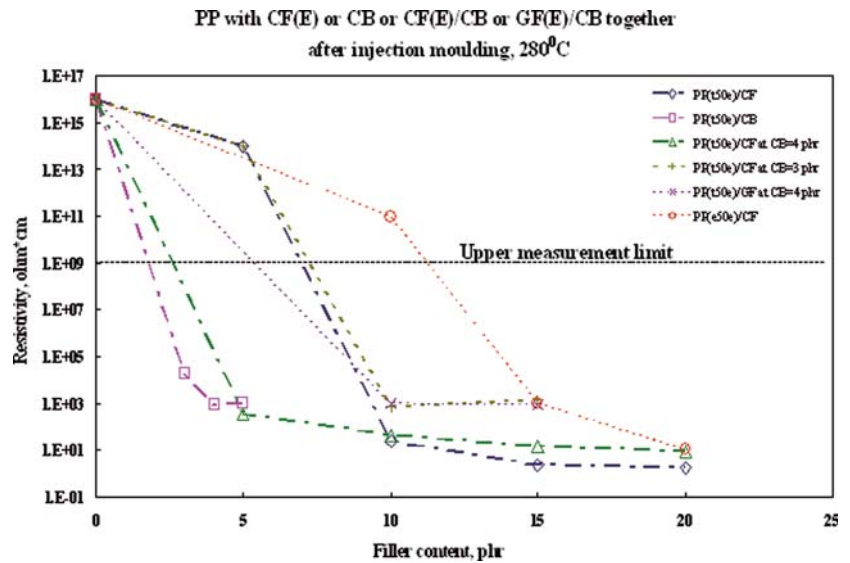


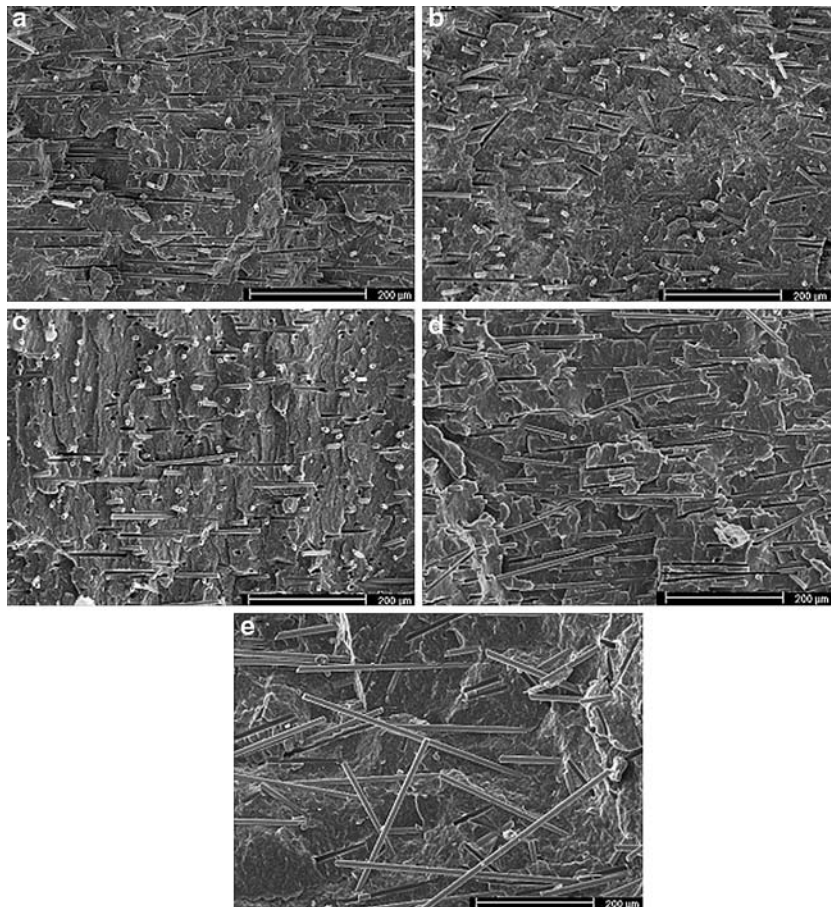
Fig. 2 Resistivity of injection molded polypropylene filled with CF, CB, CB/CF and CB-4phr/GF composites versus filler content. Points of resistivity above $1.E + 09$ ohm*cm exceed the range the measuring equipment and are depicted for illustration purposes only



As expected, the addition of CB filler particles results in an increase of the matrix polymer viscosity, as depicted in Fig. 4. Also, the viscosity of the PP (T-50-E)/CF/CB systems is higher than that of the PP (T-50-E)/CF composites. It should be noticed that

carbon black has larger effect on the matrix viscosity than CF. Hypothetically the increased viscosity coupled with the higher shear stresses required during processing should have caused higher rather than lower level of fiber orientation in the presence of CB. Hence,

Fig. 3 SEM micrographs of freeze-fractured (a) PP_{T-50-E}/CF-15phr, (b) PP_{T-50-E}/CB-3phr/CF-15phr, (c) PP_{T-50-E}/CB-4phr/CF-15phr, (d) PP_{E-50-E}/CF-15phr and (e) PP_{T-50-E}/CB-4phr/GF-15phr composites



the observed fiber disorientation in the studied two-filler systems may be related to some filler-fiber interactions and/or viscosity effects.

To investigate matrix viscosity effects on fiber orientation, and the resulting composite electrical resistance, two grades of PP were compared as matrix polymers in PP/CF composites namely, low viscosity PP (T-50-E) and higher viscosity PP E-50-E (see Fig. 4). The higher viscosity PP (E-50-E) based composites containing CF, as shown in Fig. 2, exhibit volume resistivity values higher than those of the composites based on the lower viscosity matrix (T-50-E), and a percolation threshold at a higher CF content. Relative to the PP (T-50-E)/CF system, the higher viscosity PP (E-50-E)/CF composites exhibit enhanced fiber orientation (Fig. 3a and d should be compared), reducing the number of interfiber contacts, as well as reducing the fiber length, as will be discussed below. Accordingly, since the viscosity of the PP (T-50-E)/CF/CB is higher than that of the PP (T-50-E)/CF composites, fiber orientation in the former, CB containing systems should have been higher, contrary to the present observations. Thus, the effect of the CB presence on the fiber orientation is not just through affecting the system viscosity. The fiber disorientation in the presence of CB is probably a result of some CF/CB interactions or some local disturbances of the CB particles to the flow pattern.

For comparison, the resistance of several compression molded samples, where flow during molding is minimal, was also measured. The volume resistivities of these systems are presented in Fig. 5. Interestingly, similar values of volume resistivity of the systems containing a single and two fillers are observed. The

percolation threshold of the compression molded PP (T-50-E)/CF system is lower and the volume resistivity values are higher when the results presented in Fig. 5 are compared with those of the corresponding injection molded composites (Fig. 2). The lower fiber orientation in the compression molded systems (the higher probability of the formation of three dimensional conductive networks), relatively to that in the injection molded systems is most probably responsible for these results. Similar fiber lengths can be assumed in the compression and injection molded samples, since the main fiber breakage occurs during the compounding step, common for both processes, as discussed below. Since the similarity of the volume resistivity values of the compression molded PP/CF and PP/CF/CB composites was related to the low fiber orientation in both systems, the effect of disorientation on the difference between the injection molded PP/CF and PP/CF/CB resistivity curves (Fig. 2) became more evident.

In addition to fiber orientation, fiber length (aspect ratio) is a major factor determining the resistance of a CF containing composite. Therefore, fiber length for all samples containing CF, with and without CB, was measured. Though most length reduction occurred already in the compounding step (twin extruder), some additional breakage has occurred in the injection stage. Fiber lengths following injection molding are summarized in Table 2. The minimum length values of the CF in PP (T-50-E) are nearly equal for all studied composites, independent of their composition, however, a significant reduction in the CF average length, by nearly 50%, and a narrower length distribution are observed for the CF in PP (T-50-E) containing also CB. The CF average lengths and length distributions in

Fig. 4 Viscosity versus shear rate of different types of polypropylene filled with CF, CB or CB/CF composites (280 °C)

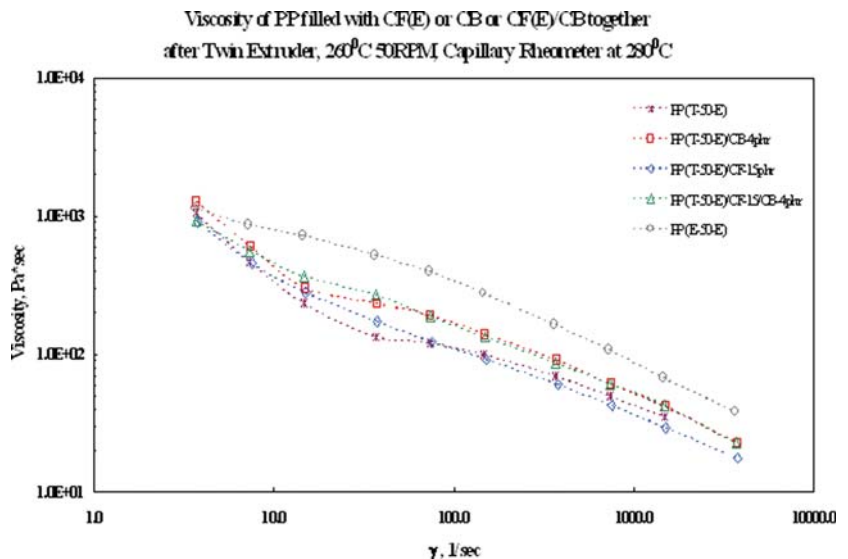
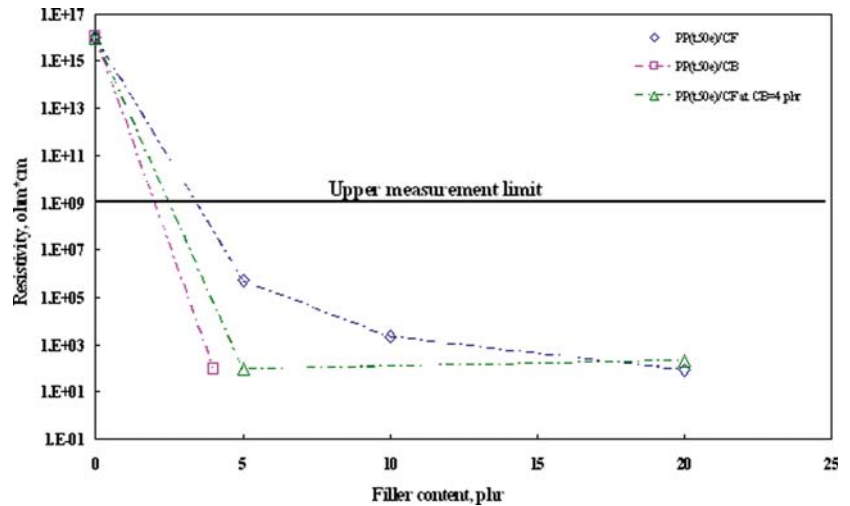


Fig. 5 Resistivity of compression molded polypropylene filled with CF, CB or CB-4phr/CF filler content



the PP/CF/CB-3phr composites are quite similar to those of the corresponding PP/CF/CB-4phr systems. The level of average fiber length reduction observed in the higher viscosity PP (E-50-E) matrix with no CB is similar to the results of PP/CF/CB composites. Enhanced fiber length reduction in PP (E-50-E)/CF, comparable to the PP (T-50-E)/CF composites, is a result of shear forces induced by the viscous matrix. However, the similarity in the width of the fiber length distribution in these systems (Table 2) indicates that the enhanced breakage of the CF in the presence of CB cannot be related only to high viscosity effects. The existence and influence of CB–CF interactions becomes evident. It is interesting to notice that fiber length in the PP/CF composites increases with fiber content emphasizing that fiber–fiber interactions are not the main cause for the fiber breakage in the PP/CF systems.

To study the effect the presence of fibers has on the contribution of carbon black to the conductivity in the hybrid composites, insulating glass fibers (GF) have been incorporated into a PP/CB system to replace the CF. In the PP/GF/CB systems only the CB contributes to their resistivity. The resistivity values of injection molded samples containing PP (T-50-E), CB-4phr and GF-10 and 15phr are depicted in Fig. 2. The resistivity

values of the samples containing both, GF and CB are slightly higher than those filled with just CB (taking into account the effective CB content). This may indicate that the incorporation of fibers into a CB filled resin has a negative effect on the CB conductive network formation. It may be a consequence of a physical barrier formed by the fibers in the conductive pathways of the CB or of a fiber stirring effect during flow resulting in a more homogeneous CB dispersion, thus disturbing the formation of a discrete network structure.

Quantitative estimation of the effect of carbon black on the formation of CF networks is more difficult. Nevertheless, comparing the resistivity curves of PP/CF/CB including 3 or 4phr CB with the resistivity of PP/CB at the respective CB contents (Fig. 2), it seems that the levels of resistivity of the formers are only slightly lower relative to the corresponding PP/CB composites. Still, it is not clear, what is the contribution of the CF and the CB to the composites conductivity.

Discussion

Based on the foregoing results, an attempt is made to clarify how the electrical conductivity is established in

Table 2 Carbon fiber length analysis in different PP/CF composites, with or without CB

	PP _{T-50-E} /CF				PP _{E-50-E} /CF			PP _{T-50-E} /CB-4phr/CF			
CF[phr]	5	10	15	20	10	15	20	5	10	15	20
Average length (μm)	136	130	183	185	115	102	172	80	106	89	76
Maximum length (μm)	778	675	731	770	819	637	678	446	950	798	583
Minimum length (μm)	20	16	20	19	8	8	14	18	21	20	13
STD	139	128	146	144	121	100	139	66	119	94	89
Skewness	2.4	2.1	1.3	1.2	2.5	2.0	1.2	2.8	3.6	3.8	3.7
Kurtosis	6.2	4.2	1.3	1.2	7.7	4.6	0.4	10.8	16.2	18.0	14.5

the studied PP based composites containing two conductive fillers, CF and CB together. The results depicted in Fig. 2 show, unexpectedly, higher volume resistivity values of the two-filler composite systems than those filled with CF only, while the CF content required to achieve composite conductivity is lowered by the presence of CB, when in contents above its own percolation threshold.

Examining the PP/CB + CF systems, one should recall that the CB contents have been initially selected to be above the percolation threshold of the PP/CB system. Hence, the lower CF content required to achieve composites conductivity in the presence of CB may be mainly due to the CB presence rather than of a synergistic effect. The slight trend of decrease in the volume resistivity of the PP/CB + CF, relative to the PP/CB composition with corresponding contents of CB, in spite of disturbances applied by the presence of fibers (see Fig. 2 PP/GF atCB-4phr), indicates the existence of some synergism between the two kinds of fillers. However, it may be just an effect of increasing the effective content of the conductive filler by the addition of CF. Analysis of the two-filler composites by investigating the effect of CB on the PP/CF resistivity curve shows lowering of the CF percolation content, which can be correlated with the loss of fiber orientation induced by the addition of CB (Fig. 3a–c) and the resulting higher probability of CF contact formation. A PP/CF system with fibers which have undergone length reduction and disorientation at a level similar to that described above for the PP/CF/CB is expected to exhibit a much higher resistivity than the studied PP/CF system. Thus, the CB presence contributes to lower the resistivity down to that of the studied PP/CF/CB. Hence, in a two fillers system with CF maintaining the original fiber length and the common fiber orientation, typical of the systems filled only with fibers, the expected resistivity synergism would have been quite clear. It is suggested, therefore, that the actual synergistic effects are shadowed by mechanical rather than electrical effects of the CB presence on the CF, i.e., the presence of CB causes disruption of the CF network structure in terms of shorter and less oriented network elements.

This conclusion requires additional confirmation, since the content of the electrically conductive filler in the two-filler composites is higher than in the single filler ones. It should be proven that the resistivity values obtained are the result of the synergistic effects rather than the overall resistivity of conductive CB and CF networks connected, for example, in parallel or in series. The conductivity magnitudes, assuming series or parallel connections of conductive CB and CF networks, were recently estimated by Balta-Calleja et al. [9]. Taking into consideration the similarity of the conductivities of the investigated injection molded PP/CF (considering fiber length reduction) and PP/CB systems (see Fig. 2), the following expressions were used:

$$\sigma_{\text{parallel}} = \frac{1}{2} (\sigma_{\text{PP/CB}} + \sigma_{\text{PP/CF}})$$

and

$$\sigma_{\text{series}} = 2 \left(\frac{\sigma_{\text{PP/CB}} \sigma_{\text{PP/CF}}}{\sigma_{\text{PP/CB}} + \sigma_{\text{PP/CF}}} \right)$$

where σ_{parallel} , σ_{series} , $\sigma_{\text{PP/CB}}$ and $\sigma_{\text{PP/CF}}$ are the conductivities of networks of CB and CF connected in parallel and series, in a PP matrix. The resistivity values estimated by applying this method and the measured ones are presented in Table 3. The resistivity values of the PP (E-50-E)/CF systems were used for the calculations (Table 3 and Fig. 2). The values of the resistivity estimated by the parallel model are higher than the experimental ones (the series model leads to even higher values). The PP/CF -20phr/CB-4phr system is unique since the measured and the calculated in parallel values are similar. This unique behavior of the 20phr CF containing system is due to its relatively high fiber length, different from the typical composites containing also CB.

Considering that the experimental values are lower than the predicted for a parallel model, one may conclude that the two fillers form a co-supporting rather than two independent conductive networks. Thus, the achieved values of the two-filler composites resistivity may be associated with the existence of a

Table 3 Estimated resistivity values of PP (T-50-E)/ CF/ CB-4phr for serial and parallel conductive network connections (corrected by PP (E-50-E)/CF resistivity values)

PP/CF/CB-4phr			
CF content [phr]	Serial connection, ρ (ohm*cm)	Parallel connection, ρ (ohm*cm)	Measured, ρ (ohm*cm)
10	$>1.0 \times 10^9$	1.7×10^3	44
15	7.7×10^2	7.6×10^2	15
20	4.2×10^2	1.8×10^1	9

synergistic effect between the two types of conductive network. The described effect is realized probably due to mutual bridging and inclusion of additional conductive regions into the overall conductive network.

Conclusions

The investigation of hybrid composite systems based on polypropylene filled with two types of carbonaceous conductive fillers, CF and CB, has shown the existence of a positive synergism between their conductive networks, shadowed by fiber disorientation and enhanced breakage of CF. It is suggested that if the CF length and orientation in the two-filler system can be preserved, at least at a level where CF is a single filler, the conductivity synergism would be more evident.

Though a desired highly electrically conductive composite material, based on a commodity matrix resin at low conductive filler loading, was not achieved, interesting indications of some intriguing interactions between the carbon black particles and the carbon fibers were discovered in the injection moldings. In the presence of carbon black particles the carbon fiber orientation is dramatically disturbed and the fiber length and length distribution are significantly altered

to shorter and narrower values than in the case of systems containing just fibers. A more detailed work is required to shed more light on the still unresolved questions, leading to better understanding the process of formation of hybrid composites in general and high electrically conductive ones in particular.

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