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Enhancing the electrical conductivity of carbon black/graphite nanoplatelets: Poly(ethylene-butyl acrylate) composites by melt extrusion

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ABSTRACT: The influence of processing parameters such as screw geometry, temperature profile, and screw speed on the electrical properties of hybrid composites consisting of graphite nanoplatelets and carbon black in ethyl butyl acrylate was studied. Two different screws were used to compound the hybrid composites at two different temperatures and two different screw speeds. A beneficial effect was noted with regard to the electrical properties when adding nanoplatelets to the filler system. The cause could be a synergistic effect due to the difference in particle shape of the two fillers. Lower percolation thresholds were obtained with the conventional screw due to less breakage of the graphite nanoplatelets compared to the barrier screw. No significant changes of the electrical properties were observed when changing the temperature profiles or the screw speeds. Furthermore, the melt viscosity of the compounds was not appreciably affected at the rather low filler contents used here. © 2015 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2016**, *133*, 42897.

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INTRODUCTION

The interest in high voltage power cables has increased in the past few years due to the increasing energy demands of a globalized world. In this type of cables, there are two semiconductive polymeric layers with a main purpose of limiting the electromagnetic field strength and by that increase the resistance against an electrical breakdown. One of these layers is situated between the conductor and the insulation (inner semiconductive layer) and the other can cover the insulation itself (outer semiconducting layer). They consist of a polymeric material highly filled (up to 40 wt %) with conductive fillers, typically carbon black (CB).[1,2] The high loading of filler required however, may be detrimental to the processability, mechanical, electrical, and surface properties of the material.[3] To decrease the amount of filler required and still have adequate electrical properties, hybrid composites based on mixtures of different carbon-based fillers have been studied. Studies on mixtures of CB/graphite nanoplatelets (GNP) or carbon nanotubes (CNT)/GNP and CNP/GNP/CB have shown positive and interesting results.[4–9] The synergistic effect that takes place when combining CB/GNP not only decreases the percolation threshold but also increases the electrical conductivity.[4]

The studies on the CB/GNP-composites have often been focused on high-structured CB in thermosets systems but recently studies on thermoplastic systems with different grades of CB have also appeared.[10] The results indicate the importance of the geometry of the fillers as the hybrids GNP/high-structured CB had a lower electrical percolation threshold than a GNP/low-structured CB system.

In hybrid systems of this type, the ability of the CB-particles to bridge the GNP flakes is believed to be important for achieving a low percolation threshold as well as a sufficiently high conductivity. A high degree of exfoliation of the GNP is then expected to be beneficial recognizing the high in-plane conductivity of these layers. The degree of GNP-exfoliation in composites produced using different methods has been studied earlier and the solvent mixing method was in that case the most successful in terms of exfoliation.[11] The solvent mixing is however quite tedious and difficult to use in a large scale production. The same study indicated the potential of using melt extrusion for mechanical exfoliation (with regard to the electrical conductivity). It is well known that it is possible to disperse and/or de-agglomerate agglomerates of filler particles in polymer melts by melt extrusion due to the shear and elongational flow fields applied to the material[12,13] and this may also contribute to an exfoliation of particles such as GNP. The geometry of the screw plays also an important role since the screw may in a sense give a too efficient dispersion of the filler particles or possibly even break them instead of providing exfoliation, cf. Ref. 11.

A homogeneous dispersion of the filler is important to obtain good mechanical properties, but it may be a disadvantage with regard to the electrical conductivity as it may increase the percolation threshold of the material.

In this work, melt mixing of GNP and CB into a thermoplastic using a single screw extruder was performed and the degree of dispersion was assessed. Two different screws, temperature profiles, and screw speeds were used to better understand how a possible exfoliation and the dispersion of the filler particles affected the percolation threshold and the electrical conductivity. The properties were compared with those of a reference material, obtained with a static mixing chamber. The effect of particle orientation on the electrical conductivity was investigated by extruding the materials through a capillary viscometer at low speeds.

EXPERIMENTAL

Materials

The polymer used as matrix material was the same grade of an ethylene-butyl acrylate copolymer as used in Ref 10. The EBA contained 17 wt % butyl acrylate (BA) and had a density of 0.925 g/cm^3. Two types of nanofillers were used, carbon black (CB) and graphite nanoplatelets (GNP).

The CB was a medium-structured carbon black (CB) ENSACO® 260G from TIMCAL Graphite and Carbon, Switzerland. The CB had a surface area of 70 m^2/g and a density of 1.8 g/cm^3.

The graphite nanoplatelets (GNP) used in this work were xGnP M5 from XG Sciences. According to the manufacturer, the platelets had a thickness of 6–8 nm, a diameter of 5 μm, a surface area of 120–150 m^2/g and a density of 2.2 g/cm^3.

Compounding of Nanocomposites

To obtain the percolation threshold curve, composites containing the pure fillers and a hybrid in which GNP and CB were combined, were manufactured with a Brabender mixing chamber with a volume of 50 cm^3. The mixing was performed at 180°C at 100 rpm for 10 min. The composition used for the hybrid material was 80–20, that is, 80 wt % of the total filler content was GNP and 20 wt % CB. The filler contents used were in the range of 6–14 vol % for the GNP and CB systems and 2–14 vol % for the GNP–CB hybrid. After mixing in the chamber, the materials were extruded in a capillary viscometer, Ceast Rheoscope 100 6742/00, Ceast SpA, Pianezza, Italy, at 170°C using a die with a length/diameter (*L/D*) ratio of 10/1 mm/mm. A piston speed of 2 mm/min corresponding to a shear rate of 24.3 s^{-1} was used. These extrudates were used for assessing the percolation threshold curve.

Masterbatches of GNP and CB were compounded with a twin screw extruder of the type Coperion ZSK 26 K 10.6 (Stuttgart, Germany) with a 10 individually controlled temperature zones. The temperature profile used was 150–170–170–170–170–170–170–170–170–175–175°C in both cases. The filler contents and the screw rotational speeds were different. In case of the CB masterbatch, the filler content was 40 wt % and the screw rotational speed was 230 rpm whereas for the GNP masterbatch the filler content was 20 wt % and the rotational speed was 120 rpm being the lowest possible for the extruder. The masterbatches were used to produce specimens with predetermined filler content by diluting them with unfilled EBA using the mixing chamber as described above and also in order to obtain the hybrid materials as described below.

The extrusion mixing of the hybrid materials was performed with a Brabender compact extruder from Brabender OHG, Duisburg, Germany, with a screw diameter $D = 19$ mm and a screw length of 25 *D*. The cylinder had three individually controlled temperatures zones and a heated circular die with a diameter of 3 mm. Two different temperature profiles were used to study how the viscosity of the melt possibly affected the dispersion of the GNP platelets and the CB and the electrical conductivity of the final composites. The profiles along the barrel from hopper to die were 90, 140, 160, and 160°C and 90, 140, 180, 180°C. Two different extruder screws were also used. A conventional screw with a compression ratio of 2:1 and a Maillefer barrier-flighted screw[14,15] with a compression ratio of 2.5:1 with a Saxton distributive mixer element at the end of the screw, both supplied by Brabender. The screw rotational speeds applied were 50 or 100 rpm. The die temperature, the screw used, and the screw speed are indicated in the sample notation: CS indicating the conventional screw and BS the barrier-flighted screw.

Characterization

Thermogravimetric Analysis. The total filler content and the thermal stability of all the compounded materials were measured by thermogravimetric analysis. The measurements were performed with a TG-DTA/DSC STA 449 F1 Jupiter, Netzsch-Gerätebau GmbH, Germany, equipped with a thermocouple Type K. Samples of approximately 30 mg were heated at 10°C/min from 30 to 600°C in an argon atmosphere. Three different samples were used and the mean value was calculated.

Scanning Electron Microscopy. Scanning electron micrographs of the fillers in powder form and also of cross sections of the compounded materials were obtained using a digital scanning electron microscope Carl Zeiss DSM 940. The samples of the compounded materials were coated with an approximately 5-nm-thick gold layer using a Sputter Coater S150B, BOC Edwards, UK.

Optical Microscopy. Photomicrographs of the compounded materials were obtained with an optical microscope Leitz DMXR, Germany. The orientation and the distribution of the platelets in extruded strings (diameter 3 mm) containing 5 and 11 vol % of the particles, produced with the different screws, were examined. To observe the cross section areas, the samples were embedded in a polymeric resin and afterwards grinded and polished with 9, 3, and 1 μm diamond pastes. Micrographs of the polished surfaces were obtained at magnifications of 100 and 500 times. Image analysis of the cross sections, that is, measurements of length and width of the platelets and distances between them, was performed with the software Axio Vision 5.1.

Electrical Measurements. The electrical measurements were performed using a two-point technique.[16] Two different types of

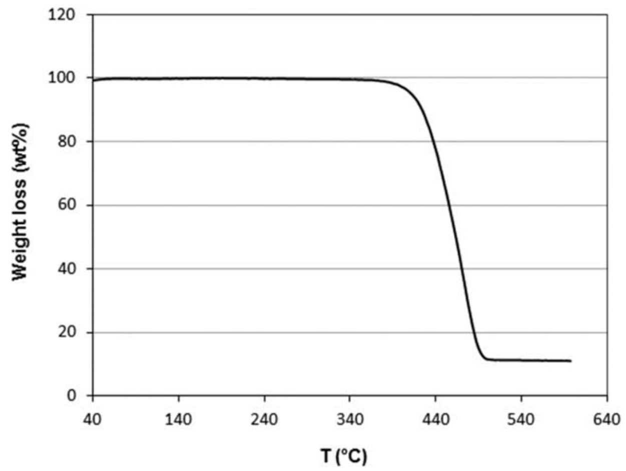

Figure 1. TGA curve for a sample with a total filler content of 5 vol % compounded with the conventional screw at 160°C and 50 rpm (160CS50).

samples were used. After extrusion mixing, some part of the materials was extruded in a capillary viscometer, Ceast Rheoscope 100 6742/00, Ceast SpA, Pianezza, Italy, at 170°C using a die with a length/diameter (*L/D*) ratio of 10/1 mm/mm. A piston speed of 2 mm/min corresponding to a shear rate of 24.3 s^{-1} was used. The extrudates obtained from the capillary and also the ones obtained from the single screw extruder were cryo-fractured in liquid nitrogen to a length l of 25 mm and afterwards the fractured surfaces were painted with silver paint. A voltage was applied over the length of the specimen and the current was measured with a digital multimeter type Fluke 8846A. From the current measurements, the resistance R was evaluated and the electrical conductivity σ was obtained as:

$$\sigma = \frac{l}{RA}, \quad (1)$$

where A is the cross section area of the specimen.

In this case, three different voltages levels were applied depending on the conductivity of the specimens. The voltage used for the materials with a conductivity higher than 10^{-3} S/cm was 10 V, 100 V for materials with conductivities between 10^{-5} and 10^{-3} S/cm and 300 V for the materials with a conductivity lower than 10^{-5} S/cm. A total of 15 different measurements were done, and the mean value is given.

X-ray Diffraction. X-ray diffractograms were obtained with a Bruker D8 Advanced X-ray diffractometer using CrKα radiation with a wavelength of 2.2897 Å. The generator was set to 35 kV and 40 mA. Spectra were recorded every 0.02° with steps of one second.

Mechanical Properties. The mechanical properties of extruded strings of EBA and composites with 3.5 and 11 vol % filler obtained with the different screws were determined with a tensile testing machine, Zwicki-Line Z2.5, Germany, equipped with a load cell of 500 N. A special fixture for the strings was used. The gauge length was set at 70 mm and the measurements were performed at 70 mm/min to obtain a deformation rate of 100%/min. A pre-load of 1.2 N was applied in all measurements. The mean value and the standard deviation of the properties were based on 10 measurements.

Rheological Properties. The shear viscosity of EBA and the compounded materials with 3.5 and 11 vol % filler content was measured by means of a Göttfert Rheograph 2002 capillary viscometer. A capillary with a flat entry and a diameter of 2 mm and a length of 20 mm was used. The rheological properties were measured at shear rates between 10 and 500 s^{-1} at 160°C. In this case, the data obtained were not subjected to any corrections as the main purpose of the study was to qualitatively assess any difference in viscosity between the different materials.

RESULTS AND DISCUSSION

Filler Content and Thermal Stability

The total filler content of the compounded materials was measured using thermogravimetric analysis. Figure 1 shows a typical thermogravimetric analysis (TGA) curve obtained for the compounded materials, in this case containing 5 vol % filler (10 wt %). The main weight loss corresponding to the EBA took place in the range 350–500°C and a residue consisting of the filler particles remained. The high thermal stability of the EBA copolymer is in agreement with that reported by others.[17]

Percolation Determination

The electrical conductivity versus the filler content (vol %) for the composites filled with the carbon black (CB), the graphite nanoplatelets (GNP), and the hybrid materials (GNP-CB) is shown in Figure 2. The onset of electrical conductivity for the CB system was higher than for the hybrid system. The percolation threshold for the CB material, that is, the point where the slope became appreciably steeper, was around 6.9 vol %. Approximately the same value was obtained for the pure GNP system.[10] The hybrid system GNP-CB had a lower percolation threshold (3 vol %) due to a synergistic effect when GNP and CB were combined. For both systems, the conductivity values leveled off around 14 vol %. In the case of the hybrid system, there were some indications of a weakly pronounced second percolation threshold around 7 vol % filler content. This

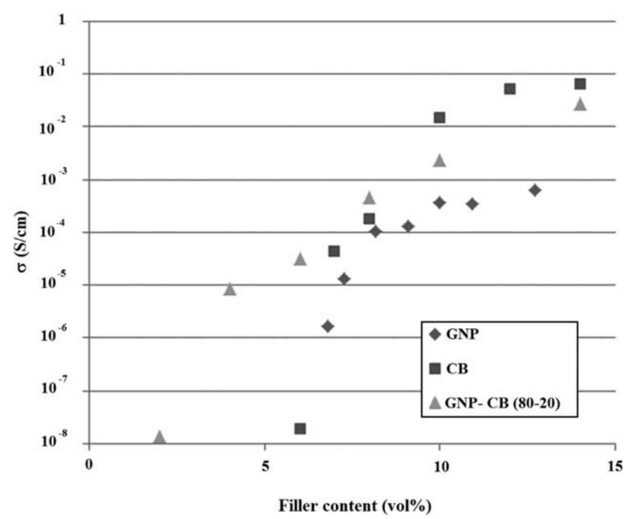

Figure 2. The electrical conductivity as a function of the filler content for the pure CB, pure GNP, and the hybrid GNP-CB systems.

Table I. Average Values of Conductivities and Standard Deviations for 5 vol % Hybrid Systems Extruded with the Conventional Screw

Sample	Conductivity (S/cm)	Standard deviation (S/cm)
160C50 5 vol % Cap	4.5×10^{-4}	2.0×10^{-4}
160C100 5 vol % Cap	1.5×10^{-4}	1.7×10^{-4}
180C50 5 vol % Cap	7.5×10^{-4}	6.1×10^{-4}
180C100 5 vol % Cap	6.6×10^{-4}	7.9×10^{-4}
160C50 5 vol %	1.4×10^{-2}	6.0×10^{-3}
160C100 5 vol %	6.1×10^{-3}	3.7×10^{-3}
180C50 5 vol %	3.6×10^{-3}	2.1×10^{-3}
180C100 5 vol %	7.3×10^{-3}	4.9×10^{-3}

threshold is very weak and further studies are required to ascertain its existence and speculate about the underlying reasons for it.

To study the processing effect on the conductivity of the hybrid system, the volume percentages of the filler were chosen to be 3.5, 5, and 11 vol %.

The Effect of Processing on the Electrical Conductivity

The average values of the conductivity are shown in Tables I and II. The notation Cap is used for the composites that had passed through the capillary viscometer after the extrusion mixing. The reference value, being slightly higher than 10^{-5} S/cm and included in Figure 3, was obtained by interpolation of the percolation threshold curve (to 5 vol %), that is, for materials compounded in the mixing chamber and then forced through the capillary viscometer as described in Experimental section.

The conductivities of the specimens obtained with the conventional screw exceeded in some cases that of the reference material (being slightly higher than 10^{-5} S/cm) with 3 orders of magnitude whereas the conductivities obtained with the barrier screw were 3 or 4 orders of magnitude lower than that of the reference material. Thus, it could be concluded that the conventional screw led to a more efficient microstructure in terms of dispersion of the fillers in the matrix than both the barrier

Table II. Average Values of Conductivities and Standard Deviations for 5 vol % Hybrid Filled Systems Extruded with the Barrier Screw

Sample	Conductivity (S/cm)	Standard deviation (S/cm)
160B50 5 vol % Cap	7.1×10^{-9}	4.0×10^{-10}
160B100 5 vol % Cap	7.6×10^{-9}	3.6×10^{-10}
180B50 5 vol % Cap	7.7×10^{-9}	3.6×10^{-9}
180B100 5 vol % Cap	8.3×10^{-9}	6.6×10^{-9}
160B50 5 vol %	8.6×10^{-10}	5.8×10^{-11}
160B100 5 vol %	7.9×10^{-10}	1.5×10^{-10}
180B50 5 vol %	9.7×10^{-10}	4.5×10^{-11}
180B100 5 vol %	8.3×10^{-10}	1.63×10^{-10}

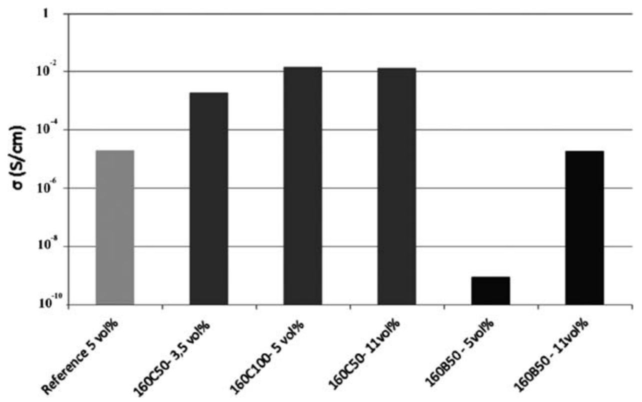

Figure 3. The electrical conductivities of hybrid systems with different filler contents extruded with the conventional screw (denoted with C) and the barrier screw (denoted with B). All samples were extruded at a screw speed of 50 rpm and a die temperature of 160°C. The reference was a specimen compounded in the mixing chamber and then forced through the capillary viscometer.

screw and the mixing chamber. For the particular case of the composites that had passed through the capillary viscometer after the extrusion mixing (denoted as Cap in the sample name), the opposite trend was observed. The conductivity of the material obtained with the conventional screw decreased whereas for the material processed with the barrier screw it increased. This could be due to an orientation effect (related to the platelets) caused by the capillary.[18] The first observation can be considered as negative for the electrical properties of the filled systems due to the loss of possible contacts between platelets. The second observation could possibly contribute positively to the electrical properties of the materials compounded with the barrier screw.

The processing temperature and the screw speed did not seem to have any major effect on the conductivity, at least not within the ranges used here. Hence, the corresponding changes in shear stresses/deformation rates due to lower temperature or higher rotational speeds were probably not too drastic.

The effect of processing on the electrical properties for materials with different filler contents and compounded with both screws at 160°C and 50 rpm is shown in Figure 3. Comparing the conductivities obtained with those from the percolation curve (Figure 2), the conductivity increased by 3 orders of magnitude for the 3.5 vol % filled system whereas for the 11 vol % filled system the increase was less than 1 order of magnitude. The results obtained with 3.5 vol %, 5 vol %, and 11 vol % of filler content described a percolation curve where the conductivity seemed to level out below 5 vol % content, reaching a similar value to the one with the highest filler contents in Figure 2. Thus, the beneficial microstructure obtained with the conventional screw extrusion appeared to be present at a filler content as low as 3.5 vol % and the conductivity leveled out at 11 vol %.

The two bars to the right in Figure 3 denote the conductivity of the 5 and 11 vol % hybrid filled systems extruded with the barrier screw. The screw speed and die temperature were again 50 rpm and 160°C, respectively. Comparing the conductivities

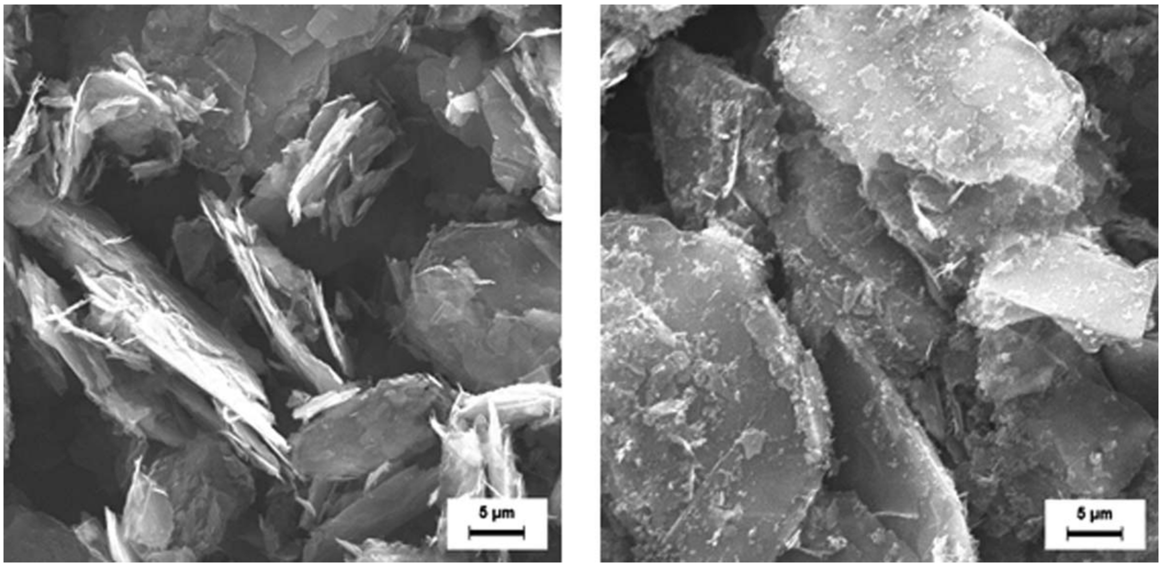

Figure 4. Scanning electron micrographs of GNP after compounding with the twin-screw extruder (left) and after barrier screw extrusion (right).

of the materials containing 5 vol % and 11 vol % filler and extruded with the barrier screw with the conductivities obtained with those from the percolation curve in Figure 2, the conductivity decreased by 3 orders of magnitude at 11 vol %. This decrease in conductivity could be due to a partial destruction of the particle network caused by the efficiency of the barrier screw in dispersing the particles.

Scanning Electron Microscopy

Scanning electron microscopy micrographs of the GNP filler before (not shown here) and after the compounding with the twin-screw extruder revealed a low degree of breakage of the nanoplatelets as many nanoplatelets retained the original size after compounding (Figure 4, left). Furthermore, using the micrographs taken of the compounds obtained with the barrier and conventional screws (Figure 4, right), it was difficult to assess the degree of breakage due to the processing. This is discussed in more detail in the section on "Optical microscopy" below.

As evident from the photos in Figure 5 indications of a rather low adhesion between the filler and the matrix were quite obvious; after fracturing voids at the interface appeared at some positions.

Optical Microscopy

Examples of optical micrographs from a cross section from samples with 11 vol % filler content extruded at 50 rpm and 160°C with the conventional screw and the barrier screw are shown in Figures 6 and 7, respectively. Several pictures were taken from different regions of the extrudates. In general, a higher amount of fillers and also a more pronounced degree of

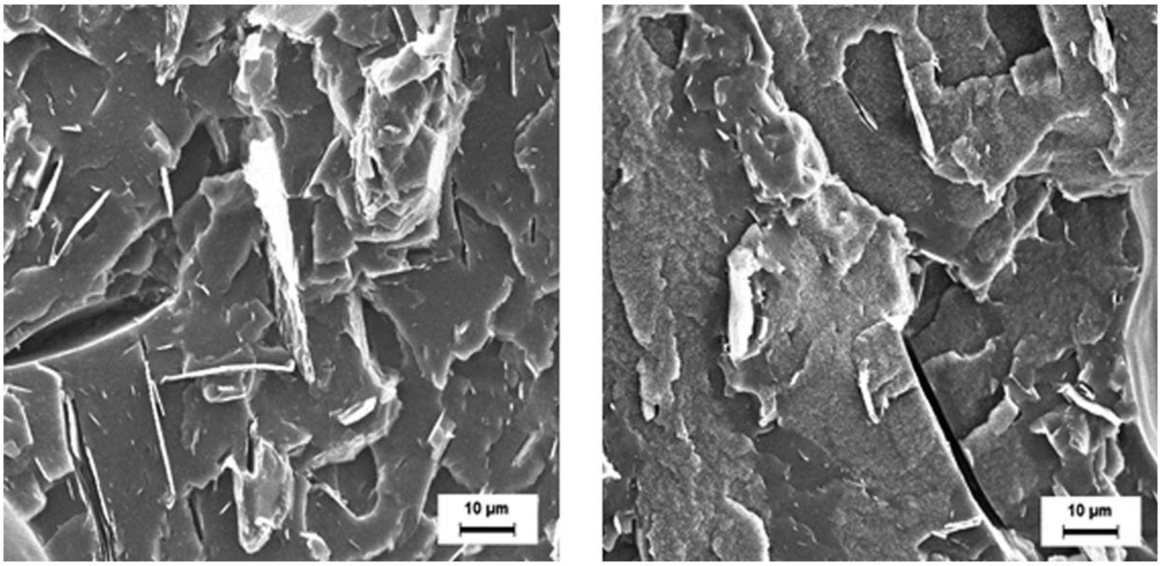

Figure 5. Scanning electron micrographs of fracture surfaces of composites based on the hybrid system. The specimens were extruded with the barrier screw (left) and the conventional screw (right).

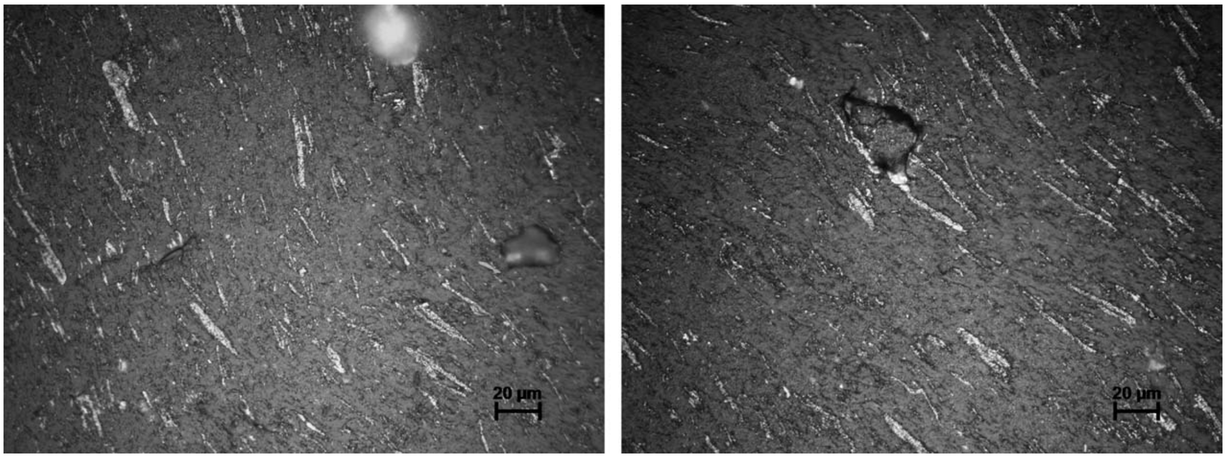

Figure 6. Optical micrograph of a conventional screw compounded sample. The sample contained 11 vol % of the hybrid filler.

particle orientation were observed in the peripheral region and a significant amount of voids was also noted. The material with higher electrical conductivity (Figure 6) contained longer nanoplatelets than the one of lower conductivity (Figure 7). Furthermore, a tendency for the agglomerates to be closer was observed in the compound with high electrical conductivity.

The optical micrographs were subjected to image analysis. The areas of the platelets/agglomerates, their lengths, and widths as well as the distance between them were measured. Figure 8 shows the length distribution for both types of compounded materials. Only platelets longer than 10 μm were included here. The material compounded with the conventional screw contained longer platelets/agglomerates than the barrier screw compounds. The same tendency was observed for the area of the platelets. Furthermore, the conventional screw yielded a higher amount of agglomerates. An excessive breakage of the nanoplatelets could therefore be the reason for the negative effect of the barrier screw on the electrical properties of the filled polymer. This is in line with the assumption that particles with a higher aspect ratio enhance the formation of conductive pathways.[19]

The width measurements, not shown here, did not reveal any significant differences between the two compounds. The distance between the filler particles was somewhat smaller in the case of the material compounded with the conventional screw.

The results from the image analysis of the materials extruded with the barrier screw were consistent with the speculations regarding network destruction from the conductivity measurements. The presence of visually detectable platelets was low and therefore a reduction of the platelets to very small sizes was suspected.

In the case of the conventional screw, the effective microstructure indicated from the conductivity results was supported by the observations of a relatively large amount of unbroken platelets with a closer distance between them. Although it could not be quantitatively measured, some exfoliation of the platelets could be speculated on; however, no definite conclusion could be drawn and further studies are needed.

X-ray Diffraction

Figure 9 shows diffractograms for EBA, two hybrid composite samples with 5 vol % filler content obtained with the different screws and the GNP masterbatch; all in pellet form.

All samples exhibited a peak at 32° which corresponds to the crystalline regions of the polymeric matrix. The second peak corresponds to the crystallographic distance between the (0 0 2)

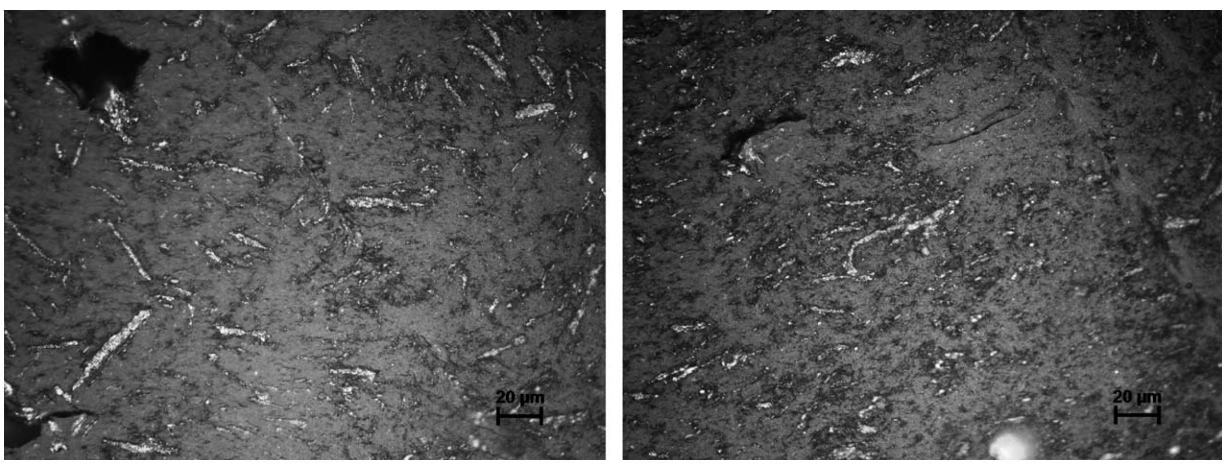

Figure 7. Optical micrograph of a barrier screw compounded sample. The sample contained 11 vol % of the hybrid filler.

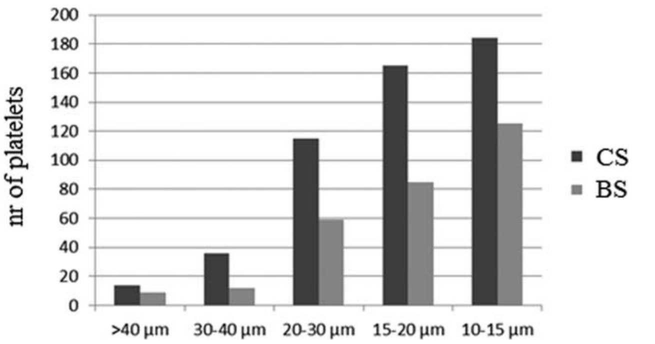

Figure 8. The length distribution of nanoplatelets/agglomerates in the conventional screw compounded and barrier screw compounded materials.

planes, that is, the distance between the graphene layers.[20] The intensity of the peaks decreased from the masterbatch to the processed materials, indicating that the diameter of the platelets was reduced by the processing, but no significant differences were observed between samples obtained with the different screws. The position of the peaks which indicates the distance between the layers was different for the composite obtained with the conventional screw. In the case of the GNP masterbatch and the composite obtained with the barrier screw (160B50 5 vol %), the peak was positioned at 40.13°, whereas for the composite obtained with the conventional screw (160C50 5 vol %) it was slightly shifted to a lower value (39.87°). This corresponds to a slight increase in the distance between the graphene layers possible due some polymer intercalation when using the conventional screw. It might be expected that the more severe treatment of the melts by the barrier screw also would lead to some intercalation. This was however not observed and the reason for this is at present not clarified.

Mechanical Properties

Table III shows the Young's modulus (E), the ultimate tensile strength (σ_b) and the elongation at break (ε_b) for the unfilled polymeric material and the hybrid filled systems containing 3.5 and 11 vol % filler. The EBA copolymer had the lowest E-value (130 MPa) but exhibited good ductile properties. Because of experimental restrictions, the elongation at break was not possible to determine for the composite materials containing 3.5 vol % filler and for the EBA, but in both cases an elongation of 800% was reached. For the same reason, the ultimate tensile strength was not determined. The modulus of the low-filler-content materials was more than twice that of the EBA with a value of 320 MPa. As expected, an increase in the stiffness of the material was observed with the addition of the rigid fillers with high aspect ratios.

Table III. Average Values of Young's Modulus (E), Ultimate Tensile Strength (σ_b), and Elongation at Break (ε_b) for the Unfilled Polymer (EBA) and Systems with Different Hybrid Filler Contents Processed with the Conventional and the Barrier Extruder

Sample	E (MPa)	σ_b (MPa)	ε_b (%)
EBA	128 (7)	–	–
160C50 3.5 vol %	318 (18)	–	–
160B50 11 vol %	559 (33)	8.1 (0.1)	72 (3)
160C50 11 vol %	539 (51)	8.1 (0.2)	71 (20)

The standard deviations are indicated in parentheses.

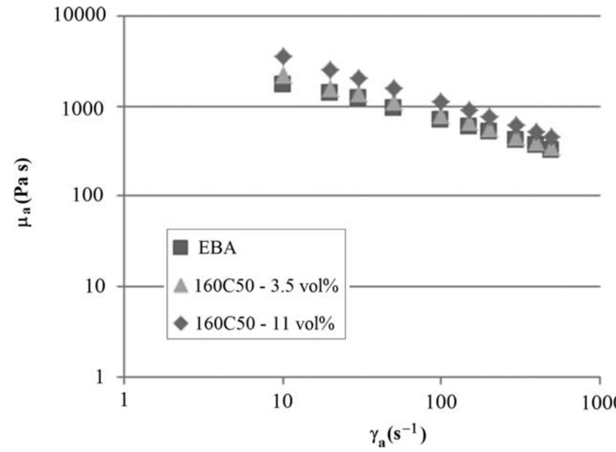

Figure 10. The apparent viscosity as a function of shear rate for unfilled EBA and composite melts processed with the conventional screw (3.5 and 11 vol % hybrid fillers).

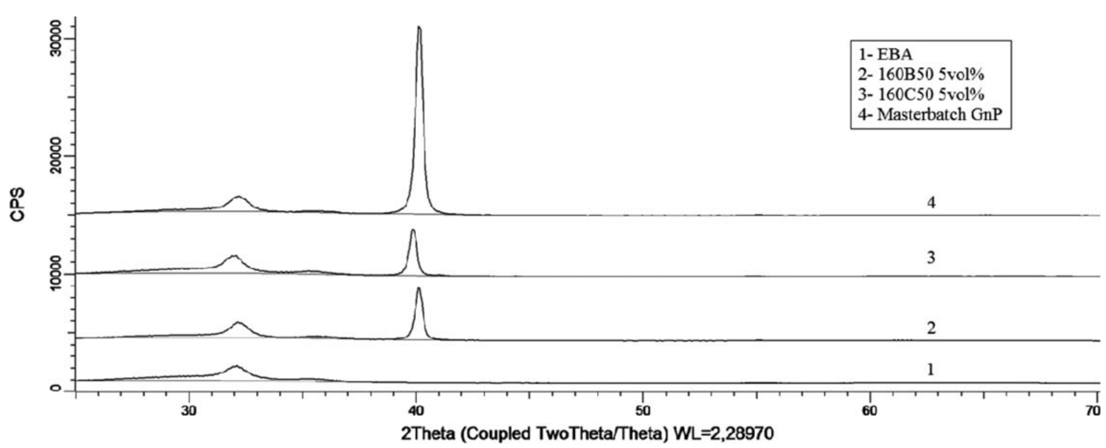

Figure 9. X-ray diffractograms for EBA and composites containing 5 vol % filler in pellet form.

In the case of 11 vol % filler, the elongation at break decreased substantially as expected compared to that of the unfilled polymer. For the two differently processed materials, the strain at break was approximately 70%. The ultimate tensile strength (σ_b) was also similar for both materials and about 8 MPa. The *E*-modulus was increased further with higher amounts of filler taking a value of approximately 560 MPa in the case of the barrier screw and 540 MPa for the conventional screw. Thus, there were no greater differences in mechanical behavior between those two composites. A possible reason for this could be the lack of adhesion between the nanoplatelets and the polymer.

The standard deviations for the experimental data are also given in Table III. As expected, because of its better dispersion capability, the properties obtained with the barrier screw exhibited lower values of the standard deviation than those produced with the conventional screw.

Rheological Properties

The results from the viscosity measurements are shown in Figure 10. The viscosity was not very much affected by low amounts of filler used here; as expected the viscosity increased when the filler content increased.

CONCLUSIONS

The main conclusions from this work can be summarized as follows:

- Combining GNP and CB into a hybrid filler can substantially reduce the electrical percolation threshold of the nanocomposite, that is, a synergistic effect is achieved.
- The processing procedure can have strong influence on the electrical conductivity and the percolation threshold of the nanocomposites.
- Here, extrusion with a conventional screw produced composites with a significantly higher electrical conductivity at a given filler content than samples manufactured with a barrier screw. Probably this can be associated with a more extensive breakage of the GNPs with the latter screw as supported with the microscopy analysis.
- Indications of polymer intercalation between the graphene layers were noted when using the conventional screw.
- Alignment of the graphite nanoplatelets, that is, orientation, due to shear/elongational flow fields during processing can be detrimental with regard to the electrical conductivity of the composite material.
- Even low amounts of the hybrid filler will change the mechanical properties of this type of nanocomposites, for example, a marked increase of the stiffness. The shear viscosity appeared to be affected to a lesser extent.

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REFERENCES

1. Jäger, K. M.; McQueen, D. H. *KGK Kautschuk Gummi Kunststoffe* **1999**, *52*, 734.
2. Jager, K. M.; Lindbom, L. *Electrical Insulation Magazine, IEEE* **2005**, *21*, 20.
3. Jeong, K. U.; Lim, J. Y.; Lee, J. Y.; Kang, S. L.; Nah, C. *Polym. Int.* **2010**, *59*, 100.
4. Fan, Z.; Zheng, C.; Wei, T.; Zhang, Y.; Luo, G. *Polym. Eng. Sci.* **2009**, *49*, 2041.
5. Ren, P. G.; Di, Y. Y.; Zhang, Q.; Li, L.; Pang, H.; Li, Z. M. *Macromol. Mater. Eng.* **2012**, *297*, 437.
6. Li, J.; Wong, P. S.; Kim, J. K. *Mater. Sci. Eng. A-Struct.* **2008**, *483–484*, 660.
7. Wei, T.; Song, L.; Zheng, C.; Wang, K.; Yan, J.; Shao, B.; Fan, Z. J. *Mater. Lett.* **2010**, *64*, 2376.
8. Kumar, S.; Sun, L. L.; Caceres, S.; Li, B.; Wood, W.; Perugini, A.; Maguire, R. G.; Zhong, W. H. *Nanotechnology* **2010**, *21*, 105702.
9. Via, M. D.; Morrison, F. A.; King, J. A.; Beach, E. A.; Wiese, K. R.; Bogucki, G. R. *Polym. Compos.* **2012**, *33*, 306.
10. Oxfall, H.; Ariu, G.; Gkourmpis, T.; Rychwalski, R. W.; Rigdahl, M. *Express Polym. Lett.* **2015**, *9*, 66.
11. Oxfall, H.; Rondin, J.; Bouquey, M.; Muller, R.; Rigdahl, M.; Rychwalski, R. W. *J. Appl. Polym. Sci.* **2013**, *128*, 2679.
12. Ariño, R.; Boldizar, A. *Polym. Eng. Sci.* **2012**, *52*, 1951.
13. Ariño, R.; Boldizar, A. *Int. Polym. Proc.* **2013**, *28*, 421.
14. Maillefer, C. E. G.B. Pat. 964,428, December 6, **1960**.
15. Maillefer, C. E. U.S. Pat. 3,358,327, December 19, **1967**.
16. Heaney, M. B. In Electrical Measurement, Signal Processing, and Displays; Webster, J. G., Eds.; CRC Press, Boca Raton, **2003**, Chapter 7, p 1.
17. Huang, N.; Wang, J. *J. Anal. Appl. Pyrol.* **2009**, *84*, 124.
18. Ausias, G.; Agassant, J. F.; Vincent, M. *Int. Polym. Proc.* **1994**, *9*, 51.
19. Kalaitzidou, K.; Fukushima, H.; Drzal, L. T. *Materials* **2010**, *3*, 1089.
20. Inagaki, M. In New Carbons-Control of Structure and Functions; Elsevier, Eds., Oxford, UK, **2000**, Chapter 1, p 1.