

# Improvement of Electrical Resistivity of Highly Filled Graphite/PP Composite Based Bipolar Plates for Fuel Cells by Addition of Carbon Black

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**Abstract.** Novel material solutions for polymer based bipolar plates in fuel cells require adapted ways to develop suitable material compositions. The common pathway to develop materials with at the same time high electrical as well as thermal conductivity is the use of conductive graphite as filler with contents up to 80-85 wt.%. However, there is a need to develop recipes with maximized conductive behavior at lowest possible content of conductive filler to enhance the mechanical properties and allow good processability. In this study, composites based on polypropylene (PP) and different filler systems were melt-mixed using a lab scale co-rotating twin-screw extruder and compression molded to bipolar type plates. As fillers synthetic (G) or expanded (EG) graphites were incorporated. At the overall filler content of 60 wt.% or 80 wt.% part of the graphite was replaced by highly conductive carbon black (CB, 2.5 wt.%, 5.0 wt.%). It was found that the addition of CB significantly reduced the electrical volume as well as the surface resistivity up to values of 0.12  $\Omega \cdot \text{cm}$  or 4 m $\Omega$ /square, respectively. For the values of thermal conductivity the kind and particle size of the selected graphite was important. If expanded graphite was partially replaced by CB, the thermal conductivity of PP/EG+CB composites decreased significantly. Otherwise, the combination of synthetic graphite and CB changed the thermal conductivity of PP composites only marginal at the same overall filler content. For both graphite types the filler with larger particle size resulted in higher thermal conductivity.

## INTRODUCTION

Despite the established commercial polymer composite materials available for producing bipolar plates for fuel cell stacks with suitable conductive properties, there are still research activities needed to develop bipolar plates with maximized electrical and thermal conductivity [1-5]. The common pathway to develop such materials is to enhance the content of conductive fillers (e.g. synthetic graphite (G)) in the composite [6-10]. Other research activities focus on the use of expanded graphites (EGs) that have high intrinsic electrical and thermal conductivity. The approach of using bimodal filler systems based on graphite and carbon black (CB) seems to be promising. Dweiri et al. described for polypropylene (PP) composites containing constant 80 wt.% carbon based filler an increase of electrical conductivity if graphite was replaced by CB. The conductivity increased from 7 S/cm (resistivity 0.14  $\text{Ohm} \cdot \text{cm}$ ) for PP/G 20/80 wt.% up to 36 S/cm (0.03  $\text{Ohm} \cdot \text{cm}$ ) for PP/G/CB 20/55/25 wt.% [10]. Király et al. [11] replaced PP by CB by holding the graphite content (vol.%) constant which resulted in an increase of electrical conductivity. At around 40 vol.% graphite, the CB addition leads to an increase from 0.1 S/cm (PP/CB/G 61.3/0/38.7 vol.%) up to 1 S/cm (PP/CB/G 57.9/2.5/39.6 vol.%) or 10 S/cm (PP/CB/G 50.7/7.8/41.6 vol.%). Derieth et al. [7] studied the influence of particle size of graphite on electrical conductivity whereas particle sizes varied between 5 and 20  $\mu\text{m}$ . It was found that composites with smaller graphite particles tend to have lower conductivities than composites containing larger graphite particles.

In this study, composites based on polypropylene (PP) and carbon based filler systems of graphite and carbon black were melt mixed using a lab scale co-rotating twin screw extruder. The measurements of the electrical volume resistivity as well as thermal conductivity of the composites were performed on model bipolar plates compression molded under industrial conditions. The influence of combinations of graphite and carbon black in the composite on both conductive properties was investigated. Additionally, the fillers were characterized concerning their particle size distribution.

## EXPERIMENTAL PART

Composites are melt-mixed using a lab scale co-rotating twin-screw extruder Zyp ZSK26Mc (Coperion) using a screw with a L/D ratio of 45 at 200°C, throughput of 10 kg/h and rotation speed of 150 min<sup>-1</sup>. The final composites contained 14 wt.% polypropylene (PP, Sabic PP579S), 6 wt.% ethylene-propylene-diene-rubber (EPDM) for improved impact behavior, and 80 wt.% filler. In a first extrusion step, the PP/EPDM blend was prepared having the mass ratio of 70 wt.% PP and 30 wt.% EPDM. In the second extrusion step the composites were extruded whereby graphite and carbon black were dosed by two side-feeders. For the mixtures of graphite and carbon black a part of the graphite was replaced by carbon black to remain the filler content constant at 60 or 80 wt.%.

As synthetic graphite Timcal Timrex<sup>®</sup> KS300-1250 and KS500 from Imerys Graphite & Carbon Switzerland Ltd., and as expanded graphite the types Sigratherm<sup>®</sup> GFG600 and GFG1000HD from SGL Group were used. As electrical conductive carbon black the type Ketjenblack<sup>®</sup> EC600JD from AkzoNobel Polymer Chemistry having a BET surface area of 1270 m<sup>2</sup>/g and a primary particle radius of 34 nm was used.

The agglomerate size distribution of the graphite powders was determined by laser diffraction using a Helos/BF particle size analyzer coupled with a RODOS dry dispersion unit and ASPIROS micro dose module (Sympatec GmbH, Germany). The measurement range is 4.5–875 µm. From the distributions the characteristic particle diameters  $x_{10}$ ,  $x_{50}$ , and  $x_{90}$  were calculated indicating that 10%, 50%, and 90% of the agglomerate particles are smaller than the given value. The mean value of particle size was calculated from three measurements.

The morphology of the graphite powders was observed by scanning electron microscopy (SEM) using the Ultra Plus from Carl Zeiss AG (Oberkochen, Germany). The powders were sputtered with 3 nm platinum.

The measurements of the electrical resistivity and thermal conductivity of the composites were performed on pressed model bipolar plates (20 cm x 22 cm). The pressing of the composites was done at 190-195°C and a pressure of 170 t. The electrical volume and surface resistivity was measured using the Loresta-GP (Mitsubishi) combined with 4-pin-electrode ESP at different locations on the plate. The mean value of electrical resistivity was calculated from five measurements. The thermal conductivity was determined by the laser flash method at 25 °C using the LFA 447 NanoFlash<sup>®</sup> (Netzsch, Germany). The mean value of thermal conductivity was calculated from two measurements.

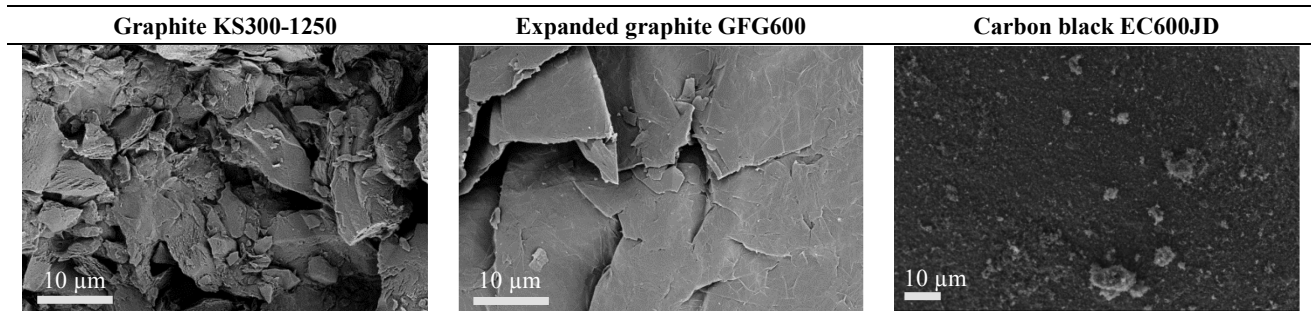
## RESULTS

The morphology of graphite and carbon black powders was characterized by measuring their particle size and the observation in a scanning electron microscope. The mean values of particle size are given in table 1. For the synthetic graphite KS300-1250 larger particles were measured compared to KS500. The particle size distribution of KS500 is much broader than for KS300-1250. For expanded graphite only the particle size of GFG600 could be determined and this material has smaller size than the synthetic graphites. The particles of GFG1000HD were too large to be measured in the used equipment. Therefore it was concluded that the particles are larger than the measuring range of 875 µm. As expected, the smallest particles size was found for carbon black EC600JD. However, the particle size distribution was bimodal having maxima at 15 µm and 215 µm.

**TABLE 1.** Particle size distribution of dry powders

| sample         | $x_{10}$ [µm]  | $x_{50}$ [µm] | $x_{90}$ [µm] | Kind of distribution                 |
|----------------|--|---------------|---------------|--------------------------------------|
| KS500 [5]      | 22.8   | 143.5         | 416.2         | monomodal                            |
| KS300-1250 [5] | 79.3   | 327.4         | 470.3         | monomodal                            |
| GFG600         | 106.1  | 268.8         | 394.6         | monomodal                            |
| GFG1000HD      | Not measurable; all particle have a particle size larger than 875 µm |               |               |                                      |
| EC600JD        | 5.6  | 65.0          | 256.2         | Bimodal: maximum at 15 µm and 215 µm |

Next to the particle size also the layer morphology plays a role for the dispersability of fillers with other fillers and with the polymer matrix. In Figure 2 the morphology of synthetic and expanded graphite as well as carbon black is exemplarily shown. The two kinds of graphite contain platelets which are much larger than those of expanded graphite. The carbon black material includes small spherical particles which are partially agglomerated. It is expected that the small carbon black particles can fill easily the place between the large platelets of graphite, leading to positive effects on the properties.



**FIGURE 1.** Scanning electron microscopy images of the carbon based fillers

The PP composite plates were characterized regarding thermal conductivity and electrical volume resistivity (Figure 2). For the interpretation of the influence of CB on the thermal conductivity and electrical resistivity of the composites, it has to be noted that the PP composites containing only 2.5 or 5.0 wt.% CB have the same thermal conductivity as unfilled PP (0.23 W/(m·K)) and are electrical non-conductive.

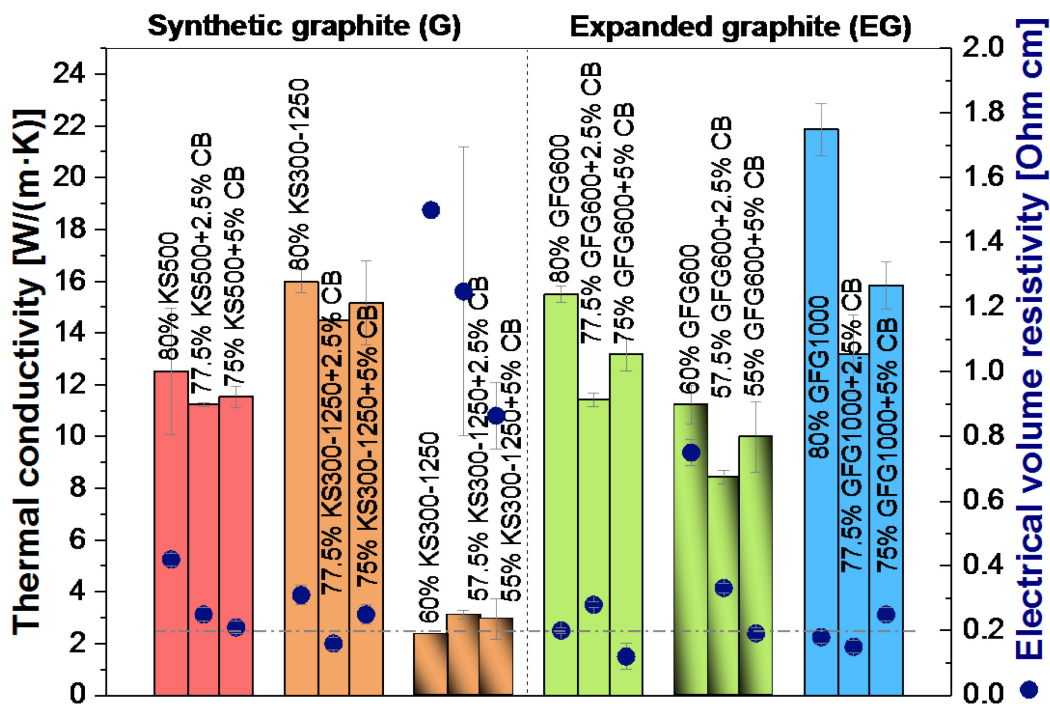
It was found that, at 80 wt% total filler content, the replacement of synthetic graphite by CB (2.5 or 5.0 wt.%) leads only to a marginal decrease of thermal conductivity from 12.5 to 11.5 W/(m·K) (KS500) or 16 to 15 W/(m·K) (KS300-1250) for the filled PP composites. As seen from these values, the graphite with larger particle size results in higher thermal conductivity values. For composites filled with 60 wt% KS300-1250 or 60 wt% KS300-1250 combined with CB, the thermal conductivity was determined to be 3.0 W/(m·K).

In case of PP composites with expanded graphite, the thermal conductivity decreases significantly if part of the EG was replaced by carbon black. For composites containing GFG1000 the mean values decreases significantly from 21.9 W/(m·K) to 13.2 (@ 2.5 wt.% CB) and 15.9 W/(m·K) (@ 5.0 wt.% CB). Also for PP/ 80 wt% GFG600 the thermal conductivity decreases from 15.5 W/(m·K) to 11.4 and 13.2 W/(m·K) if 2.5 or 5.0 wt.% CB, respectively, were added. For PP/ 60 wt% GFG600 the same tendency was detected: The thermal conductivity decreases from 12.2 W/(m·K) to 8.4 and 10.0 W/(m·K) if 2.5 or 5.0 wt.% CB, respectively, were added. Again, the composites having EG with larger particle size show higher thermal conductivity values. Especially for PP/EG composites it seems that the CB addition damages the carbon network needed for the phonon transport responsible for thermal conduction. It can be concluded that especially the larger platelets of expanded graphite GFG1000 in combination with the small CB particles were not able to form a homogeneous filler network indicated by a significantly decrease of thermal conductivity to around 60%. However, the values of thermal conductivity of PP/GFG1000+CB composites are higher than for PP/GFG600+CB composites.

Furthermore, the electrical volume and surface resistivities of the PP composites were measured and the values of volume resistivity are given in Figure 2 (blue sphere). The largest reduction of resistivity values when adding CB was found for PP/80 wt% KS500 composites. The replacement of synthetic graphite by carbon black leads to a decrease of volume resistivity from 0.42 to 0.21 Ohm·cm and of surface resistivity from 49 to 6-12 mOhm/square. The PP composite filled with KS300-1250 had with 0.31 Ohm·cm and 14 mOhm/square already lower starting resistivity values than PP/KS500. The addition of CB leads also to volume resistivities of around 0.2 Ohm·cm and 6-9 mOhm/square being in the same range like the PP/KS500+CB composites. At a total filler content of 60 wt.%; the replacement of (expanded) graphite by CB leads to a significant decrease of resistivity values. For the filler KS300-1250, the volume resistivity decreases from 1.5 Ohm·cm to 1.25 (@ 2.5 wt.% CB) or 0.86 Ohm·cm (@ 5.0 wt.% CB). For the surface resistivity the lowest values was reached for PP composites filled with 55 wt.% KS300-1250 and 5 wt.% CB having 112 Ohm/square which is significantly higher than the values for PP/80 wt.% graphite composite.

In contrast, for PP/expanded graphite composites the tendencies of the influence of CB addition on electrical properties were different. The PP/expanded graphite (GFG600 or GFG1000HD) composites without carbon black have already low volume resistivities of 0.19 or 0.18 Ohm·cm and surface resistivities of 10 or 19 mOhm/square, respectively, which is in the range of resistivity achieved in PP/G composites if CB was added. If the PP/EG composites contain CB no clear tendency of volume resistivity could be detected. For the filler combination of 75 wt.% expanded graphite GFG600 with 5 wt.% carbon black the lowest volume resistivity of this study was found, namely 0.12 Ohm·cm. For both kinds of expanded graphite the surface resistivity decreases up to 4-5 mOhm/square and is marginal lower compared to PP composites filled with synthetic graphite and carbon black. At 60 wt.% filler content, the hybrid filler system of GFG600+CB (55+5 wt.%) leads also to very low volume resistivity of 0.19 Ohm·cm which is the same range like PP/80 wt.% EG. The surface resistivity of PP/60 wt.% GFG600+CB composites was found to be 16-20 Ohm/square which is only slightly higher compared to PP/80 wt.% GFG600+CB.

It can be summarized that the replacement of graphite by carbon black leads to a significant decrease of electrical resistivities especially for PP composites containing synthetic graphite. However, the electrical resistivity values for PP/EG composites were already lower than for PP/G composites with and without carbon black.



**FIGURE 2.** Thermal conductivity (bars) and electrical volume resistivity (spheres) of composites containing 60 or 80 wt.% (graphite and carbon black) and 40 or 20 wt.% PP/EPDM (70/30), filler amount is indicated on the bars.

## SUMMARY

In this study, composites based on polypropylene (PP)/ ethylene-propylene-diene-rubber (EPDM) (70/30) blends and different filler systems were melt mixed using a lab scale co-rotating twin-screw extruder. As filler synthetic or expanded graphites were incorporated. At the overall filler content of 80 wt.%, a part of graphite was replaced by highly conductive carbon black (2.5 wt.%, 5.0 wt.%). The thermal conductivity as well as the electrical volume and surface resistivity of composites were studied on compression molded bipolar shape plates.

It was found that the replacement of graphite by carbon black significantly reduced the electrical volume as well as surface resistivity up to values of 0.12 Ohm·cm or 4 mOhm/square, respectively, (PP/GFG600/CB = 20/75/5

wt.%) which correlates with values named in literature [7, 10, 11]. The influence of CB on the reduction of electrical resistivity was more pronounced for composites filled with synthetic graphite which showed higher starting values than PP/EG composites. Interestingly, the composite filled with 55 wt.% GFG600 and 5 wt.% CB had the same volume resistivity as PP+80 wt.% GFG600. It can be assumed that the lower filler content leads to a less fragile mechanical behavior which is advantageous for the processing.

For the changes in thermal conductivity with CB replacement the kind of graphite was important. If expanded graphite was mixed with carbon black the thermal conductivity reduced to 60% of the value of PP/ 80 wt.% expanded graphite without CB. Otherwise, the combination of synthetic graphite and carbon black changed the thermal conductivity only marginal at the same overall filler content. In this comparison, the graphites with larger particle size showed significantly larger values than those with smaller sized graphite. This tendency was found for synthetic graphite as well as expanded graphite. At total filler content of 60 wt.%, the thermal conductivity of PP/G composites with or without CB was significantly decreased up to 3 W/(m·K) compared to 15 W/(m·K) @ 80 wt.% G+CB. Such reduction of thermal conductivity took also place for PP/EG composites. However, the reduction was not so pronounced compared to PP/G composites.

The use of graphite having a mean particle size of around 300 µm seems to be the best choice to generate high thermal conductivity and low electrical resistivity in PP composites.

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