Influence of Graphite and SEBS Addition on Thermal and Electrical Conductivity and Mechanical Properties of Polypropylene Composites

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Abstract. In this study, composites based on polypropylene (PP) and different graphite fillers were melt mixed using a small scale microcompounder Xplore DSM15 as well as a lab-scale co-rotating twin screw extruder Coperion ZSK26Mc. The measurements of the electrical and thermal conductivity as well as mechanical properties of the composites were performed on pressed plates. It was found that the addition of graphite powders having different particle size distributions leads to different increases of the thermal conductivity. For synthetic graphite, the PP composites filled with TIMCAL Timrex® KS500 reached the highest value of thermal conductivity of 0.52 W/(m·K) at 10 vol% loading, whereas this composite was not electrical conductive. Furthermore, the influence of a styrene-ethylene-butylene-styrene block copolymer (SEBS) based impact modifier on the mechanical properties of PP filled with 80 wt% of different synthetic graphites was investigated. For that, the proportion of SEBS in the PP component was varied systematically. The conductivities were influenced by the type of graphite and the content of impact modifier. The results indicate that the impact strength of the composite containing TIMCAL Timrex® KS300-1250 can be increased by approx. 100 % when replacing 50 wt% of the PP component by SEBS.

INTRODUCTION

In the discussion of anthropogenic climate change and efforts to replace fossil fuels with renewable energies, modern storage technologies such as fuel cells or redox-flow-batteries play an important role [1, 2]. Fuel cells and redox-flow batteries offer a high potential to convert efficiently chemical energy into electrical energy. In these systems, the costs are mainly determined by the catalyst, the membrane electrolyte unit and the bipolar plate. To replace metallic bipolar plates, which tend to corrosion and are thus restricted in their longevity, composite bipolar plates based on plastics are used increasingly. Composite bipolar plates are made of a combination of a plastic (e.g. PP) and conductive filler (e.g. graphite) prepared using conventional processing methods like hot pressing or injection molding. Compared to pure graphite, composite materials offer the possibility to produce bipolar plates with a higher flexibility in a simplified manufacturing process.

The bipolar plates must have a high electrical and thermal conductivity orthogonal to the plate dimension. Therefore, the incorporation of electrical and thermal conductive fillers in plastics is of great interest. The durability of bipolar plates based on thermoplastic composites and their production are not yet satisfactory due to the needed high proportion of the conductive filler and the resulting material embrittlement. Therefore, there is a need to reduce the proportion of the conductive filler on a high level (e.g. single or hybrid filler systems of carbon based materials) and to improve the mechanical properties by blending the plastic matrix with suitable impact modifiers [3].

EXPERIMENTAL PART

Materials

A polypropylene PP Sabic 579S (Sabic Deutschland GmbH, Düsseldorf, Germany) with a melt flow rate of 47 g/10 min (230 °C/ 2.16 kg) was used. A mixture of PP with a styrene-ethylene-butylene-styrene block copolymer (SEBS) based impact modifier was supplied by ALLOD Werkstoff GmbH & Co. KG, Burgbernheim, Germany.

As filler materials, different kinds of graphite powders having different particle size distributions were chosen, namely synthetic graphite EP1005 and EP1200 (both from Richard Anton KG, Munich, Germany) and Timcal Timrex®KS150, KS500, KS300-1250 (all from Imerys Graphite & Carbon Switzerland Ltd., Bodio, Switzerland).

Processing and Analytics

Characterization of Graphite Materials

The particle size distribution of the graphite powders was determined by laser diffraction using a Sympatec Helos/BF particle size analyzer coupled with a RODOS dry dispersion unit and ASPIROS micro dose module. The measurement range is 4.5-875 µm. The morphology of graphite powders was observed with field emission scanning electron microscopy (FESEM) using a measuring device Sigma VP from Carl Zeiss AG (Oberkochen, Germany).

The specific surface area (BET) was determined by the Autosorb-1 (Quantachrome, USA) based on a volumetric principle at a measuring temperature of 77 K (cooling in liquid nitrogen) using the adsorbate nitrogen.

Small Scale Melt Mixing

Melt compounding in small scale was performed using a conical twin screw microcompounder Xplore DSM15 at 210 °C, 150 rpm, and 5 min mixing time. Before processing, the graphite fillers were dried at 80 °C in a vacuum oven overnight. The fillers and the PP granules were pre-mixed in the solid state by shaking.

For the measurements of electrical resistivity and thermal conductivity the composite materials were compression molded in the required shape at 210 °C for 2 min using a hot press PW40EH (Otto-Paul-Weber GmbH, Germany). To perform electrical resistivity measurements on compression molded plates (diameter 60 mm, thickness 0.5 mm), a 4-point test fixture with gold contact wires combined with a Keithley electrometer E6517A was applied on strips cut (ca. 40 x 3 mm^2) from the pressed plates. For electrical resistivity values >1E7 Ω·cm, a Keithley 8009 Resistivity Test Fixture based on ring electrodes combined with a Keithley electrometer E6517A was applied on pressed circular plates.

Thermal conductivity was measured on pressed plates (diameter 12.5 mm, thickness 2 mm) using the light flash apparatus LFA 447 NanoFlash® (Netzsch-Gerätebau GmbH, Selb, Germany) at 25 °C.

Lab Scale Extrusion

The lab scale extrusion of PP-SEBS blends was performed at ALLOD Werkstoff GmbH & Co. KG (Burgbernheim, Germany) using a co-rotating twin screw extruder ZE25 A of KraussMaffei Berstorff GmbH (Hannover, Germany). The proportion of SEBS in PP was varied from 10 wt% to 50 wt%. The production of graphite-PP-SEBS composites was performed using a co-rotating twin screw extruder ZSK 26 Mc of Coperion GmbH (Stuttgart, Germany) with a screw diameter D of 26 mm and an extrusion length of 44 D at 200 °C, rotation speed of 150 rpm and throughput of 10 kg/h. The proportion of graphite was 80 wt% in all formulations.

The compounds were compression molded at 190-195 °C to plate geometries of 220 mm length, 200 mm width and a thickness of 4 mm in a heated press at Eisenhuth GmbH & Co. KG (Osterode am Harz, Germany).

To analyze the mechanical properties like impact strength, flexural strength and bending strain, corresponding sample shapes were prepared from these plates. The impact strength was measured in accordance with DIN ISO 179-1/1fU by Charpy impact test. The bending properties of the compounds were measured in a three-point bending test in accordance with DIN EN ISO 178 on a testing machine of type Zwick 1456 Zwick GmbH & Co. KG (Ulm, Germany).

The electrical volume resistivity was measured on five circular samples having a diameter of 13 mm and a thickness of 3 mm at Eisenhuth GmbH & Co. KG (Osterode am Harz, Germany).

Thermal conductivity was measured as described above.

RESULTS

Small Scale Mixing of PP/Graphite Composites

The morphology of the different graphite materials is shown in Figure 1. The FESEM images illustrate that the graphites of types EP1005 and KS150 have a plate-like structure. The graphite particles of type EP1200, KS 500 and KS300-1250 show a spherical structure. EP1200 has a larger aspect ratio than KS500 and KS300-1250.

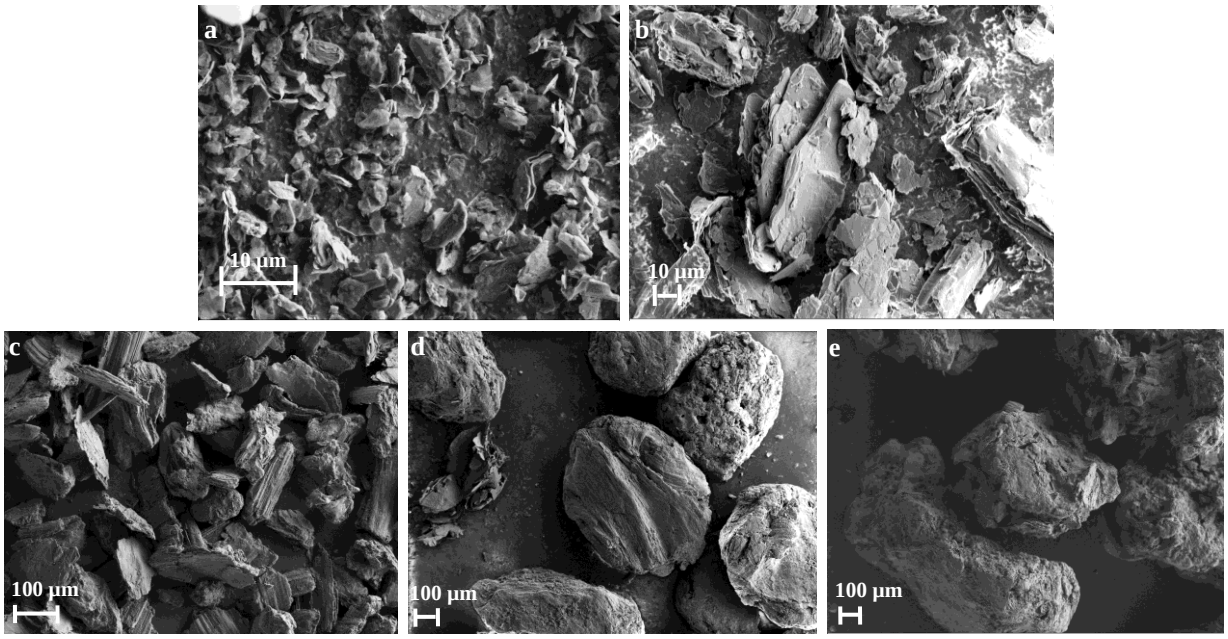

FIGURE 1. FESEM-analysis of the morphology of synthetic graphite materials: EP1005 (a), KS150 (b), EP1200 (c), KS500 (d), and KS300-1250 (e).

In Table 1 the particle size distribution and specific surface area of the different graphite types are shown. The smallest particles were measured for EP1005 having an x_{50}-value of 4.8 µm whereas also bigger particles were present indicated by an x_{90}-value of 315.8 µm. The highest particle size was found for KS300-1250 with an x_{50} of 327.4 µm. A broad particle size distribution was detected for KS150 having x-values between 9.9 and 178.7 µm. For EP1200 and KS300-1250, no very small particles were found illustrated by x_{10}-values of 69.9 or 79.3 µm, respectively. The BET value for EP1005 was with 17.4 m^2/g the highest, compared to the values of the other graphites, which were 1.1-3.5 m^2/g for EP1200, KS150, KS500 and KS300-1250.

For screening the different graphite fillers, PP composites filled with up to 10 vol% filler content were melt mixed using the microcompounder. In Table 2 thermal conductivity and electrical volume resistivity of the PP composites are summarized. The highest thermal conductivity of 0.52 W/(m·K) was found for PP/10 vol% KS500. Among the PP/graphite composites, only the PP/EP1005 composites starting at 5 vol% loading and the PP/10 vol% EP1200 composite showed lowered electrical resistivity values. It is assumed that the reason for the favourable behaviour of PP/EP1005 is the significantly higher BET value when compared to the other synthetic graphites.

TABLE 1. Values of the particle size distribution and specific surface area (BET) of different kinds of synthetic graphite

Filler name	x_{10} [µm]	x_{50} [µm]	x_{90} [µm]	BET [m^2/g]
EP1005	1.3	4.8	315.8	17.4
EP1200	69.9	123.7	205.3	1.5
KS150	9.9	54.3	178.7	3.5
KS500	22.8	143.5	416.2	1.6
KS300-1250	79.3	327.4	470.3	1.1

TABLE 2. Thermal conductivity and electrical volume resistivity of PP composites containing different fillers and amounts (the values for unfilled PP are $\lambda = 0.26$ W/(m·K) and $\rho = 1$ E+17 Ω cm).

Filler	Filler concentration [vol%]	Thermal conductivity λ [W/(m·K)]	Volume resistivity ρ [Ω·cm]
EP1005	2.5	0.27	5.7 E+14
	5	0.33	6.4 E+08
	7.5	0.42	7.3 E+08
	10	0.47	1.1 E+07
EP1200	2.5	0.26	1.1 E+17
	5	0.33	4.0 E+16
	7.5	0.38	9.9 E+14
	10	0.42	1.7 E+08
KS150	2.5	0.29	4.0 E+16
	5	0.34	4.0 E+16
	7.5	0.40	5.2 E+13
	10	0.51	1.1 E+14
KS500	2.5	0.31	4.0 E+16
	5	0.34	4.0 E+16
	7.5	0.47	4.0 E+16
	10	0.52	4.0 E+16
KS300-1250	2.5	0.36	4.0 E+16
	5	0.38	4.0 E+16
	7.5	0.44	4.0 E+16
	10	0.47	4.0 E+16

Lab Scale Preparation of PP/Graphite Composites Containing SEBS

For composite testing, the graphites EP1200, KS500 and KS300-1250 were chosen to investigate the influence of filler and SEBS on the mechanical and conductive properties. In Table 3 results are shown for the conductivity and the bending properties of the PP-SEBS composites containing 80 wt% graphite and 20 wt% PP/SEBS.

TABLE 3. PP-SEBS-composites containing 80 wt% of different fillers and various proportions of SEBS in PP: Electrical volume resistivity ρ, mechanical properties and thermal conductivity **λ**.

Filler	PP/SEBS [wt%]	ρ [Ω cm]	a [kJ/m^2]	σ_{fl} [MPa]	E_{fl} [MPa]	ε_{fl} [%]	λ [W/(m·K)]
	100/0	0.23±0.01	-*	-*	-*	-*	13.6±0.4
	90/10	0.18±0.13	1.4±0.2	25.1±1,8	6101±285	0.85±0.15	13.0±0.9
EP1200	80/20	0.25±0.02	1.5±0.5	22.6±0.7	4505±37	0.89±0.02	12.8±0.9
	70/30	0.31±0.06	2.2±0.1	17.1±0.7	3649±163	1.46±0.39	12.8±0.7
	50/50	0.46±0.03	3.2±0.4	12.5±0.8	2090±75	1.97±0.31	12.7±0.5
	100/0	-*	-*	-*	-*	-*	13.8±0.7
	90/10	0.28±0.01	1.7±0.1	21.4±0.6	5225±108	0.76±0.05	15.4±1.3
KS500	80/20	0.39±0.03	1.9±0.2	16.3±0.8	3770±108	1.04±0.15	14.1±1.6
	70/30	0.34±0.02	2.3±0.3	11.7±2.0	2229±676	1.54±0.39	14.6±0.9
	50/50	0.41±0.04	2.7±0.2	8.6±0.2	1240±36	2.06±0.06	14.6±1.1
	100/0	0.29±0.04	1.5±0.2	23.5±0.5	5726±188	0.64±0.05	16.4±1.0
	90/10	0.36±0.05	1.6±0.6	18.0±1.5	4102±83	0.90±0.11	14.8±2.9
KS300-1250	80/20	0.40±0.01	2.0±0.2	16.9±0.9	3790±192	1.01±0.04	11.7±3.0
	70/30	0.43±0.07	2.2±0.2	11.5±1.2	2210±173	0.98±0.18	13.4±2.3
	50/50	0.63±0.11	2.9±0.2	8.8±1.1	1336±187	2.33±0.35	15.8±0.2

ρ – electrical volume resistivity; **a** – Charpy impact strength; σ_{fl} – flexural strength; E_{fl} – flexural modulus; ε_{fl} – bending strain; **λ** - thermal conductivity; *) composite was not processable due to the high brittleness

The results in Table 3 show that with increasing amount of SEBS in PP, the impact strength of the highly filled composites can be improved. The addition of 50 wt% SEBS in PP leads to a maximum value of the Charpy impact strength of 3.2 kJ/m^2 when using the graphite type EP1200. This represents a strength increase by 128 % compared to the PP/SEBS (90/10) + EP1200 composite. EP1200 has a larger aspect ratio compared to the spherical graphites

KS500 and KS 300-1250. For fillers with a high aspect ratio, the impact energy can be dissipated in a better way in the composite [4]. By the incorporation of SEBS, the bending properties are significantly modified. Pressed plates with a proportion of 30 wt% SEBS in PP already exhibit a significantly improved flexibility (increased bending strain) compared to plates without SEBS. Flexural strength σ_{fl} and modulus E_{fl} of the composites decrease as expected with increasing content of SEBS in PP. The incorporation of 50 wt% SEBS in PP leads to a decrease in the flexural strength to 50 % for EP1200, 40 % for KS500, and 49 % for KS300-1250 compared to the PP composite containing 10 wt% SEBS. For the graphite KS300-1250 the comparison between PP without SEBS and with 50 wt% SEBS shows a decrease in σ_{fl} to 37 %. The addition of 50 wt% SEBS leads to a minimum flexural strength of 8.6 MPa for PP/KS500 composites. The incorporation of SEBS in PP has a significant effect on the bending strain ε_{fl}. The addition of 50 wt% SEBS leads to an increase of the bending strain by 132 % for EP1200 and 171 % with KS500 in comparison to composites with 10 wt% SEBS. The maximum bending strain of 2.33 % is achieved when graphite KS300-1250 was used.

However, the improvement in mechanical properties by the incorporation of the impact modifier SEBS is connected with undesired lower electrical conductivity. The incorporation of 50 wt% SEBS in PP/graphite composites leads to a significant increase of the volume resistivity by approximately 100 % from 0.29 Ω cm to 0.63 Ω·cm using KS300-1250 or from 0.23 Ω·cm to 0.46 Ω·cm using EP1200. The lowest value of the volume resistivity for composites with 50 wt% SEBS in PP was achieved with KS500 reaching 0.41 Ω cm.

The thermal conductivity λ (Table 3) of PP/EP1200 composites with different contents of SEBS was determined to be around 13 W/(m·K). Higher thermal conductivity values were measured for PP/SEBS composites containing graphite having larger particle sizes (KS500 with 13.8-15.4 W/(m·K) or KS300-1250 with 11.7-16.4 W/(m·K)). However, beside the differences of the values using different graphite fillers no clear correlation between thermal conductivity and SEBS content in PP could be observed.

SUMMARY AND CONCLUSION

In small scale microcompounder experiments, PP/graphite composites were melt mixed to screen different kinds of synthetic graphites having different particle size distribution and shape. The highest thermal conductivity of 0.52 W/(m·K) was found when adding 10 vol% of the graphite type KS500. A significant decrease in electrical volume resistivity was measured only for PP composites filled with 5 vol% and more EP1005 or 10 vol% EP1200.

Composite materials based on PP and SEBS containing 80 wt% graphite were prepared in laboratory scale in a compounding process. Selected graphite with different particle size distributions were used and the influence of graphite and SEBS on different composite properties was examined. By adding SEBS in PP, the impact strength and bending strain could be significantly increased. For PP/SEBS (50/50) filled with 80 wt% graphite EP1200 a maximum impact strength of 3.2 kJ/m^2 was obtained. The highest bending strain with 2.33 % was achieved using graphite KS300-1250 in the PP/SEBS blend having 50 wt% SEBS. However, the incorporation of SEBS into PP results in an increase of the electrical volume resistivity. The thermal conductivity of PP/ 80 wt% graphite composites was independent of the content of SEBS and was found to be around 13-16 W/(m·K). The development of composites with impact modification represents a compromise between electrical and mechanical properties. In order to improve the electrical conductivity also other conductive fillers or combinations should be investigated.

ACKNOWLEDGMENTS

The authors thank German Federal Ministry of Education and Research (BMBF) for financial support (project No. 01LY1307B). The authors thank Mr. Geißler and Mrs. Albrecht for the determination of particle size and specific surface area (both IPF).

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