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ELECTRICAL, MECHANICAL AND MORPHOLOGICAL PROPERTIES OF CONDUCTIVE POLYMER COMPOSITES

Summary of the Thesis

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1. Introduction

Nowadays, in addition to traditional uses, polymers may find new applications by using additives, fillers and reinforcements. The development of electrically conductive fillers containing polymer composites (also known as: conductive polymer composites (CPCs)) is very promising and is being studied increasingly widely. Because of their corrosion resistance and low density, CPCs may replace metals in several applications, thus increasing the useful life of the equipment. Significant weight reduction can be achieved by their use, accompanied by cost reduction.

Electrically conductive polymers can be divided into two groups. One of them is the intrinsically conductive polymers the other is the conductive polymer composites which are conductive because of the electrically conductive fillers embedded in the insulating polymer matrix. Intrinsically conductive polymers can be used in corrosion protection, sensors, batteries, controlled drug delivery systems, light emitting diodes and as radar absorbent coatings. While CPCs are used in self-regulating heating systems, sensors, electromagnetic and radiofrequency interference shielding, electrostatic discharge protection and fuel cells [1-6].

Conductive polymers are more and more frequently used for the preparation of mono- and bipolar plates in fuel cells. More and more people use biethanol in their cars, solar cells and wind energy for generating electricity and solar collectors for heating to reduce the consumption of non-renewable energy sources. Generating electricity by fuel cells is a very promising field of environmentally conscious energy production. Fuel cells produce electricity directly by chemical reactions, by using hydrogen gas as "fuel", resulting in water as a byproduct. As the process does not involve burning, there is no smoke emission. Mono- and bipolar plates are key parts of the fuel cells. These plates were traditionally made from metal but their electrochemical stability was not satisfactory [7]. To improve the corrosion resistance of the plates they were coated with protective coatings or they were made from graphite. However, graphite plates were fragile and protective coatings decreased the conductivity of the plates and were vulnerable, thus conductive polymer composites got in the focus of attention [8].

In this work conductive filler containing polymer composites were developed and examined. These conductive polymer composites can be used as mono-and bipolar plates in fuel cells. The composites were made by compression and injection molding and the effect of the processing technology on the mechanical, electrical and morphological properties of composites were studied. Furthermore, the effect of different fillers on each other and the effect of temperature on the electrical properties of composites were examined.

2. Short analysis of the literature, aims of the dissertation

The increase of the electrical conductivity of polymers is studied more frequently. Articles and books are dealing mostly with increasing the electrical conductivity of the CPCs as greatly as it is possible and with decreasing the amount of filler at the percolation threshold. In case of hybrid; two, three or four types of filler containing composites the goal is to achieve synergistic effect between the fillers in order to prepare more conductive composites than the one type of filler containing ones. However, what really is causing the synergistic effect is not studied. The conductivity of the composites is measured mostly by four point probe method. Results are published as a function of the volume fraction or weight fraction of the fillers, thus it is hard to compare these results since the properties of the fillers are not in every case accessible. The most frequently used fillers are graphite, carbon black, carbon nanotube and graphene and the most frequently used matrices are thermoplastic (depending on the operating temperature) and thermoset polymers. In case of thermoplastic polymers, mixing of the matrix and the fillers can be solved by special (e.g. wet lay method) and conventional (e.g. injection molding, compression molding) methods. The processing technology significantly affects the electrical properties of the processed composites.

The mechanical properties of the CPCs are studied by bending, tensile and impact strength tests. In fact, the explanations are only speculations since they are not based on morphological analysis. The dispersion state of the fillers in the composite is examined by scanning electron microscopy which is - in my opinion - not the best method.

In this dissertation the mechanical, electrical and morphological properties of conductive polymer composites were studied. The different types of fillers (graphite, carbon black and carbon nanotubes) containing composites were injection and compression molded using polypropylene, poly(buthylene terephtalate) and polycarbonate as matrix. The goals of the dissertation were:

1. Study the electrical, mechanical and morphological properties of one type of filler containing conductive polymer composites using amorphous and semi-crystalline thermoplastic polymers as matrix.
2. Study the electrical, mechanical and morphological properties of two and three types of fillers containing conductive polymer composites using amorphous and semi-crystalline thermoplastic polymers as matrix. Analyze the effect of the different fillers on each other.
3. Study the electrical, mechanical and morphological properties of compression and injection molded conductive polymer composites. Analyze the effect of the processing technology on the conductivity of the composites.

4. Develope an image processing method in order to help understand the connection between electrical and mechanical properties of conductive polymer composites.
5. Study the effect of temperature on the electrical properties of differently composed conductive polymer composites.

3. Overview of the used materials and test methods

TVK Tipplen H949A polypropylene (PP), TVK Tipplen R959 A polypropylene (rPP); Lanxess Pocan B 1305 poly(buthylene terephtalate) (PBT) and Bayer Apec 1695 polycarbonate (PC) were used as matrix materias in the experiments. The graphite powder used to increase the conductivity (Carbosint Ltd.; specific surface area: 6 m^2/g; density: 2.1 g/cm^3) was crystalline natural graphite powder. The carbon black used was Ketjenblack EC-600 JD (AkzoNobel; specific surface area: 1400 m^2/g; density: 1.7 g/cm^3), and the multi-walled carbon nanotubes used were Baytubes C150P (Bayer).

Firstly, simple filled (graphite, carbon black and carbon nanotubes) composites were made using PP, PBT and PC as matrix. Then, in order to increase the conductivity of the composites, graphite-carbon black filled composites were made using PP, PBT and PC as matrix. Keeping the graphite content constant (0; 40 and 60 w%) the amount of carbon black was increased constantly. As the properties are mainly determined by the volume fraction of the fillers, the amounts used are usually given in this form. In order to do so, when evaluating the trends appearing in the material groups containing 40 w% and 60 w% graphite the volume fraction of graphite was taken as constant, minor deviations were neglected: In the case of 40 w% graphite: 22.8±1 vol%; in the case of 60 w% graphite: 40.6±2 vol%).

Furthermore, graphite-carbon black-carbon nanotubes filled hybrid composites were made using PP, PBT and PC as matrix. 5 and 10 vol% carbon black/carbon nanotube mixtures were used at three different, constant levels of graphite (0, 20 and 40 vol%) content. In the carbon black/carbon nanotube mixtures the ratio of the two fillers was varied by 20% steps between 100% carbon black and 100% carbon nanotube content.

To the comparison of injection molded and compression molded specimens 3 vol% carbon black, 50 vol% graphite and 50 vol% graphite + 3 vol% carbon black containing composites were made using rPP and PBT as matrix.

The various compositions were mixed in a Brabender kneader with a chamber of 50 cm^3 at 240ºC (for PP), 250°C (for PBT) and 340°C (for PC) for 12 min at 25 rpm. From the melt-mixed materials, 120 mm x 120 mm x 2 mm and 80 mm x 80 mm x 2 mm plates were compression molded at 160 bar using a Collin P 200E mold. 80 mm x 80 mm x 2 mm plates were injection molded using an Arburg Allrounder Advance 370S 700-290 injection molding machine.

Electrical measurements

Bulk conductivity was measured on 120x120x2 mm plates using a four-probe resistivity testing method with an Agilent 34970A, an Agilent 4333B milliohmmeter and a 34901A module. A special head was prepared for this measurement, four gold-plated Ingun probes were embedded in a distance of 2 cm from each other in an insulator plate [9-11].

Further electrical characterization of the specimens was carried out by means of current-voltage characteristics analysis. The current was generated by a GW Insteak GPS-4303 power supply from 0.01 to 0.15 A with a step of 0.01 A. The voltage was measured by an Agilent 34970A milliohmmeter.

Morphological analysis

Specimens were embedded in epoxy resin and the cross sections of the test specimens were polished with a Buehler Beta twin polishing instrument in 6 steps. An Olympus PMG3 optical microscope was used for optical microscopy, and the data were evaluated by analySIS Steel Factory 5.0 software. As a first step the images were binarized then in the binarized images the graphite agglomerates were detected.

SEM analysis was carried out to study the dispersion state of nano sized filler content and the structure of the CPCs using a JEOL JSM-6380LA scanning electron microscope.

DSC was performed on a TA Q2000-type calorimeter operating under a N_2 atmosphere using 4–6 mg of the samples. The degree of crystallinity of the differently processed composites was determined by heating the samples to 250°C at a rate of 10°C/min. To determine the sample’s crystallization temperature (T_c), its thermal history was cancelled by a 5 min long isothermal treatment at 250°C; subsequently the sample was cooled to room temperature at a rate of 25°C/min.

Wide-angle X-ray diffractograms (WAXD) were generated using a PANalytical X’pert Pro MPD diffractometer; Cu Kα radiation with a wavelength λ = 1.54 Ǻ was used. The radiation was monochromatized by a Ni filter. A work tension of 40 kV and a current of 30 mA were applied during scanning.

Mechanical tests

Three-point bending tests were performed on a Zwick Z020 universal loading machine on 120 mm x10 mm x 2 mm specimens with a 64 mm span-length and a 5 mm/min deformation rate at room temperature according to EN ISO 178:2003.

Tensile tests were performed on a Zwick Z020 universal tester with a 40 mm clamping length and a 10 mm/min deformation rate at room temperature on 120 mm x10 mm x 2 mm specimens.

Impact strength tests were made using a CEAST Resil Impactor Junior equipment with 2 J hammer, at room temperature on 120 mm x10 mm x 2 mm unnotched specimens according to EN ISO 179:1-2001.

Thermomechanical analysis

Dynamic mechanical analysis (DMA) was made by a DMA Q800 dynamic mechanical analyzer (TA Instruments) with a three point bending clamp. The applied amplitude was 20 μm, the frequency was 1 Hz and the DMA curve was measured from -0 to 160°C at a heating rate of 5°C/min.

Apparent thermal expansion was measured by a DMA Q800 dynamic mechanical analyzer (TA Instruments) with a tension clamp. The applied force was 0.001 N and the apparent thermal expansion was measured from -20 to 130°C (for PP), from 30 to 130°C (for PBT) and from 30 to 160°C (for PC) at a heating rate of 5°C/min.

Moisture content measurement

The moisture content of the graphite powder was measured by an Aboni FMX HydroTracer moisture meter on a 0.22 g sample at 27.0°C and 31.9% relative humidity.

4. References

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5. Theses

In my work graphite (particle size: 16-21 µm; specific surface area: 6 m^2/g), carbon black (particle size: 0.035 µm; specific surface area: 1400 m^2/g) and multi-walled carbon nanotubes (diameter: 0.015 µm; specific surface area: 300 m^2/g) were used as fillers. The materials were mixed in a Brabender kneader. My theses are the following:

1. I demonstrated, that in the case of the same amount of graphite (22.8 and 40.6 vol%) and carbon black (0.0-8.9 and 0.0-10.6 vol%) containing compression molded, conductive, hybrid thermoplastic polymer (PP, PBT, PC) composites the dispersion of the graphite is dependent of the matrix material. Comparing the various amount of graphite containing composites it can be stated that:
   a) in the examined filler content range the different dispersion state of graphite compensated the flexural strength reduction at PP matrix in the whole studied carbon black content range, at PBT matrix between 2 and 6 vol% carbon black content and in the case of PC matrix above 5 vol% carbon black content.
   b) in the examined filler content range the different dispersion state of graphite compensated the impact strength reduction at PP matrix between 2 and 6 vol% carbon black content, at PBT matrix between 2 and 5 vol% carbon black content and in the case of PC matrix above 5 vol% carbon black content.

   It can be stated, that the changes of the flexural strength and impact strength as a function of the filler content cannot be considered as matrix-independent phenomena [12, 13, 19].

2. By optical microscopy, I demonstrated that in the case of compression molded, hybrid filled, conductive thermoplastic polymer (PP, PBT, PC) composites there is a statistically proven correlation in the studied filler content range independently of the matrix material:
   a) between the flexural modulus and the average area of the graphite agglomerates of the graphite-carbon black filled, and the graphite-carbon black-carbon nanotubes filled conductive thermoplastic polymer composites.
   b) between the conductivity and the average area of the graphite agglomerates of graphite-carbon black-carbon nanotubes filled conductive thermoplastic polymer composites [18-20].

3. By optical microscopy and scanning electron microscopy, I proved that in the case of compression molded, conductive thermoplastic polymer (PP, PBT, PC) composites filled with graphite, carbon black and carbon nanotubes the following connections can be observed between the composition and the properties of composites:
   - The greater the graphite content, the larger the average area of the graphite agglomerates.
   - Carbon nanotubes have a greater dispersion-supporting effect on graphite than carbon black does.
   - The increasing graphite content helps disperse the nano fillers, especially in the case of carbon black.
   - The increasing nano filler content redounds a better graphite dispersion.

   These statements were conformed by the higher flexural strength of the graphite containing hybrid composites [18, 20].

4. By bulk conductivity measurements performed in different depths of the specimens, I demonstrated that in case of the injection molded conductive polymer composites the conductivity of the composites is significantly changing along the thickness of the specimens because of the skin-core structure formed during injection molding. In case of the graphite filled polypropylene composites the conductivity of the core is higher by 45% than that of the skin. While in case of the graphite-carbon black filled polypropylene composites the difference is only 15% due to the better filler dispersion. By scanning electron microscopy I proved that the conductivity of the compression molded specimens does not change along the thickness of the specimens because of the homogeneous structure of the composites. Thus, conductivity of the compression molded composites is two to seven times higher than that of the injection molded ones [15, 21, 22].

5. By studying the current-voltage characteristic, I proved that in the case of compression molded, graphite filled conductive polymer composites ohmic conductivity is the dominant charge transport mechanism, while in carbon black containing conductive polymer composites the dominant charge transport mechanism is tunneling and hopping conductivity. The conductivity of the graphite filled composites decreased as a function of the increasing temperature, while the conductivity of the carbon black filled composites did not change significantly in the examined temperature range (PP matrix: -20-130°C; PBT

matrix: 30-130°C; PC matrix: 30-160°C) due to the thermal activation of the charge carriers which compensated the conductivity reducing effect of temperature [20, 23].

6. List of the publications related to the theses

12. **Király A.**, Ronkay F.: Hibridtöltésű vezetőképes műanyagok vizsgálata. Műanyag és Gumi, **48**, 441-444 (2011).
13. **Király A.**, Ronkay F.: Szénalapú töltőanyagokat tartalmazó polipropilén bipoláris lemezek üzemanyagcellákhoz: kompromisszum a vezetőképesség és a feldolgozhatóság között. Műanyagipari Szemle, **8**, 75-83 (2011).
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