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Stability of Electrical Properties of Conducting Polymer Composites

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Summary: The effect of slow cycle heating and cooling on the stability of electrical properties of two polymer composites– polypropylene/polypyrrole (PP/PPy) and polypropylene/carbon black (PP/CB) – was investigated. Conductivity in composites was measured in heating/cooling cycles in the temperature range from 16 °C to 105 °C in PP/PPy and to 125 °C in PP/CB, respectively. It was found that the thermal treatment caused the decrease of PP/PPy conductivity while in case of PP/CB the treatment increased the electrical conductivity. The positive effect was explained by increased crystallinity in the thermally treated composite.

Introduction

Practical usage of conducting polymers such as polypyrrole, polythiophene, polyaniline is limited particularly because of their poor mechanical properties and processability[1-3]. However, the composites prepared by mixing of conducting polymers or conducting fillers with conventional polymers such as polyolefins can be used as antistatic packaging materials, anticorrosion protection paints or materials for electromagnetic shielding[4-6]. Carbon-based fillers (carbon black, graphite or carbon fibres) are the most frequently used conductive fillers because of their high conductivity, relatively low price, and good ultimate and processing properties of the conductive composites [7-8]. Final electrical and mechanical properties of the composites are considerably affected by the way of polymer preparation[9-10]. Stability of composite polymers and mixtures is a crucial property for all potential usage.

Our contribution presents a study of electrical properties and stability of electrical

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conductivity of two polymer composites with the same polypropylene (PP) matrix. The first composite (PP/PPy) contained polypyrrole (PPy) as the conducting component. The second one (PP/CB) contained carbon black (CB) as the conducting component. Concentration of the conducting component was 10% in both composites. Our goal was to investigate the effect of repeated thermal treatment on stability of composites – particularly ageing characteristics with respect to the perspective composites application possibilities.

Experimental

Materials

Pyrrole (Merck-Schuchardt, Germany) was distilled twice under reduced pressure and stored in a refrigerator at about 4°C before use. Polypropylene (Tatren TF-411, MFI = 10g/10 min., M_W = 210 000 g/mol, M_n = 25 100 g/mol, Slovnaft, Slovak Republic), anhydrous ferric chloride (Fluka, Switzerland), methyl alcohol, p.a. (Jansen Chimica, Belgium), and carbon black (VULCAN® XC-72R, Cabot Corp., USA) were used as received. Water was distilled before use.

Preparation

PP/CB composites were prepared by mixing polypropylene with carbon black in a 50 ml mixing chamber at 75 rpm for 10 min. at 200°C using the Plasti-Corder kneading machine PLE 330 (Brabender, Germany).

PP/PPy composites were prepared by chemical modification of PP particles. PP particles of 30 to 200 μm in diameter were dispersed in a water-methanol mixture and then $FeCl_3$ was added. Pyrrole was dissolved in methanol and inserted dropwise under vigorous stirring. All compounds were stirred for 4 hours. The reaction product was filtered off and washed with distilled water and methanol.

All prepared composites and PP samples were processed by compression moulding followed by cooling at ambient conditions.

Electrical conductivity measurement

Electrical conductivity was measured by the four-point van der Pauw method. The experimental setup included the current source Keithley 238, the scanner Keithley 706 with the matrix cards and the Solartron-Schlumberger 7081 voltmeter. The sample holder was placed in the thermostat chamber Heraeus-Vötsch VMT 07/3. Both, the temperature and time scale of the experiment were controlled by the computer. The temperature step between the measurements was 5°C. By one cycle we understand the heating up to the desired temperature and the cooling down to 16°C. The set of four such cycles constituted one temperature run. Similar runs followed the first run (4 cycles) up to 85°C, 105°C, and 125°C. The heating or cooling rate during the thermal treatment was 1°C /200 s.

WAXS

Wide-angle diffractograms were taken using an automatic HZG4A powder diffractometer (Freiberg Präzisionsmechanik GmbH, Germany). Cu K_{α} radiation was registered using a scintillation counter and monochromatized by a Ni filter and a pulse-height analyzer. Diffractograms were taken in the range of scattering angle interval $2\theta = 4 - 60°$.

Results and discussion

Cycle temperature dependence conductivity measurements in our composite samples PP/9.8 wt.% PPy and PP/10 wt.% CB showed very different behavior in the process of slow heating and cooling. Conductivity in PP/PPy composite similarly like in the pure PPy increases when it is heated. This is a generally known fact for conjugated conductive polymers and their composites. It is also known that heating of conjugated polymers in the air leads to the polymer degradation that results into conductivity decrease due to the polymer dedoping[11]. The slow cycle heating and cooling experiment makes both effects perfectly visible. Fig. 1a shows two runs. The first one contains four heating-cooling cycles up to 85 °C. The second one shows similar cycles up to 105 °C.

The curves have leaf-like shapes. At the end of each cycle when the conductivity reached the initial temperature the conductivity value was lower than the value at the same temperature at the beginning of the cycle. We have already published similar curves in PPy polymers earlier[9] and also other authors observed such effects with polyaniline composites [12]. Fig. 1b shows conductivity changes in individual cycles within both runs at 60 °C. The column height represents the difference in conductivity read from the lower curve and from the upper curve at the same temperature, 60 °C, in the corresponding cycle. As it can be seen from the Fig. 1b each cycle

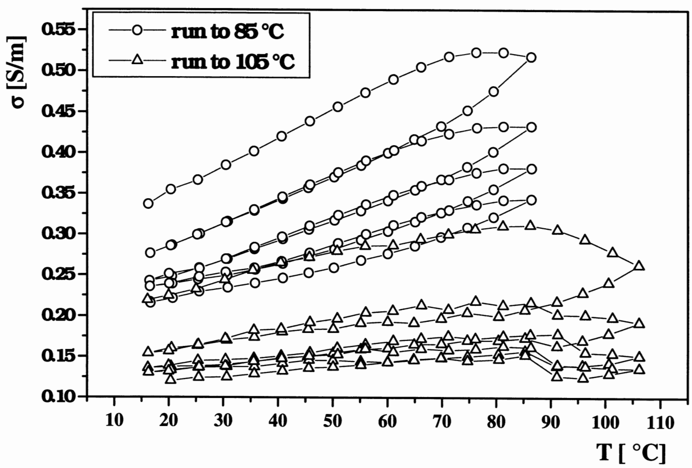

Figure 1a. Temperature dependence of conductivity in PP/9.8 wt.% PPy composite – 4 cycles, 2 runs.

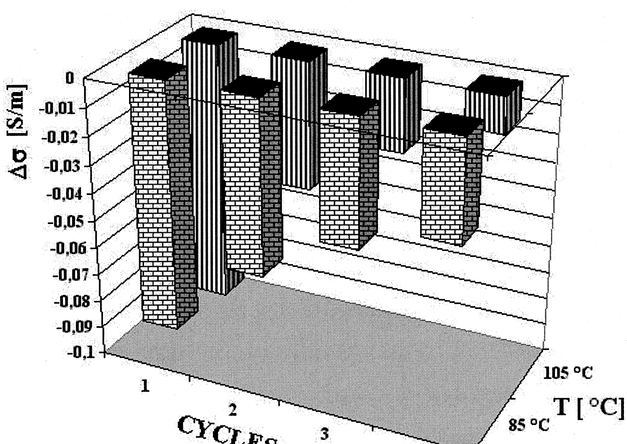

Figure 1b. Conductivity changes in PP/9.8 wt.% PPy composite – 4 cycles, 2 runs.

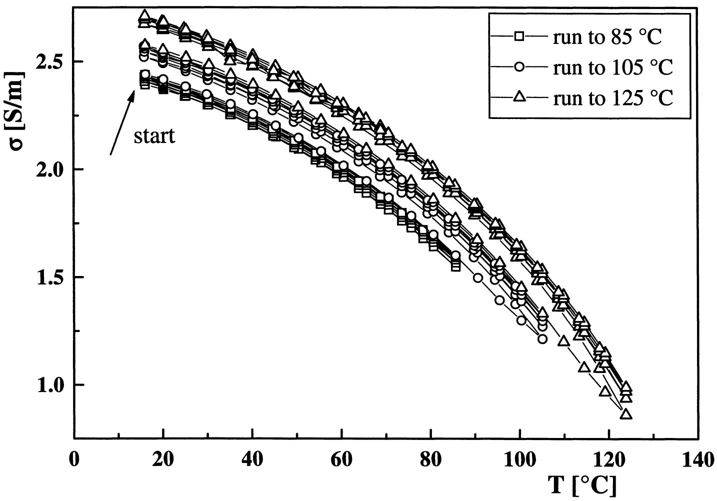

Figure 2a. Temperature dependence of conductivity in PP/10 wt.% CB composite – 4 cycles, 3 runs.

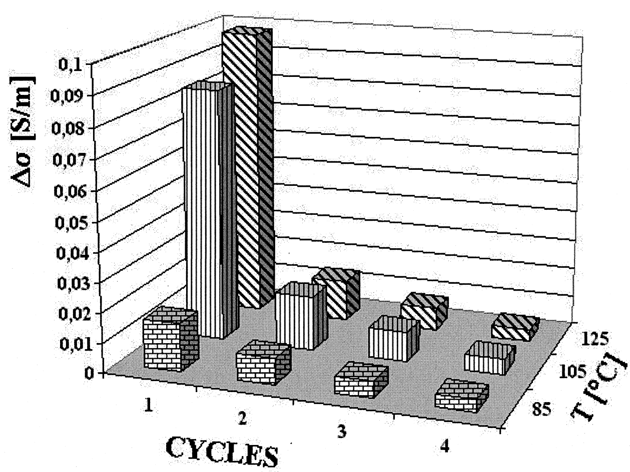

Figure 2b. Conductivity changes in PP/10 wt.% CB composite - 4 cycles, 3 runs.

contributed to the conductivity decrease. The first cycle always caused the highest change. There was no significant difference between two runs.

The behavior of the PP/10 % CB composite during the same experiment was very different. Its conductivity decreased when the composite was heated (Fig. 2a). This fact (positive temperature coefficient of resistivity) is in agreement with the behavior of majority of composite polymers filled with carbon black for comparable CB concentrations and temperature ranges[13]. Unlike in the PP/PPy composite the cooling curve in PP/CB composite is drawn above the heating curve (Fig. 2b). As it can be seen from this figure, the conductivity value in cooled state increased after each heating/cooling cycle. The sample behaved similarly in all three runs.

Alike in PP/PPy we have drawn the changes in conductivity at 60 °C in each cycle. Column heights in Fig. 2b represent the difference in the conductivity value at 60 °C read from the cooling curve (upper one) with respect to the value read from the heating curve. As it can be seen the changes are positive. The first cycle always caused the most significant change and, the higher the temperature in the run, the larger the effect.

Such behavior in the PP/CB composite can be explained by the heating effect on the polymer crystallinity. Crystallinity increase leads to the increased concentration of CB in amorphous polymer phase. This fact results in improving of conducting paths formed by CB particles and final conductivity increase. The relative increase of conductivity at 60°C was found to be 18 % after the third heating-cooling run up to 125 °C.

The previous explanation of the PP/CB composite behavior is confirmed by the results of WAXS investigations in virgin PP and PP/CB composites. A special investigation was done in heating-cooling cycle up to 130 °C. Samples were slowly heated up to 130 °C. The samples were kept in the chamber at this temperature for 28 hours. Then they were cooled down to 16 °C.

WAXS diffractograms of virgin PP and PP/10 % CB composite before and after the thermal treatment are shown on Fig. 3 and Fig. 4. WAXS diffractograms were processed in a usual way (subtracted background and amorphous noise and calculated areas related to crystal reflections and amorphous content). The crystallinity degree in untreated (original) samples was found to be 0.52 ± 0.02 for both, the pure PP and PP/10% CB composite. The crystallinity degree increased in both samples to 0.58 ± 0.02 after thermal treatment. The difference represents 11.5%. We are aware of possible inaccuracy of this result. It is generally known that crystallinity degree found by various methods may differ. Therefore, we plan to confirm this result by DSC measurements.

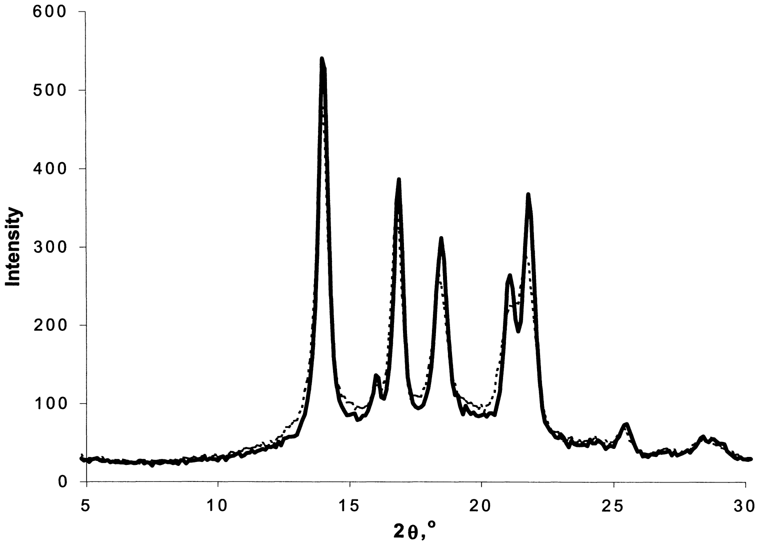

Figure 3. Wide-angle diffractograms of PP (- - - -) and PP after thermal treatment (——).

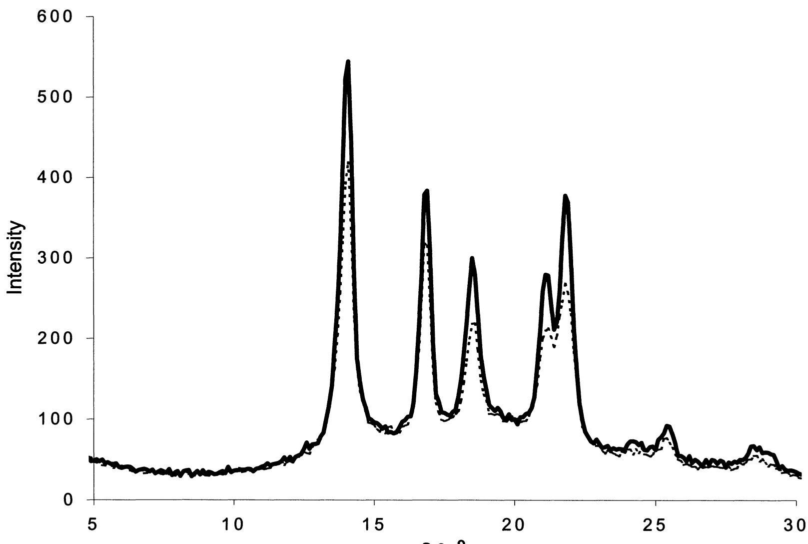

Figure 4. Wide-angle diffractograms of PP/CB composite containing 10 wt. % CB (- - - -) and the same composite after thermal treatment (——).

Conclusions

Thermal treatment of polypropropylene/9.8 % polypyrrole and polypropylene/10% carbon black composites in the temperature range from 16 °C to 105 °C in PP/PPy and from 16 °C to 125 °C in PP/CB has shown considerably different effect in these two composites. While the cycle heating–cooling in the PP/PPy composite resulted into the decreased conductivity due to the degradation processes in conducting (PPy) component the same treatment improved the electrical conductivity in the PP/CB composite. A significant increase of conductivity was found in the whole temperature range. The relative increase of conductivity at 60 °C was found to be 18 % after the third heating-cooling run up to 125 °C.

The latter effect can be explained by the crystallization processes in the non-conductive polypropylene matrix. Wide angle X-ray diffraction technique proved the crystallinity increase in the treated polymer matrix.

The above described effects must be taken into account when practical usage of these composites is considered.

Acknowledgement

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