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Stability of Electrical and Mechanical Properties of Polyethylene/Carbon Black Composites

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Summary: The stability of electrical and mechanical properties of two kinds of polymer composites – polyethylene/carbon black and polyethylene/carbon black modified by polypyrrole – was investigated during slow cycle heating and cooling. Conductivity in composites was measured in heating/cooling cycles in the temperature range from 16°C to 125°C. It was found that the thermal treatment resulted in the conductivity changes and the mechanical properties of treated composites have also been influenced. The effect was explained by increased crystallinity in the polymer matrix of thermally treated composites.

Introduction

An addition of a filler into a thermoplastic matrix significantly affects properties of composite materials, particularly regarding mechanical properties and processing characteristics[1,2]. The extent of the properties changes depends on the concentration of the filler and preparation conditions. Addition of conducting particles such as metals particles, carbon blacks, short carbon fibres or graphite into conventional polymers enables preparation of new materials with unique electrical properties[3,4]. Carbon blacks have been widely use as fillers in various polymer matrices e.g. polyolefins,[5,6] rubbers[7,8], and others. This filler is chosen for its good electrical conductivity and low cost. The electrical and mechanical properties are also affected significantly by way of preparation of composites. Carbon black filled polymers are very attractive because of their numerous application in industry. Nevertheless, all applications of electrically conducting polymer composites and blends depend on the material stability.

Our contribution deals with electrical conductivity and its stability of two kinds of polymer composites with the same polyethylene (PE) matrix during repeated thermal heating and cooling. The electrical properties of polyethylene/carbon black (PE/CB)

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and the polyethylene/carbon black modified by polypyrrole (PE/CB-PPy) composites were measured during treatment. Mechanical properties of prepared composites were investigated before and after thermal treatment.

Experimental

Materials

Pyrrole (Merck-Schuchardt, Germany) was distilled twice under reduced pressure and stored in a refrigerator at about 4°C before use. Low density polyethylene (Bralen RA2-19, MFI = 1,704 g/10 min., T_m = 109.3°C, Slovnaft, Slovakia), ferric sulphide (Fluka, Switzerland), and carbon black (VULCAN® XC-72R, Cabot Corp., USA) were used as received. Water was distilled before use.

Modification of carbon black by polypyrrole

Carbon black particles were dispersed in water with surfactant (dodecylbenzenesulfonic acid sodium salt). $Fe_2(SO_4)_3$ was added as oxidant. Pyrrole was inserted dropwise under vigorous stirring of CB in reaction vessel. The polymerization of pyrrole proceeded for 2 hours. The resulting CB-PPy was filtered out and dried. The modified CB contained 10 wt.% polypyrrole.

Composite preparation

PE/CB and PE/CB-PPy composites were prepared by mixing of polyethylene with carbon black, or with modified carbon black in a 50 ml mixing chamber of a Plasti-Corder kneading machine PLE 330 (Brabender, Germany) at 75 rpm for 10 min. at 170 °C. Testing samples were prepared by compression moulding at 160 °C for 4 min. 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 Precision Voltmeter. The sample holder was placed in the thermostat chamber Heraeus-Vötsch VMT 07/35. Both, the temperature and time scale of the experiment were controlled by the computer. The temperature step between the measurements was 5 °C. One cycle means the heating up to the peak temperature and the cooling down to 16 °C. The set of four cycles constituted one temperature run. Each sample underwent several runs (four cycles each) with the increasing peak temperature, up to 85 °C, 105 °C, and 125 °C. The heating or cooling rate during the thermal treatment was about 1 °C/200 s.

DSC measurement

Thermal stability of samples was measured by instrument DSC 821^e (Mettler-Toledo) in nitrogen atmosphere from 5 to 180 °C. Heating and cooling rate was 10 °C/min.

Results and discussion

First, the conductivity of prepared composites has been measured. Concentration of the conducting component was 30 wt.% in both composites. At room temperature, the conductivity of PE/CB composite and PE/CB-PPy composite is 35.6 S/m and 1.6 S/m, respectively. The difference, about one order of magnitude, is caused by a presence of polypyrrole on CB surface. The conductivity of chemically synthesized PPy is within this range.

We investigated the effect of repeated thermal treatment on stability of composites regarding their conductivity and mechanical properties. The samples were placed in the thermostated chamber and measured in heating-cooling cycles. The thermal treatment in four cycles up to 85 °C, was followed by second run to 105 °C. The composites in the third run were measured in cycles from 40 °C to 125 °C, what is about 15 °C above the melting point of polyethylene matrix.

Significant increase of conductivity of both composites was observed during first heating-cooling cycle in the first and second run of the cycle stability testing, as shown in Fig. 1 and Fig. 2.

Figs. 1b and 2b illustrate the conductivity changes at 60 °C in individual cycles within all runs. The column height represents the difference in the conductivity value at 60 °C read from the cooling curve with respect to the value read from the heating curve. The first cycle leads always to the most significant and positive conductivity change. No significant difference was found between the first two runs for both composites. At 60°C the relative change after first run was 18.7 % in the PE/CB composite that

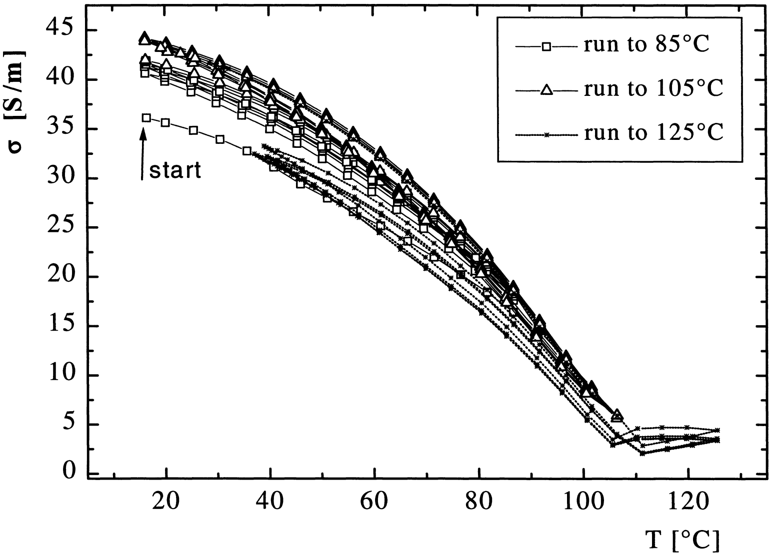

Figure 1a. Temperature dependence of conductivity in PE/30 wt.% CB composite; 4 cycles, 3 runs.

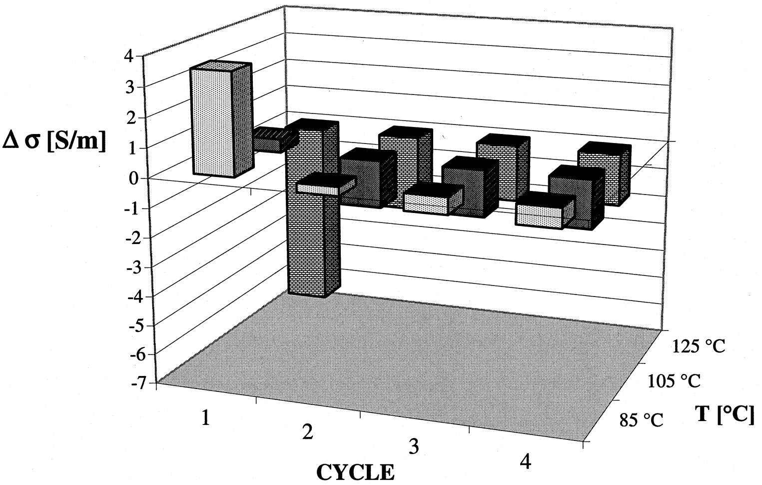

Figure 1b. Conductivity changes at 60°C in PE/30% wt.% CB composite for the individual cycles; 4 cycles, 3 runs.

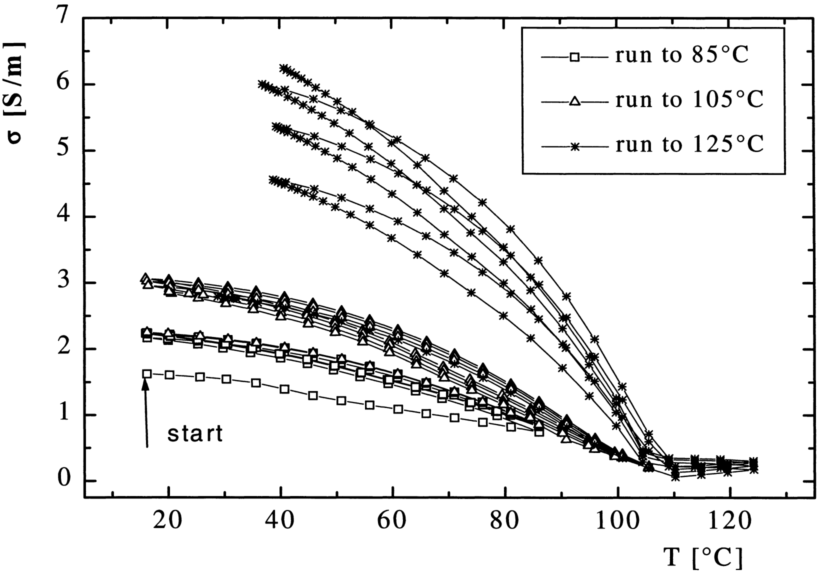

Figure 2a. Temperature dependence of conductivity in PE/30 wt.% CB-PPy composite; 4 cycles, 3 runs.

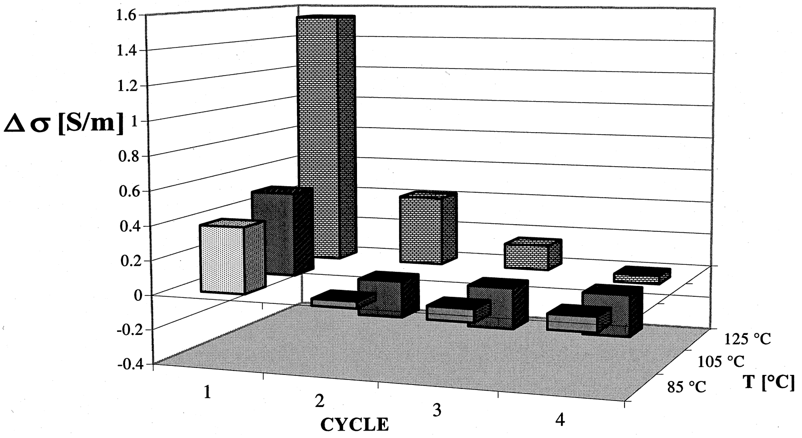

Figure 2b. Conductivity changes at 60 °C in PE/30%CB-PPy composite for the individual cycles; 4 cycles, 3 runs.

contained 30 % of carbon black. Even higher increase, 41.1 % was found in the PE/CB-PPy composite that contained the same amount of modified carbon black as seen in Table 1. The increase of conductivity in second run is higher in composite containing modified carbon black (Table 1).

Table 1. Comparison of changes of conductivity after thermal treatment for PE/30 % CB and PE/30 % CB-PPy composites.

Sample	PE/30 % CB Change of conductivity (%)	PE/30 % CB-PPy Change of conductivity (%)
After the first run to 85°C	18.7	41.1
After the second run to 105°C	21.2	78.6
After the third run to 125°C	-2.9	370.4

Usually heating of conductive composites containing CB above the melting point of polymer matrix results in conductivity changes by several orders of magnitude. This behavior is related to the positive temperature coefficient (PTC) effect[9, 10]. PTC effect is strongly influenced by polymer matrix as well as by the amount of the filler. During four heating-cooling cycles up to 125 °C the conductivity of PE/30 % CB composite decreases as shown in Figs. 1a and 1b. The conductivity value after this treatment is by 2.9 % lower compared to the sample conductivity before thermal treatment. Behavior of the PE/30 % CB-PPy composite during the same experiment was different. Its conductivity increased when the composite was heated in third run up to 125 °C (Fig. 2a). This is influenced by presence of polypyrrole on the carbon black surface. Our former study[4] revealed that polypyrrole filler in polypropylene/polypyrrole composites creates more perfect and temperature resistant conductive filler network compared to CB network in the same matrix, which leads to the increase of viscosity of the PPy containing composite. Therefore, the reason of different behavior of PE/CB-PPy composite apparently consists in a presence of PPy on CB surface, which responds by different way upon treatment above the melting temperature of matrix.

We suppose that the effect of conductivity increase in investigated composites during first heating-cooling cycle of every run was caused by the re-crystallization of the polymer matrix during the process of slow cooling. The samples were first prepared by compression moulding and cooled at ambient conditions which means a rather fast cooling and then thermally treated in heating-cooling cycles with quite slow rate

1°C/200 s. The re-crystallization may lead to the certain restructuring of charge transport conducting paths formed by the conductive filler in the amorphous parts of polyethylene matrix.

The above mentioned explanation of the PE/CB composites behaviour is confirmed by the DSC investigations in virgin PE and PE/CB composites. For DSC investigations and mechanical properties testing, the virgin PE and composites containing 5, 7.5, 10, 15, 20, and 30 % of CB or CB-PPy were treated thermally for 24 hours at 100 °C, i.e. below the melting point of polyethylene matrix. Heating and cooling rate was 1 °C/min in this case.

In Table 2 the crystalline portion in PE and PE/CB composites before and after thermal treatment is shown, as calculated from DSC measurements. The crystalline portion in PE increased from the original 46.2 % up to 50.2 % after the thermal treatment. Similar tendency was observed for all the PE/CB composites. The relative increase in crystallinity degree after thermal treatment is from 8 to 11 % for each sample.

Table 2. Crystallinity of the samples calculated from the first heat of DSC measurement.

SAMPLE	Crystallinity of the samples (%)	
	original	after thermal treatment
PE	46.2	50.2
PE/5 % CB	46.1	50.3
PE/15 % CB	45.9	49.5
PE/30 % CB	43.7	48.8

The thermal treatment also affected mechanical properties of the composites. The thermally treated composites showed a decrease in elongation at break, as shown in Fig. 3a, and Fig. 4a. An increase of the Young's modulus in the treated composites was also observed (Fig. 3b and Fig. 4b). This effect should be ascribed mainly to the changes in crystallinity, although the influence of partial degradation of the polymer matrix must be taken into account as well. Nevertheless, in the case of polyethylene this effect may be considered as less important regarding the temperatures and times of the sample treatment.

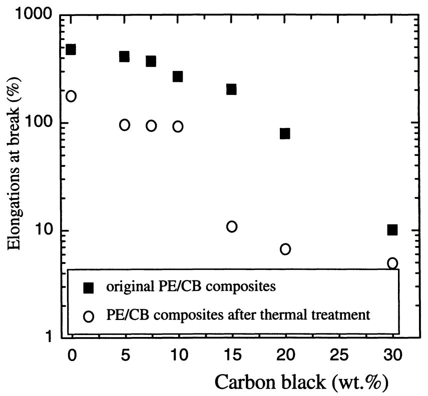

Figure 3a. Dependence of elongation at break on CB content in PE/CB composites.

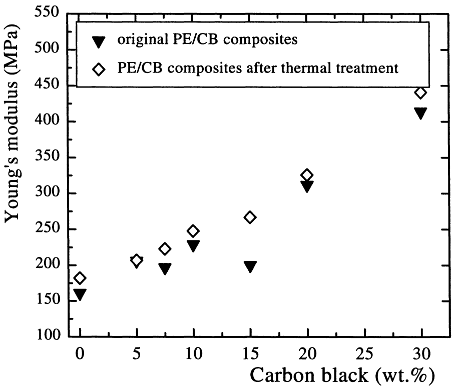

Figure 3b. Dependence of Young's modulus on CB content in PE/CB composites.

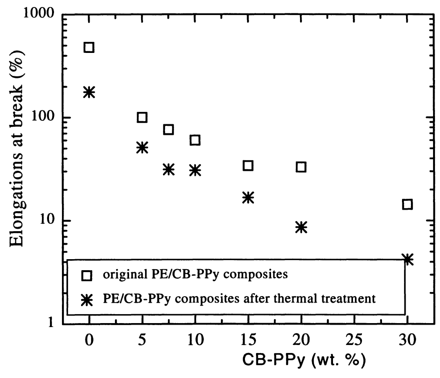

Figure 4a. Dependence of elongation at break on filler content in PE/CB-PPy composites.

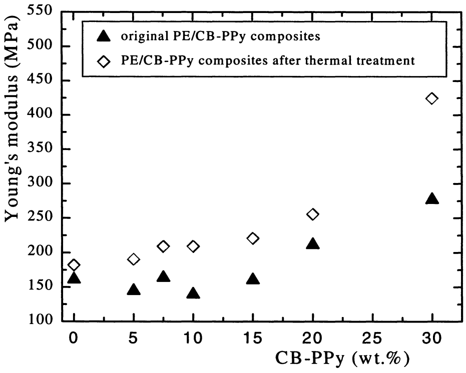

Figure 4b. Dependence of Young's modulus on filler content in PE/CB-PPy composites.

Conclusions

We investigated the effect of repeated thermal treatment on stability of composites – particularly on stability of electrical and mechanical properties.

A significant increase of conductivity was found in composites during cycling thermal treatment in the whole temperature range below temperature of melting point of polyethylene matrix. The effect can be explained by the re-crystallization processes in the non-conductive polyethylene matrix during slow cooling. Crystallinity increase leads to the increased concentration of conductive filler in amorphous polymer phase. This fact results in improving of conducting paths formed by filler particles and final conductivity increases.

The thermally treated composites showed the decrease of elongation at break, and increase of the Young's modulus.

The above described effects must be taken into account if any application of these composites is considered.

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