Electrical properties of foamed polypropylene/carbon black composites

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Abstract. Polypropylene composites containing carbon black fillers were produced by vibration assisted extrusion process. Solid (unfoamed) composite samples were molded by conventional injection molding method, while structural foams were molded by a low pressure process. The foamed samples were evidenced to have a solid skin-foamed core structure which main parameters were found to depend on the quantity of material injected in the mold. The average bubbles’ sizes and their distribution were investigated by scanning electron microscopy. It is established that the conductivity of the foamed samples gradually decreases when reducing the sample density. Nevertheless, the conductivity is found to be lower than the conductivity of the unfoamed samples both being of the same order. The flexural properties of the composites were studied and the results were discussed in the context of the structure parameters of the foamed samples.

1. Introduction

Polymers are known to be principally insulating materials. Their electrical conductivity can be enhanced by the addition of electrically conductive carbon fillers. The relationship of conductivity versus filler concentration clearly demonstrates a relatively narrow filler concentration range where a small increase in its content results in a drastic increase of the conductivity. This point called electrical percolation threshold denotes formation of a filler network that enables successful and faster conveyance of electrons throughout the samples. Further increase of the carbon filler content causes only slight increase of the electrical conductivity till a fixed value, i.e. reaching a plateau [1].

According to the conducting mechanism, to enable conductive pathways through composites the filler particles do not necessarily need any physical contact, because a small gap of several nanometers in width between them is sufficient to cause electron jumping [2]. The types of polymer matrix, conductive filler and processing parameters are main factors that influence the percolation behavior. Changing conditions for the preparation of particular polymer composites one could achieve better or worse filler dispersion or lower or higher filler concentration at the percolation point, respectively [2-5]. Lots of different methods for achieving better distribution of filler particles have been tried so far; however their successful dispersion still remains a challenge. Melt compounding is an efficient, rapid and environmentally friendly method for a good-quality dispersion of fillers in the polymer matrix.
Most mixers and plastic processing machines operate mainly under shear conditions. This way, any increase of the shear intensity in extruders could be a rational way for improving their mixing ability. Efficient melt compounding can be realized using an extrusion mixing die where the molten polymer composites will be subjected to continuously changing shear and extensional deformations created by vibrations of a moveable mandrel [6]. The polypropylene/carbon black (PP/CB) composites fabricated by this vibration assisted processing method exhibit better filler dispersion and percolation point at lower filler concentration than the composites compounded by conventional extrusion [7].

From a practical point of view it is important to produce above mentioned polypropylene composites with a possibly lower density. Structural foams are important achievements of such polymer processing. In contrast to conventional polymer foams their densities are relatively high (usually in the range of 0.6-0.9 the nominal polymer density). The structural foams are known to consist of three basic elements, unfoamed solid smooth skin, foamed core and transitional layer. This type of structure ensures a relatively greater bending strength in comparison with such strength of the unfoamed plastics.

Since foamed PP/CB composites would take place in advanced technological goods, for example in antistatic products or as a part in electromagnetic shields, it is important to know their electrical properties in comparison with the properties of unfoamed PP composites.

2. Materials and testing methods

2.1. Materials
Foamed PP/carbon filler composites were used as objects in current investigation. The polymer used is isotactic PP „Buplen“ 6531 produced by Lukoil Neftochim Co., Bulgaria, having melt flow index MFI (230, 2.16) = 4,1 g/10 min. PP composites were filled with a carbon black filler, Ketjen black EC-300J produced by Akzo Nobel Polymer Chemicals with specific surface area of 803 m²/g measured by BET techniques, pore volume of 325 ml/100 g measured by dibuthylphthalate absorption and size of basic/primary carbonic particles of 30 - 100 nm. Azo-dicarbonamide type Genitron AC4 produced by Fisons Ltd. was used as a blowing agent, which decomposition temperature region falls between 200 and 230 °C.

2.2. Melt compounding and sample preparation,
Composite of 90 wt. % PP and 10 wt. % CB were fabricated using an extrusion system, containing a new mixing die, where the polymer melt was subjected to axial vibrations that resulted into improved dispersion of the filler in the polymer matrix [6, 7]. The melt compounding was carried out under the following process conditions: the temperature profile of the barrel was 170, 180, 190, 200, 205 ºC; screw speed of 20 rpm, vibration amplitude of 0.3 mm and vibration frequency of 10 Hz. After exiting the mixing die the extrudates were cooled and then pelletized using a Vespa 22/40 cutting machine. Plates with dimensions of 100×80×4 mm used for electrical and mechanical measurements were produced on KuASY 25×32/1 injection molding machine. Foamed samples were prepared by a low pressure injection molding process of the PP/CB composites containing 1 wt. % azodicarbonamide under the manufacturing conditions as follows: melt temperature 230 °C, mold temperature 20 °C, injection pressure 15 MPa, packing time 5 s and cooling time 20 s. Mold filling during low pressure injection molding was two-stage process. The first stage was partial filling of molds with “short-shot” of polymer melt containing gaseous phase. The second stage was full filling of the molds realized by foaming of the polymer melt after injection shot.
Table 1. Relationship of the overall density and effective cross-section vs. the short-shot.

| Short-shot, g | 21.9 | 24.5 | 26.4 | 28.3 | 28.9 |
|---------------|------|------|------|------|------|
| Overall density, kg/m³ | 670  | 750  | 810  | 870  | 890  |
| Effective cross-section, % | 72.8 | 82.6 | 83.8 | 84.9 | 85.4 |

Varying the short-shot, different sample densities were obtained (table 1). Unfoamed samples obtained by conventional injection molding process were used as reference.

2.3. Characterization

Scanning electron microscopy (SEM) observations were carried out in a secondary electron flow regime at a 10 kV accelerating voltage on a JEOL 5510 microscope. The examined cross sections were obtained by cutting off the samples using a metal knife of a microtome device type Reinchert, Austria and coating them with 2 nm layer of Au in argon atmosphere. Bubble size and bubble area occupied the cross-section of the sample were determined from the SEM images.

The DC electrical resistivity was measured at ambient temperature of 25 ºC and humidity 50 % by the four-probe Van der Pauw technique [10]. This technique makes use of four isolated contacts on the boundary of an arbitrarily-shaped lamilar sample. In our case, the four probes were located in the four edges of the test samples. A total of eight measurements are made around the sample as shown in figure 1. Silver paste was used to ensure good contact of the sample with the copper electrodes.

![Van der Pauw resistivity measurements](image)

Figure 1. Van der Pauw resistivity measurements.
Flexural properties were determined according to EN ISO 178 at a test speed of 2 mm/min and a temperature of 20 °C. Specimens with dimensions of 80×10×4 mm were cut from the plates and tested at a length of span between supports of 64 mm. Ten specimens were used for the measurements. The flexural strength, $\sigma_{fM}$ and flexural strain at the flexural strength, $\varepsilon_{fM}$ were calculated using following equations:

$$\sigma_{fM} = \frac{3FL}{2bh^2}$$ and $$\varepsilon_{fM} = \frac{600lh}{L^2},$$ (1)

where $F$ is the maximum force applied during the test; $L$ is the span; $b$ is the width of the specimen; $h$ is the thickness of the specimen; $l$ is the deflection.

3. Results and discussion

3.1. Composites structure

From a macroscopic point of view the specimens produced by low pressure injection molding have a sandwich-like structure consisting of a solid skin and cellular core. SEM images in figure 2 show cross sections of the plates produced at varying short-shot. Parts of the cross-sections with dimension 4×4 mm located at the center of the plates demonstrate the different overall density of the specimens and different bubbles morphology of the core, respectively. When the overall density is relatively high (figures 2a, 2b) the bubble shape is close to spherical. In contrast, bubbles with highly extended shapes oriented along the flow direction are observed in the composites with overall density of 750 kg/m$^3$ (figure 2c) and 670 kg/m$^3$ (figure 2d). Another feature has to be noted for the sample of the lowest density: there can be clearly evidenced that in practice there is not any solid skin in its structure. It is well-known that the resistivity of the sample is strongly dependent on its cross sectional area. That is why the effective cross sectional area, i. e. the full cross section reduced by the bubble area, was additionally calculated and presented in Table 1. From the table it can be seen that the bigger the short-shot, the higher the overall density and the effective cross-section.

3.2. Electrical properties

Our earlier experiments proved that PP/CB composites demonstrated typical relationship between resistivity and filler concentration [7, 8]. There was established the percolation threshold to depend on the melt flow index of the polymer that for the PP6531 should lie in the region between 8 and 9 wt. %. To ensure that experiments would proceed above percolation threshold foamed samples at CB concentration of 10 wt. % are used in current work. The volume resistivity of the samples, $r$ measured by the four-probe Van der Pauw technique and conductivity of the samples, $s$ calculated using equation (2) are presented in Table 2.

$$s = \frac{1}{r}. \tag{2}$$
Table 2. Resistivity and conductivity of the samples.

| Overall density, $\text{kg/m}^3$ | Resistivity, $\Omega \text{m}$ | Conductivity, $\text{S/m}$ |
|----------------------------------|-------------------------------|-----------------------------|
| 670                              | 0.80                          | 1.25                        |
| 750                              | 0.48                          | 2.08                        |
| 810                              | 0.53                          | 1.89                        |
| 870                              | 0.49                          | 2.04                        |
| 890                              | 0.39                          | 2.56                        |
| 980                              | 0.39                          | 2.56                        |

As can be seen from the table, the lower the density, the lower the conductivity. A possible reason for such behavior can be the reduced effective cross section of the foamed samples. In contrast to the foamed core, the density of the sample solid skin is close to the value of the unfoamed composite this way including a key influence on the conductivity. Since the sample conductivity depends on its cross section we have referred to a relative conductivity as conductivity divided by the effective cross sectional area. Such way calculated values are plotted vs. overall density and are presented on the figure 3. As is seen from the figure they are close to the unfoamed samples conductivity. The sample with the lowest density is a sharp exception. Its relative conductivity is significantly lower than the relative conductivity of the other samples.
3.3. Flexural properties

Some important mechanical properties enrich above presented electrical properties. In practice, during the use of moldings as constructive materials their flexural properties are the most valuable features one should examine. Such properties of foamed PP/CB composites are presented in the figure 4. It is seen that the flexural strength of foamed samples (curve 2 □) grows up with a growing overall density whilst their deformation (curve 1 ●) remains lower than that of the solid samples. Relative flexural

Figure 3. Relative conductivity vs. overall density of the samples.

Figure 4. Flexural properties of the foamed samples.
strength calculation is a simple method used for comparing strengths of different density samples [9] following equation:

$$\sigma_{rF} = \frac{\sigma_{FM}}{\rho / \rho_{\text{comp}}}$$

where $\rho$ is the foamed composite density, $\rho_{\text{comp}}$ is the unfoamed composite density (in our case it is 980 kg/m$^3$). The values of calculated relative flexural strength are shown in figure 4, (curve 3 ▲). The structure of foamed samples and mainly existence of a skin affirm their strengths to be close or even higher than those of the unfoamed ones. Here, another exception appears again. The value of the relative flexural strength of sample with the lowest density not having any skin is too low.

4. Conclusions
The presented experimental results proved that PP/CB structural foams produced by the low pressure injection molding can be used for production of technical articles with antistatic and electroconducting properties. The presence of a skin in studied structural foams leads to obtaining of better mechanical and electric parameters that are comparable to the properties of unfoamed products.

Acknowledgements.
The authors of this article would like to thank to INSTITUTE OF SOLID STATE PHYSICS - BAS, Project INERA/FP7-REGPOT-2012-2013-1 NMP (Research and Innovation Capacity Strengthening of ISSP-BAS in Multifunctional Nanostructures) and National Science Fund of MYES of Bulgaria Contract No. DO 02-202.

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