

Development of electrically conductive polymers

Anett Király^{1,a}; Ferenc Ronkay^{1,b}

¹Department of Polymer Engineering, Budapest University of Technology and Economics, H-1111
Budapest, Muegyetem rkp. 3, Hungary

^ae-mail: kiraly@pt.bme.hu

^be-mail: ronkay@pt.bme.hu (corresponding author)

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Abstract

Conducting composites based on graphite, carbon black and polypropylene have been prepared and the effect of composition on the flexural modulus and electrical conductivity has been studied. The conductivity of polymers containing only one kind of filler did not increase significantly, their modulus of elasticity was the highest for graphite filling, and the lowest for nanotube filling. The conductivity of dual filler hybrids increased significantly due to the synergetic interaction between the two fillers. At lower graphite contents, because of the better dispersion of graphite, the material became more flexible, but at higher carbon black contents the stiffness increased significantly. In the case of triple filler hybrids, if keeping the graphite content at a certain level and varying only the carbon black/nanotube ratio, the conductivity and the flexural modulus varied according to exponential and linear rules respectively.

Introduction

Development of conductive polymers is becoming more and more popular. Due to their corrosion resistance and low density they may replace metals in several applications, thus improving the life span of various equipments and decreasing the costs and the weight of the parts.

One potential field of application is the production of bipolar plates of fuel cells. 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.

Bipolar plate is one of the most important parts of the fuel cell, as it determines the lifetime of the cell. One of its tasks is to establish contact between the individual cells in order to maintain the required voltage, it conducts the electrons from the anode to the cathode, it supplies the anode with hydrogen and the cathode with oxygen, it separates hydrogen and oxygen from each other and conducts the electrical current form the membranes [1,2]. In order to perform these tasks completely at low pH, high humidity even at 80 °C they have to meet certain criteria, most important of which include good conductivity (> 100 S/cm), good corrosion resistance, acceptable mechanical properties and good chemical and electrochemical stability [3].

The conductivity of the polymer increases significantly if the added filler forms a continuous conductive network in the matrix, this process called percolation that can be explained by percolation theory. Below the so-called percolation threshold the material behaves as an insulator, while above the percolation threshold infinite conducting network is formed in the matrix, thus the material becomes conductive. The maximum conductivity is achieved theoretically at 100% filler content. Between the percolation threshold and the maximum the conductivity value increases steeply [4].

Most frequently used fillers to increase the conductivity include graphite, carbon black and carbon nanotubes [5-10]. Due to their different particle sizes and specific areas they can saturate the matrices in different proportions therefore their maximum loading values can be very different. By adding only one of the mentioned fillers it is not possible to achieve a proper increase of the conductivity, for this it is better to use hybrid fillers. The advantage of hybrid filler systems is that

smaller filler particles may fill matrix-resin rich areas between the large particles, therefore a continuous conducting network may form in the composite, and the percolation threshold may be realized at lower filler loading [4,6].

The goal of this study is to determine the effect of various fillers on the conductivity and on the mechanical properties for composites containing one, two or three kinds of fillers.

Materials and methods

Materials

Tipplén H949A polypropylene (TVK, Hungary) with an MFR value of 45g/10 min was used as a matrix material in the experiments. The graphite powder used to increase the conductivity (Carbosint Ltd. Hungary) was a crystalline natural graphite. The carbon black used was Ketjenblack EC-600 JD (Akzo Nobel), the carbon nanotube was Baytubes C150P (Bayer). The properties of the fillers used are summarized in Table 1.

Table 1. Properties of the fillers used [11,12]

	Graphite (G)	Carbon black (CB)	Carbon nanotubes (CNT)
Apparent bulk density [g/cm ³]	0.40	0.11	0.15
Density [g/cm ³]	2.24	1.80	1.50
Average particle size [μm]	diameter: 10-20 thickness: 0.1-1	0.035	diameter: 0.015 length: 0.3 - 1
Specific surface [m ² /g]	6	1400	300

The various compositions were mixed by a Brabender internal mixer at 240°C for 12 min at 25 rpm. From the melt-mixed materials 2 mm thick plates were compression molded at 250°C and 160 bar using a Collin P 200E mold.

In the case of materials containing only one filler the graphite content varied between 0 and 63 vol%, carbon black content between 0 and 8.5 vol% and the carbon nanotube content between 0 and 12 vol%. In the case of dual filler hybrids the loading of carbon black was varied between 0 and 12 vol% at three different, constant levels of graphite (0, 20 and 40 vol%). Finally in triple filler hybrids 5 and 10 vol% carbon black/carbon nanotube mixtures were used also at three different, constant levels of graphite (0, 20 and 40 vol%). In the carbon black/carbon nanotube mixtures the ratio of the two fillers was varied by 20% steps between 0% and 100% carbon nanotube content.

Test methods-

The conductivity was measured using a four probe resistivity test using an Agilent 4333B type milliohmmeter device. Three point bending tests were performed on a Zwick Z020 type universal tester with 64 mm span length, at 5 mm/min deformation rate, at room temperature.

Results and discussion

Conductivity test results

As a first step the conductivity of polymers containing a single filler was studied. As shown by Figure 1, in the case of the PP matrix carbon black increased the conductivity to the highest degree and graphite proved to be the least effective. The percolation threshold appeared at 1.6 vol% for carbon black, at 7.5 vol% for carbon nanotube and at 30 vol% for graphite.

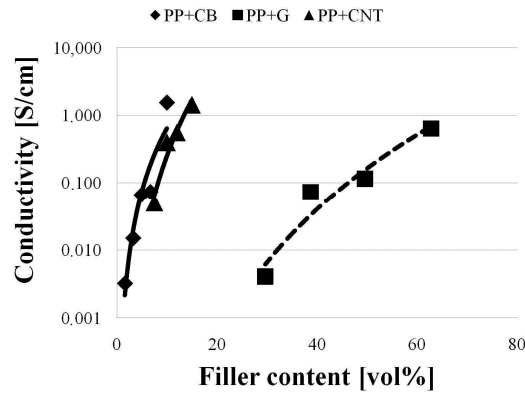


Figure 1. Variation of the conductivity vs. the filler content for graphite, carbon black and carbon nanotube filled systems

Figure 2 shows the specific volume conductivity of the hybrid composites plotted against the carbon black content. It can be seen that the conductivity of the hybrid filled materials is considerably higher than that of the samples containing only one kind of filler. At comparable graphite contents the conductivity increases with the carbon black content. This increase is less significant above 4.9 vol% carbon black content at 0 vol% graphite content and from 6.5 vol% carbon black content at 22.8 vol% graphite content. One possible reason for this is that the graphite content also influences the dispersion of the carbon black, and the more even distribution caused by the graphite content ensures higher conductivity.

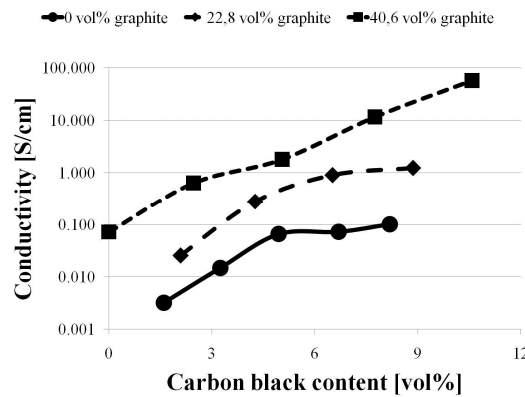


Figure 2. The specific conductivity of the dual hybrid composites plotted against the carbon black content

Figure 3. shows the variation of conductivity of composites containing triple hybrid filler loading. Figure 3/a plots the conductivity of composites containing 5 vol% CNT-CB at various graphite loadings (the conductivity of the sample containing only carbon nanotube could not be measured). At all three graphite loadings the conductivity decreases according to the exponential mixture rule (1). Figure 3/b shows the changes of conductivity of composites with 10 vol% CNT-CB content, where again a decreasing tendency according to equation (1) can be observed as a function of the CNT loading.

$$\sigma_C = \sigma_{CB} \exp \left(V_{CNT} \ln \frac{\sigma_{CNT}}{\sigma_{CB}} \right), \quad (1)$$

where σ_c is the conductivity of the composite, σ_{CB} is the conductivity of the material containing carbon black alone, σ_{CNT} is that of the material containing nanotube alone, V_{CNT} is the volume fraction of the nanotube within the carbon black-nanotube mixture.

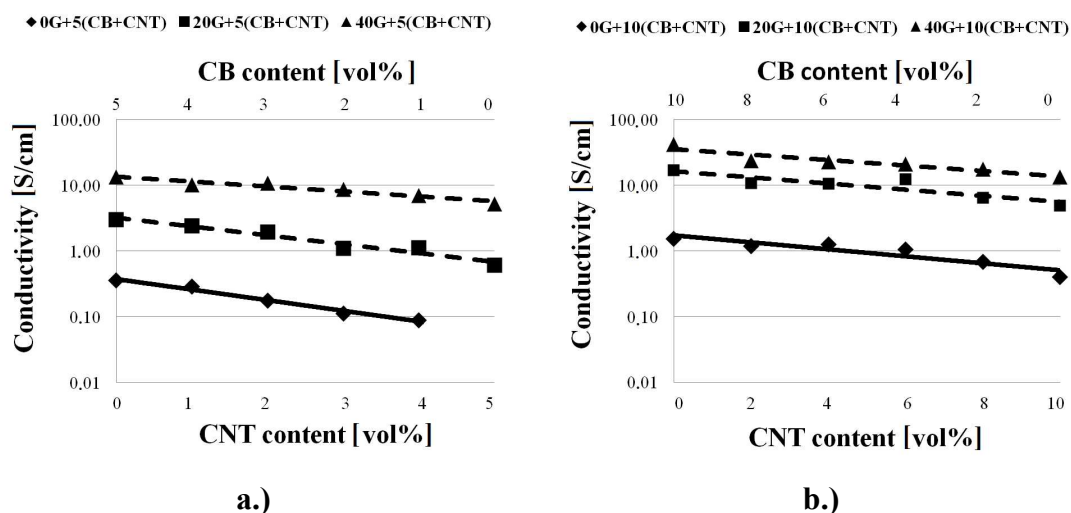


Figure 3. Changes of conductivity in triple hybrid materials

Results of the flexural tests

Figure 4 shows the changes of the flexural modulus of elasticity of polymers containing a single filler vs. the filler content. All three fillers increased the stiffness, the highest value could be achieved with graphite filled systems, the lowest one with nanotube filled ones.

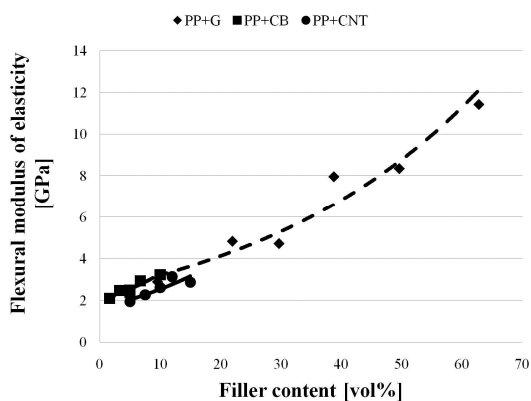


Figure 4. Variation of the flexural modulus of elasticity vs. the filler content for graphite, carbon black and carbon nanotube loaded systems

Figure 5 shows the changes of the flexural modulus of elasticity of systems containing dual hybrid fillers vs. the carbon black content. Taking the moduli of the materials containing carbon black only it can be seen that the carbon black content is less dominant in determining the stiffness.

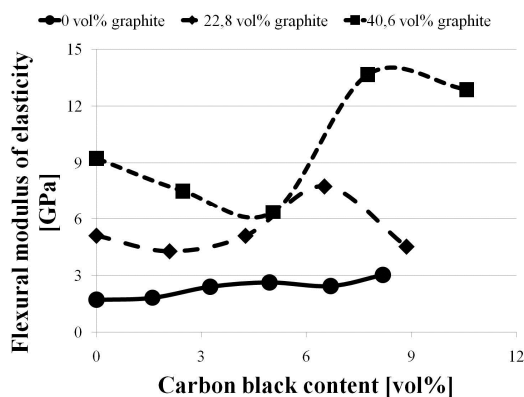


Figure 5. Changes of the flexural modulus of elasticity of systems containing dual hybrid fillers vs. the carbon black content.

Figure 6 shows the flexural moduli of elasticity for composites with triple hybrid fillers vs. the CNT content. The curves decrease according to the linear mixture rule (2). The reason for this is that decreasing the amount of carbon black dispersing well in polypropylene the hindrance of the molecular chains decreases, the material becomes more flexible.

$$E_C = V_{CNT}(E_{CNT} - E_{CB}) + E_{CB}, \quad (2)$$

where E_C is the flexural modulus of elasticity of the composite, E_{CB} is that of the material containing carbon black, E_{CNT} is that containing nanotubes alone, while V_{CNT} is volume fraction of the carbon nanotube within the carbon black - nanotube mixture.

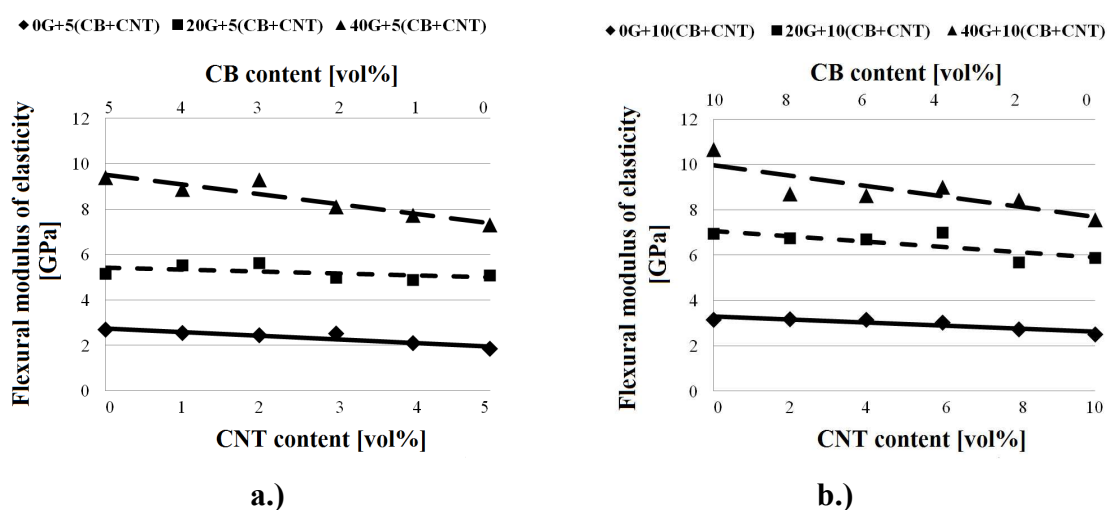


Figure 6. Changes of the flexural modulus of elasticity with triple hybrid fillers

Conclusion

In this work conducting composites based on graphite, carbon black, carbon nanotubes and polypropylene have been prepared and the effect of composition on the flexural modulus and electrical conductivity has been studied.

In the case of polymers loaded with only a single filler, in accordance with the literature significant increase of the conductivity could be achieved. In the case of composites containing dual fillers the two fillers exhibited synergism, at higher graphite contents the increase of the carbon black content increased the conductivity more effectively. In the case of composites containing triple hybrid fillers at various graphite contents the ratio of the added carbon black and nanotube were varied. Conductivity decreased according to the exponential mixture rule (1), the flexural modulus of elasticity according to the linear mixture rule (2) with the CNT ratio at all graphite contents.

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