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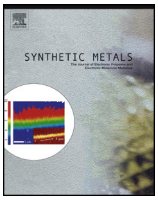

The electrical conductivity of ethylene butyl-acrylate/carbon black composites: The effect of foaming on the percolation threshold

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ABSTRACT

The main objective of this work is to study the influence of foaming on the percolation threshold of carbon black-filled polymer composites. The electrical conductivity, structure and tensile strength properties of solid and foamed ethylene butyl-acrylate/carbon black composites were investigated. The percolation threshold of solid composites was 10.9 vol.%, whereas for composite foams it decreased to 5.8 vol.% of carbon black. It was found that the charge transport mechanism of composites was not affected by the foaming. The reported decrease of the percolation threshold is attributed rather to the volume exclusion effect and carbon black redistribution. As a result, a conducting composite with a reduced specific volume and filler content can be prepared.

1. Introduction

The use of fillers is common practice in the plastics industry for improving physical properties, such as heat distortion temperature, hardness, toughness, stiffness or electrical conductivity. Recently, nanofillers have attracted much interest for their potential to provide novel performances. The enormous interfacial area of nanofillers influences nanocomposite properties to a great extent, even at low filler concentrations [1]. Among first nanofillers were carbon blacks (CB) [2].

The need to reduce weights of materials is increasing, especially in the automotive, transportation, electrical and aerospace industries, which leads to a wider use of polymer foams. Polymer foams or cellular plastics have many attractive characteristics, such as low density, flexibility, thermal insulation, impact damping, and good structure stability.

Polymer composite foams have received increased attention since the combination of functional nanofillers and foaming technology has the potential to generate new class of multifunctional materials [3,4]. Cell morphology and density of polymer foams can be significantly affected by the blowing agent solubility, saturation pressure, foaming time, foaming temperature, pressure drop rate and the presence of nucleating agents [5–8]. Thus foams with various density levels and physical characteristics can be prepared by the selection of appropriate foaming conditions and filler.

Over several decades, considerable effort has been devoted to experimental studies of conducting polymer composites (CPCs) [9–14]. Electrical conductivity of CPCs depends on the intrinsic conductivity of used filler, on the concentration, size, and shape of filler particles and as well as the homogeneity of particle distribution in the polymer matrix [15]. The percolation theory is usually used to describe the conductor–insulator transition in CPCs. Its main parameter percolation threshold, ϕ_C, is the critical concentration of conductive filler where the transition from the insulating to the conductive state is observed. This concentration region is characterized by a steep increase of conductivity, σ. According to this concept, the change in conductivity with an increasing concentration of conductive filler in a matrix is described by the following formulas:

$$\sigma = \sigma_f(\phi - \phi_C)^t \tag{1}$$

$$\sigma = \sigma_m(\phi_C - \phi)^{-s}, \tag{2}$$

where σ depends on the content of the conducting phase ϕ and the intrinsic conductivity of the filler (matrix) $\sigma_{f(m)}$ [16].

The possibility to influence the conductivity of CPCs through the modification of their structure represents a powerful trend in polymer composite research. Except the use of nanofillers, the phase-separated structure of polymer composites or multiple filler

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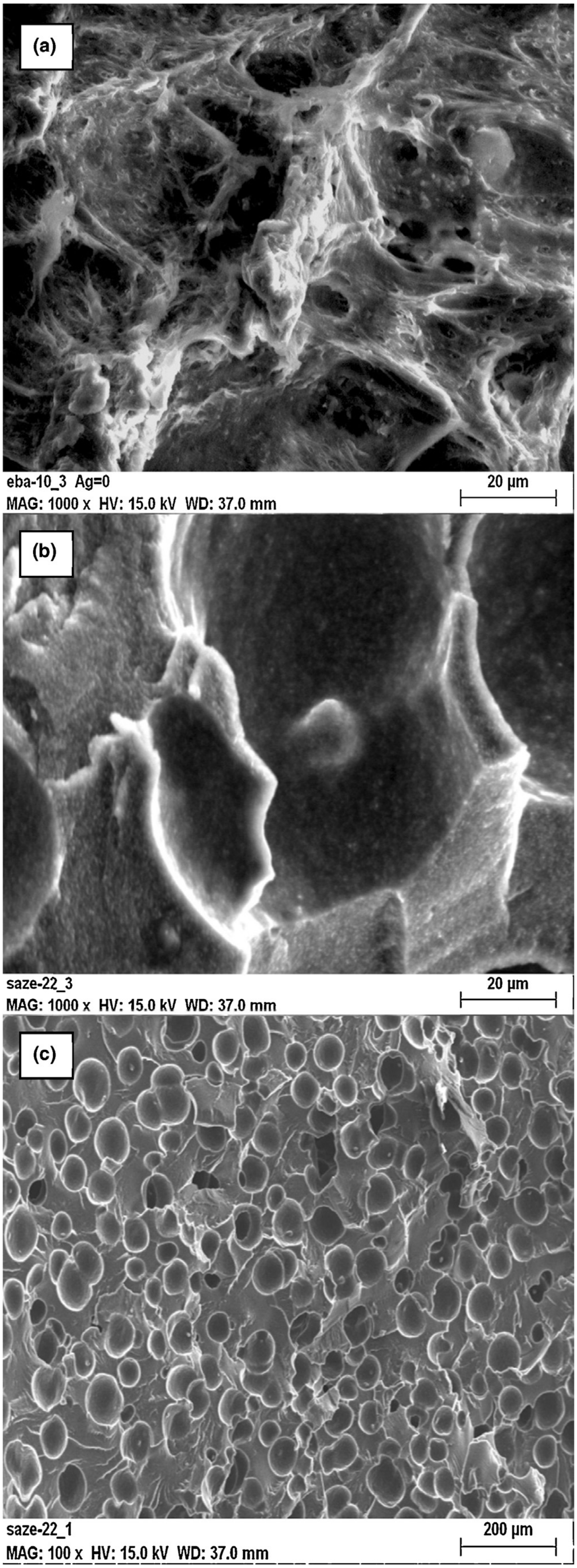

Fig. 1. SEM images of EBA/CB composites with (a) non-foamed composite with 10 wt.% of CB; (b) composite foam with 18 wt.% of CB; and (c) composite foam with 18 wt.% of CB – lower magnification.

systems belong to the most often used development strategies to adjust the electrical properties of composites [17–23]. Foaming is another possibility, but it is so far less frequently presented in literature [12,13,24–27]. Electroconductive polymer foams can be prepared by various synthetic methods [18,24] or by conventional processes for thermosetting [6,26] and thermoplastic polymers [25,37,38] using physical or chemical foaming method. Just as conducting polymer composite foams (CPCF) differ in method of preparation, they can be varied in the degree of lightening or hardness. The most of studied CPCF represented in literature contain carbonaceous nanofillers [6,24–27,37,38]. To achieve the desirable dispersion of nanofillers, that affects the resulting electrical properties, it is a problem in itself. In most cases, the percolation threshold was achieved in the range from 2 to 5 wt.% of carbonaceous nanofillers. Only a few articles (e.g. [25]) report about the lowering of the percolation threshold due to the foaming of nanofiller-composite. However, it is evident that fabrication of CPCF encounters a great practical challenge, since the nature of porous structure can limit the formation of an effective conductive network. This might be the reason why CPCF with conventional carbonaceous fillers (carbon black, graphite, etc.) has been rarely reported in the open literature [27]. In one case the electrical properties of foamed cyclic olefin copolymer filled with short carbon fibers or carbon black were studied [31,39,40]. It was found that studied composites remained electrically conductive after foaming. Nevertheless, the anisotropy of the conductivity properties was improved due to more effective conducting network formation during the growth of pores [31,39]. However, the influence of foaming on the percolation threshold was not reported. The aim of this study was to examine the influence of foaming on electrical properties (particularly the percolation threshold) and mechanical properties (Young modulus, elongation) of carbon black-filled polymer composites produced by conventional processing method with the use of blowing agent.

2. Experimental

2.1. Materials and composites preparation

For the sample preparation, ethylene butyl-acrylate (EBA) granulates with various amounts of acetylene CB were used (EBA density 925 kg/m^3, CB density 1800 kg/m^3). Azodicarbonamide (ACD) obtained from Sigma–Aldrich® was utilized as a chemical blowing agent.

Two series of composites, differing in CB concentration, were prepared: non-foamed (solid) EBA/CB composites and EBA/CB composite foames. In the case of the foamed composites, granulates were premixed with 1.5 phr of ACD at 100 °C employing a Brabender GmbH & Co. KG internal mixer. Afterwards, at the same temparature, they were hot-pressed. To initiate the foaming process, sheets were hot-pressed at the decomposition temperature of ACD, i.e., 200 °C, and cooled down to room temperature, in order to ensure convenient solidification. Although the material for composites preparation was received in a form of well-mixed granules for each concentration of carbon black, granules for solid composite samples were also premixed in order to ensure the same thermal history.

2.2. Foams characterization

The density of the composites was determined according to the ASTM D792 method. Then the expansion ratio was calculated as:

$$\mathrm{ER} = \frac{\rho_s}{\rho_f} \tag{3}$$