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Electrical conductivity and mechanical properties of melt-spun ternary composites comprising PMMA, carbon fibers and carbon black

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ABSTRACT

In this study, the electrical conductivity of melt spun composites consisting of PMMA containing both aligned carbon fibers (CF) and carbon black (CB) has been investigated. A broad range of composite compositions (up to 50 vol % CF and 20 vol % CB) was studied. The percolation thresholds of binary PMMA/CF and PMMA/CB composites were determined to 31.8 and 3.9 vol %, respectively. Experimental conductivity contour plots for PMMA/CF/CB ternary composites were presented for the first time. Additionally, based on a model for predicting the percolation threshold of ternary composites, a novel equation was proposed to predict the conductivity of ternary composites, showing results in agreement with corresponding experimental data. Finally, two mechanical contour plots for elastic modulus and tensile strength were presented, showing how the decreasing tensile strength and increasing E-modulus of the PMMA/CF/CB ternary composites was depending on the CB and CF filling fractions. The systematic measurements and novel equations presented in this work are especially valuable when designing ternary conductive polymer composites with two different fillers.

1. Introduction

Conductive polymer composites (CPCs) have been widely used in many fields, such as anti-static materials, electromagnetic interference (EMI) shielding, sensor and conductors. CPCs have been extensively investigated in both academia and industry, because the combination of promising material properties and comparatively simple manufacturing processes often imply commercially interesting materials [1,2]. Nowadays, the conductivity of CPCs is generally explained by “conductive pathways” in the composites, which are formed by conductive fillers [3–6]. As the fillers fraction increases, the number of “conductive pathways” growth, and consequently, the conductivity of the composite also increases. An electrical percolation threshold is defined as a certain critical value filler fraction when the conductivity of the composite increases by several orders of magnitude [7–9].

Carbon black (CB) and carbon fibers (CFs) are the most commonly used conductive fillers, which can be incorporated into a polymer matrix for facilitating the formation of a CPCs. The CF are elongated while the primary CB particles are spherical. This kind of CB (XE2) is however highly structured and the primary particles are fused to small aggregates which in turn form agglomerates [10], resulting in a significantly reduced percolation threshold.

Synergistic effects of CPCs containing both CFs and CB have been reported [11–16]. In a system with randomly dispersed CFs and CB particles, clusters of CB may form short “conductive pathways” between the CFs. Therefore, the conductivity of composites containing both fillers can be enhanced, as compared to those with only CFs or CB at the same concentration of fillers.

However, in a CPC system with randomly dispersed fillers (Fig. 1a), the conductive pathways formed between CFs also contribute to the conductive networks [11–16]. To evaluate the real synergic effect between CFs and CB, the effect of the CF-pathways in a PMMA/CB/CF system should be minimized. Therefore, the melt

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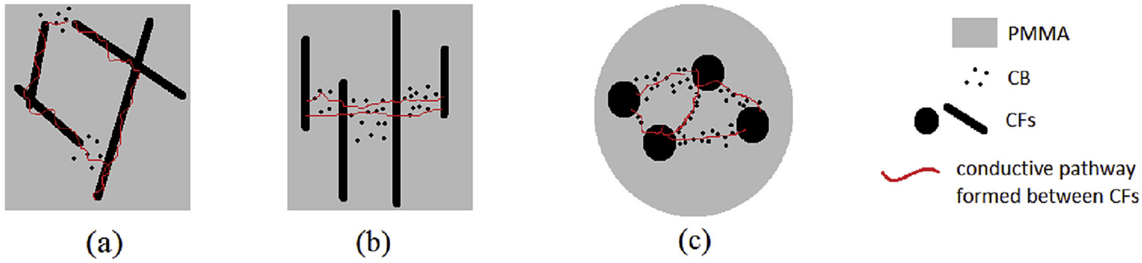

Fig. 1. Schematic of the conductive pathway formed by CB and CFs in the CPCs. (a) CPCs with randomly dispersed CFs, conductive pathway are contributed also by CFs themselves; (b) CPCs with highly orientated CFs, the contacts between CFs are reduced. With the addition of CB particles, a fence-like structure can be formed; (c) cross section view of fiber composites with fence-like structure.

spinning process [25] is applied in this study, in order to induce a maximum alignment of the CFs in the CPCs and consequently, to reduce the contacts between the CFs. With the addition of CB particles, "conductive pathways" can also be formed between the parallel CFs, such that fence-like structure is formed. (A side view and a cross section view of an idealized fence-like geometry is shown in Fig. 1b and c, respectively). Then the real synergistic effect between CB and CFs can be revealed.

Synergistic effects were also reported between CB and carbon nanotubes (CNT) in ternary composites [17–19]. CNT and CF are both suitable conductive 1-D fillers. In this study CFs were chosen due to their (1) improved melt mixing dispersion (2) more distinct cylindrical shape, (3) larger size, which simplifies microscopy analysis and (4) higher percolation threshold, which enabled a more genuine validation of our analytical conductivity model.

Several theories [20,21] have been suggested to describe the conductivity of binary composites, but few models consider the conductivity of ternary composites with two conductive fillers. Sun et al. [24] have proposed a percolation threshold model based on the assumption that the excluded volume of the two fillers can be added together linearly. The percolation threshold of a conductive composite with two fillers can then be predicted as:

$$\frac{\phi_A}{\phi_{c,A}}+\frac{\phi_B}{\phi_{c,B}}=K \qquad (1)$$

where ϕ_A and ϕ_B are the volume fractions of filler A and filler B in ternary composites, respectively, while $\phi_{c,A}$ and $\phi_{c,B}$ are the corresponding percolation concentrations when filler A or B is used alone in binary composites. When $K=1$, the percolation threshold is just reached. When $K>1$ the fillers in the composites connect each other (i.e. the composites are conductive) and when $K<1$ the composites are insulating. Based on this model, the potential synergic effects between CFs and CB have been discussed [13], defining "synergy" as a lower percolation threshold of the mixture than predicted by Eq. (1) with $K=1$. It should be noted that, according to Eq. (1), a linear relationship between volume fractions ϕ_A and ϕ_B can be established once the percolation thresholds $\phi_{c,A}$ and $\phi_{c,B}$ are determined. Therefore, a conductivity contour plot versus ϕ_{CFs} and ϕ_{CB} was presented in this work, such that the linear equation (Eq. (1)) could be evaluated.

Since the experimental conductivity measurements did not fully support Eq. (1), an improved original equation was proposed in this work for predicting the electrical percolation threshold of ternary composites containing two different conductive fillers. In addition, based on the improved percolation threshold equation, a novel equation for predicting the electrical conductivity of ternary composite was also developed.

2. Experimental methods

2.1. Materials

The polymer matrix was PMMA Plexiglas 7N from Evonik Röhm GmbH (Germany), with a weight-average molar mass of 99 kg/mol, a polydispersity index of 1.52, and a density 1.19 g/cm^3. CF segments were obtained from Tenax® - JHT C493 6 mm (Toho Tenax Europe GmbH) with a diameter of 7 μm, a specific resistance of 1.7×10^{-3} Ω/cm, and a density 1.79 g/cm^3. CB was Printex XE2 from Evonik Degussa, with a specific surface area of 900 m^2/g measured by the BET-method. The mean diameter of the primary CB particles was around 35 nm and the density at room temperature was 2.13 g/cm^3.

2.2. Sample preparation

All the materials were dried in vacuum at 80 °C prior to processing. Both the PMMA/CF composites (with parallel fiber orientations) and the PMMA/CB composites were prepared by melt mixing in an internal kneader PolyDrive (Haake, 557–8310) at a temperature of 200 °C and a rotation speed of 60 rpm, 20 min. Composites with 50 vol % CFs were treated as master batches, and further diluted with pure PMMA or PMMA/CB. Using this two-step melt mixing procedure, PMMA/CF binary composites with CFs concentration varies from 10 vol % to 50 vol % were produced, and the aspect ratio (AR = 9.2 ± 1.3) of CFs from different samples was well controlled (Fig. 2) [25]. After melt mixing, all the composites were ground into granules and dried under vacuum at 80 °C for 24 h.

After drying, the composite granules were melt spun at 200 °C in a capillary rheometer (Göttfert, Rheograph 2003), with a die 10 mm long and 1 mm in diameter, at an extrusion speed of 0.08 mm/s. The following nomenclature is used for the samples: *a*CB and *b*CF denote the composites with a % volume fraction of CB, and b % volume fraction of CFs, respectively. Thus, the sample with the name aCBbCF presents the ternary composite filled with a vol. % CB and b vol. % CFs and (100-a-b) vol. % PMMA. In this study, a ∈ [0, 20], and b ∈ [0, 50].

2.3. Sample characterization

The melt-spun composite samples were fractured in liquid nitrogen, the broken sections were sputtered with a thin layer of palladium, and were then analyzed using a SEM (Leica, LEO 435VP) equipped with a secondary electron detector at an acceleration voltage of 3 kV.

The fiber composites were cut into samples of 20 mm length and their end-sections were polished in order to remove isolate