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Processing and characterization of conductive composites based on poly(styrene-b-ethylene-ran-butylene-b-styrene) (SEBS) and carbon additives: A comparative study of expanded graphite and carbon black

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ABSTRACT

Electrically conductive polymer composites (ECPCs) based on poly(styrene-b-ethylene-ran-butylene-b-styrene) (SEBS) and expanded graphite (EG) or carbon black (CB) were prepared through melt blending using a torque rheometer equipped with a mixing chamber. Variations in parameters such as temperature, rotation speed and mixing time were investigated in order to define the most suitable processing conditions. The processing parameters investigated did not exert significant influence on the electrical conductivity for SEBS/EG composites, except for the mixture processed at 230 °C and 150 rpm for 15 min. On the other hand, it can be stated that the conductivity of the SEBS/CB depends on the processing temperature and mixing time. The electrical conductivity, morphology, dynamic mechanical, dielectric and rheological properties as well as electromagnetic interference shielding effectiveness (EMI-SE) of the SEBS/EG and SEBS/CB composites prepared under the same processing conditions were evaluated and compared. The insulator–conductor transition of SEBS/CB was very sharp and the electrical percolation threshold at room temperature was about 5 wt.% of CB, which was significantly lower than that of 9 wt.% for SEBS/EG composites. It was also observed that EMI SE value depends on its electrical conductivity. The EMI SE acceptable value for SEBS/CB composite with 15 wt.% of CB indicates that this materials are promising candidates for shielding applications.

1. Introduction

Electrically conductive polymer composites (ECPCs) consisting of an insulating polymer matrix filled with a conductive material, such as nickel, aluminum or silver particles, conductive carbon black (CB), carbon fibers and graphite (G), have been extensively investigated due to the combination of the mechanical properties and the processability of polymers with the electrical and magnetic properties of a conductive material. These materials have many applications, for instance, in electronic devices, static charge dissipation, electromagnetic shielding and chemical, thermal, mechanical and biological sensors [1–11].

A major challenge in relation to the incorporation of conductive additives into polymer matrices is the development of conductive mixtures containing the proportion of the additive as low as possible, in order to preserve the mechanical properties of the matrix, minimizing processing problems and reducing costs [8,12]. The critical amount of conductive additive in mixtures with insulating polymers, after which the conductivity of the system changes abruptly, is known as the electrical percolation threshold. The electrical percolation threshold is strongly dependent on the volume fraction of the conductive filler, the morphology, the intrinsic properties of the components, and the compatibility between the insulating polymer matrix and the conductive filler. The characteristics of the filler, such as particle shape, aspect ratio and orientation, and also the interfacial tension between the conducting and insulating phase, the dispersion and distribution of the conductive fillers in the polymer matrix, the rheological properties of the mixture and the processing methods have also been shown to influence the electrical conductivity of the resulting polymer

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composite [6–8,12–14]. Thus, there are several strategies available to reduce the electrical percolation threshold in ECPCs, including the adequate choice of the system phases and the use of the most suitable processing conditions.

The use of poly(styrene-b-ethylene-ran-butylene-b-styrene) (SEBS) as a matrix is an interesting alternative for the production of ECPCs. SEBS is a thermoplastic elastomer which allows properties similar to a vulcanized rubber without the need to go through the process of vulcanization. It also offers easy processability and features which allow its application in, for instance, electromagnetic shielding materials, anti-corrosive coatings, and conductive adhesives [4,15].

On the other hand, conductive additives such as intercalated graphite and expanded graphite (EG) have been intensively studied for incorporation into polymer matrices because of the possibility of obtaining CPCEs with a low electrical percolation threshold and appropriate physicochemical properties [6,7,9,14,16,17]. Chen et al. [17] have demonstrated that polystyrene/expanded graphite (PS/EG) composites have a lower electrical percolation threshold (1 wt.%) than polystyrene/conventional graphite (PS/G) composites (7 wt.%). According to the authors, the difference between the electrical percolation threshold of the PS/EG and PS/G composites can be attributed to the higher aspect ratio and better dispersion and distribution of the EG in the polymer matrix when compared to graphite. Chung [6] demonstrated the potential application of polymer composites based on expanded graphite as electromagnetic interference (EMI) shielding materials, due to the high electrical conductivity and surface area (typically 10 −15 $m^2 g^{-1}$) of the expanded graphite.

Carbon black (CB) as a conductive additive is one of the most widely used fillers to obtain ECPCs with low percolation threshold and is also suitable for EMI shielding applications. Zois, Apekis and Omastová [18] prepared composites of polypropylene (PP) and CB by melt mixing and obtained samples with electrical percolation thresholds of 6.2 wt.% of CB. Zheng and Wong [14] obtained composites of poly(methylmethacrylate) (PMMA) and CB with electrical percolation thresholds of 8 wt.% of CB. Ramôa et al. [12] obtained electrical percolation thresholds of 1.7 wt.% of CB for composites with thermoplastic polyurethane (TPU). As it can be seen, for the composites mentioned above the electrical percolation thresholds varied considerably, which may be related to the use of different polymer matrices and different mixing conditions.

In ECPCs, parameters such as the mixing temperature, speed and time tend to exert minimal influence on the final electrical conductivity values of the composites [1,19]. Krause et al. [19] conducted studies on the processing conditions for composites of polyamide 6 and polyamide 66 with multi-walled carbon nanotubes obtained by melt mixing. These researchers suggested that the use of high temperature, low speed and prolonged mixing time was the most appropriate combination of processing conditions for these composites as it resulted in lower electrical percolation thresholds.

In this context, the focus of this research was to obtain polymer composites of SEBS filled with two different conductive additives, EG and CB, after determining the most suitable processing conditions for the preparation via melt mixing. The electrical conductivity, morphology and rheological properties of the composites obtained were characterized and the feasibility of using these composites for electromagnetic interference shielding was verified.

2. Experimental

2.1. Materials

Poly(styrene-b-ethylene-ran-butylene-b-styrene) (SEBS) (Kraton G-1650; number-average molecular weight = 54,000 g mol^{-1}; polystyrene content = 30 wt.%) was kindly donated by Kraton Polymers do Brasil Ind.Com. Prod. Petr. Ltda. The expanded graphite (EG) (Micrograf HC 30; surface area = 26 $m^2 g^{-1}$; density = 1.8 g cm^{-3}) was provided by Nacional de Grafite Ltda. Conductive carbon black (CB) (Printex XE 2B; n-dibutyl phthalate absorption number (DBP) = 370 mL (100 g)$^{-1}$, Brunauer–Emmett–Teller (BET) = 1000 $m^2 g^{-1}$; density = 1.7–1.9 g cm^{-3}) was supplied by Degussa-Brazil.

2.2. Composites preparation

Composites were obtained in a torque rheometer (Haake Rheocord) coupled to a mixing chamber (RHEOMIX 600p) using roller rotors. Firstly, studies were performed with pre-fixed conductive additive concentrations (15 wt.% and 7 wt.% for SEBS/EG and SEBS/CB composites, respectively). The processing parameters were described as follows: temperatures of 230 and 260 °C, rotation speeds of 50 and 150 rpm and mixing times of 7 and 15 min. These processing parameters and pre-fixed additive concentrations were based on the experimental results observed by our research group and those reported in the literature for other ECPCs [4,7,9,14–18,20–25]. After defining the optimal processing parameters for each particular system (SEBS/EG and SEBS/CB), studies were performed with different conductive additive concentrations. SEBS/EG and SEBS/CB composites were manufactured at various weight fractions of EG and CB content.

The composites were compression molded in a Bovenau hydraulic press, model ST P15, at a temperature of 230 °C and pressure of around 20 MPa, for 10 min. Films were obtained with different geometries (square and circle) and thicknesses (1 and 5 mm), depending on the type of characterization to be performed.

2.3. Characterization

The morphology of the conductive composites was evaluated by scanning electron microscopy (SEM) for SEBS/EG samples and by field emission scanning electron microscopy (FEG-SEM) for SEBS/CB samples. SEM analysis was performed using a JEOL JSM - 6390LV instrument at an acceleration voltage of 15 kV. The FEG-SEM analysis was carried out using a JEOL JSM-6701 F field instrument at an acceleration voltage of 10 kV. Samples of the SEBS/EG (15 wt.% of EG) and SEBS/CB (7 wt.% of CB) composites were cryogenically fractured in liquid nitrogen and placed in an aluminum sample holder containing a double-sided conductive carbon adhesive tape and coated with gold for cross-sectional analysis.

The electrical conductivity of pure SEBS and SEBS composites with different weight fractions of conductive additives was determined by the two-probe and four-probe methods. For pure SEBS and high resistivity composites, the electrical conductivity measurements were performed using the two-probe standard method with a Keithley 6517A electrometer connected to a Keithley 8009 test fixture. The electrical conductivity of the conductive fillers and low resistivity composites were measured using the four-probe standard method with a Keithley 6220 current source to apply the current and a Keithley 6517A electrometer to measure the potential difference. All measurements were performed at room temperature five times and the electrical conductivity values were averaged.

The dynamic-mechanical properties of the composites and SEBS were studied using a dynamic-mechanical analyzer (DMA Q800 from TA Instruments Inc.). The DMA measurements were carried out at a heating rate of 3 °C min^{-1} and at 1 Hz, using single cantilever clamp.

The rheological behavior of SEBS and the composites was analyzed in the molten state using a Physica MRC302 rheometer