

Processing, characterization and properties of conducting polyaniline-sulfonated SEBS block copolymers

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Abstract

Incorporation of polyaniline (PAni) into thermoplastic elastomers can be used to produce materials that potentially combine the good mechanical properties and processability of thermoplastic elastomers with electrical, magnetic and optical characteristics of PAni. In this work, a polystyrene-block-poly(ethylene-ran-butylene)-block-polystyrene copolymer (SEBS) was chemically modified by grafting a sulfonic group onto the chain backbone in order to promote higher levels of compatibility between the thermoplastic elastomer and polyaniline. The sulfonation process was performed by reacting SEBS with acetyl sulfate. Infrared spectroscopy and titration were used to monitor the amount of sulfonic groups successfully grafted on SEBS. Mechanical tests performed in sulfonated SEBS showed that sulfonation levels lower than 15% did not reduce substantially the mechanical properties of SEBS. PAni doped with dodecylbenzenesulfonic acid (PAni-DBSA), used in the preparation of the blends, was prepared by the “*in situ* doping polymerization” method. PAni-DBSA was then blended in solution with SEBS having different levels of sulfonation. The introduction of sulfonic group into the structure of SEBS improved coulombic interactions between the phases in the blend and enhanced compatibility. As a consequence, higher values of electrical conductivity (measured by the four-probe method) were achieved in blends with sulfonic groups grafted onto polymer chains. Concentrations as low as 20 wt% of PAni were able to lead to electrical conductivities of PAni-DBSA/sulfonated SEBS blends close to 1.2 S/cm. Optical micrographs of the blends showed that PAni-DBSA/sulfonated SEBS microstructure is composed of a very disperse group of small conducting particles. This type of microstructure would then be responsible for the enhanced electrical conductivity and low percolation threshold of PAni-DBSA/sulfonated SEBS, when compared to PAni-DBSA/SEBS blends.

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1. Introduction

Over the last decade, significant progress has been achieved to improve the processability and mechanical

properties of conducting polyaniline (PAni). The incorporation of PAni into an electrical insulating conventional polymer matrix has received attention due to the possibility of combining the good processability and mechanical performance of the conventional polymer with the electrical and optical properties of PAni. These blends are normally obtained by *in situ* polymerization of aniline in the presence of the insulating polymer or by blending soluble or fusible polyaniline with other

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polymers in solution or melts [1,2]. Blending of PANi with conventional polymers through solution processing has recently been reported to be efficient when both polymers are soluble in a common solvent. The solubility of PANi in common solvents has been first achieved by Cao et al. [3–5] through a counter ion induced processability method, where a specific functionalized protonic acid is used as protonating agent. These dopants improve the solubility of PANi in common organic solvents and enable the formulation of conducting blends in which polyaniline and insulation polymers are dissolved and blended in a common solvent. An example of such a functionalized acid is dodecylbenzenesulfonic acid (DBSA), that has long alkyl chains that increase the solubility of PANi-DBSA in toluene, xylene, etc, and acts as a surfactant, inducing compatibility with polymer matrices with similar structure [3]. PANi-DBSA complex is normally used in melt blends, due to its relatively high thermal stability [6–8].

The use of rubbers in blends with conducting polymers is very attractive because of their unique mechanical properties. Conducting blends of polyaniline with poly(ethylene-co-propylene-co-diene-monomer) (EPDM) [9], nitrile rubber [10] and polychloroprene [11] have been reported in literature. However, the reported values of conductivity of these blends were not so high probably because the vulcanization process may contribute to dedoping/degradation of polyaniline. The use of thermoplastic elastomers, such as polystyrene-block-polybutadiene-block-polystyrene (SBS) or polystyrene-block-poly(ethylene-ran-butylene)-block-polystyrene copolymers as the insulating matrix, can be advantageous due to the combination of good mechanical properties and processability that does not require vulcanization. Some papers in the literature discuss the electrical and mechanical properties of SBS-based conducting blends using polyaniline as the conducting polymer component. Ruckenstein and coworkers have employed the “*in situ*” chemical polymerization of aniline in the presence of SBS, to prepare polyaniline SBS composites [12]. Xie et al. have also employed the “*in situ*” oxidative polymerization of aniline in an emulsion of SBS, using dodecylbenzene sulfonic acid as emulsifier and dopant [13,14]. Solution cast blends of PANi and SBS were also studied by Leyva et al. [15]. The SBS/PANi-DBSA blends, prepared in solution, displayed conductivity values close to the PANi-DBSA [15]. According to these authors, the conductivity of solution-cast PANi/polymer blends depends upon the ability of the solvent to disperse the conducting polymer when blended with the insulation polymer solution.

However, polyaniline is usually immiscible when blended with other polymers, and a phase separation process ended up restricting the formulation of more integrated materials. If the compatibility of these blends is enhanced then the electrical properties would poten-

tially increase. The morphology in immiscible blends is determined by various parameters, such as interfacial tension, volume fractions, and viscosity ratios [16]. Methods to improve compatibility in polymer blends include the use of compatibilizers such as block copolymers, or by introducing ionic polymers [17]. Lee et al. blended sulfonated polycarbonate (SPC) with polyaniline [18,19]. The compatibility between the components was improved by the presence of the sulfonic groups in the polymer matrix which interact with polyaniline. According to these authors, the degree of phase separation in this system was reduced when the sulfonic group content in the polymer chains was increased. Less phase separated blends led to materials with enhanced mechanical and electrical properties [19,20].

On the basis of these results, we decided to investigate the effect of the introduction of ionic group in polystyrene-block-poly(ethylene-ran-butylene)-block-polystyrene block copolymers (SEBS) chains on the electrical behavior and morphology of SEBS/PANi-DBSA blends. For this purpose, we synthesized a partially sulfonated SEBS (SSEBS), which was used in solution-cast blends with PANi-DBSA. This method required that both components were soluble in a common solvent. For this reason, PANi-DBSA was prepared by a method known as “*in situ* doping polymerization” where aniline is polymerized in an emulsion medium consisted by a small amount of water, a nonpolar or weakly polar organic solvent and DBSA which can act simultaneously as a surfactant and protonating agent for PANi.

2. Experimental

2.1. Materials

Aniline (analytical grade, Merck) was distilled twice under vacuum and stored under nitrogen in a refrigerator. Ammonium peroxydisulfate (APS) (analytical grade, Merck), and dodecylbenzenesulfonic acid (DBSA) (technical grade, Pro-Química do Brazil) were used without purification. The polymer used in this work was a block copolymer with styrene hard segments and ethylene-butadiene rubbery segments. The polymer, commercially designated Kraton G1652, was kindly supplied by Shell Química (Brazil) and contains 29 wt% styrene units. Acetyl sulfate, prepared by reaction of excess of acetic anhydride and concentrated sulfuric acid (96%), was used as the sulfonation reagent. Sulfonation of SEBS was carried out in 1,2-dichloroethane, previously dried using molecular sieves.

2.2. Sulfonation procedure

A series of sulfonated SEBS (SSEBS) was synthesized following the procedure reported in the literature

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