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Piezoresistive response of extruded polyaniline/(styrene-butadiene-styrene) polymer blends for force and deformation sensors

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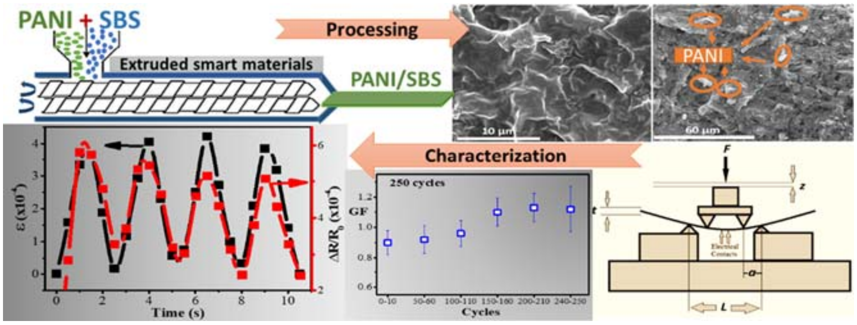
HIGHLIGHTS

- Conductive PANI can be an alternative to nanofillers in piezoresistive polymer composites for smart materials applications
- Extruded PANI/SBS blends show good mechanical, electrical and piezoresistive properties
- The percolation threshold is near 30 wt% polyaniline and the highest electrical conductivity is 0.1 S/m
- Mechanical strain reaches near 60% and the samples withstand large number of piezoresistive cycles
- Piezoresistive response shows a Gauge Factor ≈1, with linear resistance variation with the applied strain

GRAPHICAL ABSTRACT



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ABSTRACT

Smart materials for sensor applications are increasingly being used in a wide variety of applications ranging from engineering to medical devices. This work reports on piezoresistive sensors based on conductive polyaniline and thermoplastic elastomer processed by conventional polymer extrusion. The material presents excellent processability and piezoresistive performance offering an alternative to traditional composites with conductive nanofillers for sensor applications.

The polyaniline/styrene-butadiene-styrene (PANI/SBS) conductive polymer blends present good mechanical properties, high electrical conductivity and piezoresistive response. The maximum strain reaches ≈60% for 30 weight percentage (wt%) PANI content and the electrical conductivity is $\sigma \approx 0.1$ S/m for blends with 40 wt% PANI content. Further, the sample with 40 wt% PANI content shows a piezoresistive gauge factor GF ≈ 1 for deformation measurements between 0.1 and 3 mm in bending cycles.

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1. Introduction

Materials with piezoresistive properties represent a key engineering technology for device applications, being commonly used in industry and consumer products with ever growing demand [1–3]. Pressure or strain moldable sensors must be low profile and flexible to conform to arbitrary surfaces [4].

Most of the commercial piezoresistive sensors used in industrial applications are based on metallic films characterized by low flexibility and stretchability, limiting their range of applications [2,5]. Semiconductor materials show high piezoresistive sensitivity but poor mechanical properties [1,4]. In order to overcome these mechanical limitations, polymer-based smart materials have been developed due to their flexibility, low temperature processability and low cost [2,6]. Further, these materials show simpler device integration and allow tailoring their overall physico-chemical properties for specific applications. Their outstanding properties result in a broad spectrum of engineering materials [5,7] for sensors and actuators [8,9], optoelectronics [10], low weight structures [11], antistatic dissipations [11] and dielectric devices [12], among others.

Promising applications of these materials are related to strain sensing technology for structural health monitoring and biomedical applications [4,13]. Polymer composites with specific conductive characteristics can be developed using different materials (polymers and nanofillers) and strategies (processing methods and conditions). Extrinsically conducting polymers (ECPs) are based on conductive nanoparticles embedded in insulating polymer matrices. The most used conductive nanofillers are mostly based on carbonaceous materials, including carbon black, carbon nanofibers or nanotubes and graphene [7,14]. The electrical conductivity of polymer composites as a function of nanofiller content is characterized by different well-defined zones. The zone showing a strong increase of the electrical conductivity is identified as the percolation threshold (PT) and strongly depends on the nanofiller type and the composite processing method [15]. Thus, the PT can be as low as 0.01 wt% [15] for composites prepared by solvent casting or between 1 and 3 wt% for composites based on polymers with carbon nanotubes (CNT) processed with industrially viable methods such as melt compounding and extrusion [16]. Therefore, up scaled industrial processing for composite preparation typically lead to an increase of carbonaceous nanofiller loading content for achieving similar electrical properties when compared with laboratory methods.

In addition to ECPs, intrinsically conducting polymers (ICPs) also show piezoresistive properties and can be considered regarded a suitable alternative in terms of electrical conductivity and piezoresistive behavior response. Polyaniline (PANI), poly(3,4-ethylenedioxythiophene) (PEDOT), PEDOT modified with polystyrenesulfonate acid (PEDOT/PSS) and polypyrrole (PPy) [5] are examples of ICPs. These types of polymers can be used as piezoresistive sensors. In this way, the piezoresistive behavior of ICPs opens a new concept for piezoresistive sensors applications [17] but, on the other hand, ICPs present several limitations that need to be overcome. In particular with respect to their mechanical properties and longtime stability of the ICPs [17]. From the many available ICPs, PANI has been implemented in a wide variety of applications, including biosensors [18], anti-static materials [19] and batteries [20], among others. PANI shows easy processing, low cost and stability, allied to the doping/dedoping mechanism, allowing to further tune material physico-chemical properties, makes the PANI one of the most interesting ICPs [5,17].

Further, stretchable conductive composites are growing attention to replace the traditional rigid conductor materials, due to their applicability in flexible and stretchable devices [21]. Elastomer or thermoplastic elastomers (TPEs) polymer matrices are interesting materials in this context. TPEs are an important class of polymers that combine the mechanical properties of rubbers (e.g., stretchable materials) with the processability and recyclability of thermoplastics [22]. Additionally TPEs do not need vulcanization [6]. Styrene-butadiene-styrene (SBS) tri-block copolymer is an interesting TPE for the development of stress/strain sensors for large strain, robotic and industrial automation applications in order to replace silicone-like materials that are not capable of sustaining large deformations and sudden impacts [6]. Since SBS can be processed without the use of vulcanization, the properties of the corresponding composites do not deteriorate during their processing in composite materials [15]. With respect to the thermal behavior, SBS has two T_g at -86 and 76 °C, assigned to the glass transitions of polybutadiene and polystyrene, respectively [22,23].

In fact SBS and (styrene-ethylene/butylene-styrene) SEBS composites with CNT have been prepared by several methods, including solvent casting, electrospinning [24] and extrusion [15]. The different processing methods allow preparing composites with excellent piezoresistive properties with gauge factors (GF) up to ≈ 120 and deformation up to 30% under uniaxial stress [8]. Elastomeric polymer composite with piezoresistive properties can be processed using other conductive carbon nanofillers such as graphene or carbon black within different rubber-like materials [25,26]. Natural rubber/CNT composites show linear behavior with mechanical stress for strains up to 250%, unlike graphene composites for lower strains [25]. The main drawback of composites with nanocarbonaceous fillers is the agglomeration of the nanofillers, which can be up to tens of micrometres in size [27,28]. Another issue with respect to polymer composites is their poor adhesion of the polymer to fibre surfaces, being necessary the use of supplementary binders, which increase price and decrease electrical conductivity [29]. The agglomerates are defective structures that reduce the electrical and mechanical properties of the composite, leading to difficult reproducibility of the properties of the materials under the same manufacturing conditions. Further, the presence of large nanofiller agglomerates hinders the use of specific sensors integration processes, such as printing techniques [30,31].

Thus, PANI/TPE blends are an interesting alternative to polymer-based composites with conductive nanocarbonaceous fillers, due increased compatibility between the conductive polymer and the polymer matrix [32]. Further, the polymer blend can be processed by extrusion that, when compared to solvent-casting, commonly used for the preparation of piezoresistive polymer composites [15], has the advantage of being a purely mechanical process for polymer mixing which does not rely on the use of any chemical solvent. Further, it is a continuous process and allows the molding of the resultant products.

The present work reports on extruded blend composites based on intrinsic conductive PANI embedded one a thermoplastic elastomer (SBS). The morphologic, electrical, mechanical and electro-mechanical properties of the PANI/SBS blends are reported as a function of PANI and compatibilizer content.

2. Experimental

2.1. Material synthesis

Aniline and potassium peroxodisulfate (APS) were purchased from Fluka (Steinheim, Germany). Dodecylbenzensulfonic acid (DBSA) 70 wt% solution in 2-propanol and acetone were obtained from Scharlau (Sentmenat, Spain). Chloroform and methanol were supplied from Merck (Darmstadt, Germany) and Octyl Gallate (OG) compatibilizer was acquired on Sigma-Aldrich (Madrid, Spain). All the solvents and reagents except DBSA were at least of 99% purity. Water was purified on a Milli-QUltrapure 109 system (Millipore, Molsheim, France).

Thermoplastic elastomer (TPE) copolymer based in styrene-butadiene-styrene (SBS) with reference Calprene 718 (75/25 butadiene/styrene ratio with a radial structure) was provided by Dynasol.

2.2. Processing of the conductive polymer and the polymer blend

Polyaniline (PANI-DBSA) was processed via indirect route with "dedoping-redoping" steps, as detailed in [19]. A doped polymer of