Composite films based on shape memory polyurethanes and nanostructured polyaniline or cellulose–polyaniline particles

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A B S T R A C T

Conducting polyaniline (PANI) and PANI coated cellulose (PANI-NC) nanofibers doped with hydrochloric acid were synthesized by a sonochemical method and re-dispersed in methyl isobutyl ketone (MIBK) by ultrasonication. Composite films were prepared by mixing the dispersions with a segmented polyurethane (SMPu) solution in MIBK, followed by casting and solvent evaporation. PANI-NC fibers resulted more conductive than neat PANI ones and the same behavior was found for the resulting composite films, being the last ones in the range of semi-conductive polymers. As the concentration of nanofibers was maintained under 5 wt%, the thermal, mechanical and shape memory properties of the polyurethane matrix were not negatively affected or even slightly improved with the addition of nanofibers. In particular, the addition of any of the fibers led to an increase in the tensile modulus without decreasing the elongation at break, while the use of PANI ones resulted in an increase of the recovery capacity of the samples and the incorporation of PANI-NC fibers led to an increase in the recovery force. However, the transparency of the neat SMPu was lost, since even the less concentrated composite films resulted homogeneously green colored. On the other hand, no evidence of nanofiber percolation through the matrix was found.

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1. Introduction

In recent years, conducting polymers have attracted much attention due to the variety of possible commercial applications [1]. Among intrinsically conducting polymers, polyaniline (PANI) is unique due to its good environmental stability, straightforward synthesis, and adjustable electrical properties [1–4]. The emeraldine base form can be easily doped by means of protic acid treatments to obtain protonated emeraldine, which is green in color and electrically conductive. However, the intractability of PANI has limited its application, especially in its pure, inherently conductive form. Processing difficulties can seriously restrict devices manufacture and function [5]. On the other hand, low-dimensional nanostructured PANI, such as nanoparticles, nanofibers and nanotubes, nanosheets and nanobelts, have received considerable attention owing to the huge number of potential applications, especially in polymeric conducting molecular wires [6], light-emitting and electronic devices [7], chemical sensors [8], and biosensors [9]. For some applications, however, conducting polymers present certain deficiencies regarding specially the mechanical performance [1]. Recently, PANI nanofibers were prepared by a series of

novel template-free methods like interfacial polymerization [10], rapid mixing reaction method [11], radiolytic synthesis [12] and sonochemical synthesis [13,14]. These nanostructures demonstrate special physical and chemical properties like superior conducting and photothermal effects [15], differing from the bulk material. Furthermore, some of these nanostructures exhibit excellent dispersibility in water as shown by Jing et al. [14] and Li and Kaner [16]. Wang and Jing [4] demonstrated also that PANI nanofibers sonochemically synthesized in sulfuric acid can be easily dispersed in isobutyl ketone (MIBK) with ultrasonication to fabricate transparent conductive films based on poly(methyl methacrylate) (PMMA).

Technological uses of neat conducting polymers are not very likely because of their poor mechanical properties, which rarely meet technological expectations. However, the unique combination of electronic and mechanical properties of blends of conducting polymers with conventional polymers seems to have great promise for many applications [17].

In a two-component system comprising dispersion of a conductive polymer in a non-conductive matrix, the conductivity of the resulting blend is governed by bulk conductivity of the conducting polymer as well as the percolation behavior of the conducting polymer in the non-conductive matrix [18].

The percolation threshold depends greatly on the size of the particles as well as on the efficiency of mixing and uniformity of size [17]. In blends of doped polyaniline [17] with conventional

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insulating polymers, very low (∼5%) percolation thresholds were observed. It is believed that percolation is reached at a very low level since the continuous conducting polymer forms a network within the host polymer, thus forming a fine continuous conducting matrix throughout the bulk material.

The most important field of applications of conducting blends are antistatic materials [17]. Conductivities for antistatic applications need not to be high (10^{-6}–10^{-5} S/cm ranges are sufficient). Some materials using polythiophene or doped polyaniline have been already introduced for packaging of electronic items. Another very important application is electromagnetic shielding which requires higher conductivities (10^{-3}–10^{-1} S/cm, typically in anti-radar protection). Blends of conducting polymers in conventional polymers are very promising materials for this purpose. The third potentially important application of the conducting blends is their use as membranes for gas separation of high selectivity.

Chemical polymerization of conducting polymer on cellulose fiber has attracted attention recently for the manufacturing of conducting composite films and applications based on such materials [19]. Cellulose is one of the most abundant materials in nature and it naturally forms nanofibrils that can be extracted from different plants. Cellulose nanofibrils possess several advantages such as low cost, low density, non-toxicity, renewable nature, biodegradability, capability of forming stable aqueous suspensions and remarkable mechanical properties that allows improving mechanical performance of polymers at quite low fiber concentrations [20–22]. In addition to these advantages, cellulose-based nano-reinforcements are entirely organic, providing some of the mechanical improvements observed in the use of nanoclays and the added versatility of easy modification by applying well-understood cellulose chemistry [21]. Moreover, Mattoso et al. [21] prepared polyaniline coated cellulose by in situ polymerization of aniline onto "never-dried" nano cellulose fibers and demonstrated that the resulting aqueous suspensions were much more stable than PANI ones and thus, shining films with interesting electrical conductivities were obtained.

In a previous work [23], we reported the properties of composites based on a commercial shape memory polyurethane (SMPu) and PANI coated nanocellulose fibers. In that case we noticed that the changes of the material properties associated with the percolation of the coated fibrils appeared at higher concentrations than previously observed for non-modified cellulose nanofibers, which suggests that fibril agglomeration is occurring due to the PANI coating. The shape memory behavior of the composites was maintained at about the same level as that of the unfilled polyurethane only up to 4 wt% of fibrils. At higher concentrations, the rigidity of the nanofibrils as well as their interaction with the hard-segment phase and the increasing difficulty of dispersing them in the polymer collaborated to produce early breakage of the specimens when stretched at temperatures above the melting point of the soft segments [23]. In the present work, the behavior of the filler dispersion in the polymeric matrix was investigated by comparing the performance of neat PANI particles with respect to PANI coated cellulose nanofibers. Moreover, the effect of the concentration of each filler on the mechanical, thermal and dielectric properties of the resulting composites was evaluated.

2. Experimental

2.1. Preparation of cellulose nanofibers

Aqueous suspensions of cellulose crystals were prepared from commercial microcrystalline cellulose (Aldrich, Cat. No. 31,069-7) by acid hydrolysis, using an optimized procedure [20]. The microcrystalline cellulose was mixed with aqueous sulfuric acid (64 wt%) in a ratio of microcrystalline cellulose to acid of 1:8.75 g/ml. The

mixture was then held at 45 °C for 0.5 h under strong stirring. The resulting suspension was diluted with an equal volume of water and dialyzed using a cellulose dialysis membrane (Spectra/Por 2, SpectrumLabs, Unitek de Argentina, molecular weight cut off = 12–14,000 Da) to pH = 5–6 to eliminate the excess of acid. The final suspension was stabilized by ultrasonic treatment (0.5 h, Elmasonic P 60H, Elma). The concentration of this suspension was determined by drying aliquots of known volume and determining the fiber weight.

2.2. Synthesis of PANI and PANI–cellulose nanofibers

PANI fibers were synthesized by the sonochemical method proposed by Jing et al. [13] and adapted with small modifications. Aniline (ANI, Carlo Erba) was doubly distilled in presence of zinc powders. Ammonium persulfate (APS. Anedra, RA-ACS) and hydrochloric acid (HCl, 36–37 wt%, Anedra, RA- ACS) were used as received. In a typical procedure, a 0.2 M solution of ANI in HCl (1 M) was prepared in a beaker and sonicated by placing the beaker in an ultrasonic cleaning bath (Elmasonic P 60H, Elma), using a power of 160 W and operated at 37 kHz. Then, 0.2 moles of APS were dissolved in 100 ml HCl (1 M) and dropwise added to the ANI containing beaker, which was kept at 25 °C during the 4 h of reaction. After that, the acid suspension was dialyzed using the membrane already described until the dialyzed water became colorless. PANI was doped in HCl (1 M, ∼2 g PANI in 50 ml HCl solution) for 3 h with magnetic stirring. Finally, PANI was separated from the HCl solution by ultra-centrifugation (20 min at 12,000 rpm), washed once with distilled water and freeze-dried to yield a green powder.

The same procedure was used to synthesize PANI coated nanocellulose (PANI-NC) fibers, but in this case the nanocellulose fiber suspension (1 g/L) was previously dispersed in the ANI solution by ultrasonication. A ratio of 9.3 g ANI/g nanocellulose particles was used during synthesis.

2.3. Preparation of composite films

Composite films were prepared by suspension casting. The thermoplastic Pu (IROGRAN A60 E4902, Hunstman) was first dissolved in methyl isobutyl ketone (MIBK, Dorwill, PA) at 5 wt% and 60 °C by mild mechanical agitation (200 rpm) for 3 days. Simultaneously, PANI-MIBK and PANI-NC-MIBK suspensions at 1 wt% were prepared by ultrasonication during 2 h. The polymer solution and a selected volume of each suspension were mixed by magnetic stirring during 12 h at 95 °C. Partial evaporation of the MIBK solvent took place during this step. Then, the mixtures were sonicated during 30 min and cast onto glass plates. After 12 h drying at 65 °C in a convective oven, films of 0.4–0.5 mm thickness and containing up to 5 wt% of PANI or PANI-NC fibers were obtained.

2.4. Characterization techniques

2.4.1. Fourier transform infrared spectroscopy (FTIR)
FTIR spectra of neat SMPu, PANI and PANI-NC composites were recorded using a ThermoScientific Nicolet 6700 FTIR spectrometer in ATR mode at 32 scans with a resolution of 4 cm^{-1}.

2.4.2. UV–visible spectroscopy (UV–Vis)
UV–visible spectrum of solutions/suspensions of SMPu, PANI and PANI-NC fibers and composite samples containing 10 wt% fibers in MIBK, in the wave length range 300–1000 nm were obtained using an Agilent UV–Vis spectrometer, model 8453. Solutions and suspensions were prepared at the concentration of 0.4 g/L.