Short communication

Organic dispersion of polyaniline and single-walled carbon nanotubes and polyblends with poly(methyl methacrylate)

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ABSTRACT

Traditionally, in situ polymerization has been used to make polymer-carbon nanotube composites. Here, we report a simple method of mixing polyaniline with single-walled carbon nanotubes in a variety of organic solvents via ultrasonication. The maximum loading fraction of SWCNTs in the composites is determined by the conformation of the polyaniline chains. The type of solvent used has the greatest influence on the conformation of the polyaniline chains. Furthermore, the composites can be easily blended with poly(methyl methacrylate) (PMMA), to form polyblends. The electrical conductivities and transparencies of the polyblend films are reported.

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1. Introduction

Since its rediscovery, polyaniline (PANI) has been one of the most studied conducting polymers due to its excellent chemical stability, relatively high conductivity and low cost. Conducting PANI solutions can be prepared in select organic solvents including toluene, m-cresol and chloroform, with the use of a compatible protonic acid, such as dodecylbenzene sulfonic acid (DBSA) or camphorsulfonic acid (CSA) [1]. This counter-ion induced process-ability enables the creation of solution processable conductive polyblends of PANI and the desired insulating bulk polymer. However, the conductivity of PANI is lower than most metals, and its low strength may also hinder the mechanical properties of the polyblends [2,3]. A good alternative to PANI as a conductive filler is carbon nanotubes (CNTs), a lightweight nanomaterial, which ex-hibits high electrical conductivities and excellent mechanical properties [2,4–6]. Unfortunately poor processability limits the applications of CNTs. Although the use of non-conductive surfac-tants [7] or the introduction of functional groups [8] can improve the solubility of CNTs in a variety of solvents, the conductivity will inevitably be diminished due to the insulating nature of the

surfactants [9] and the destruction of long range π conjugation [10]. On the other hand, several studies [11,12] indicate that PANI and CNTs can interact strongly through π-π interactions between the conjugated polymer chains and the carbon nanotube walls. Thus, it seems logical that a dispersible PANI-CNT composite could over-come the limitations of each component. Progress has been made in recent years to prepare PANI/CNT composites dispersed in either aqueous or organic media [13–18]. Yet most syntheses have focused on a single solvent and adopted an in situ polymerization method [19–21], which makes control over CNT loading difficult. Moreover, there are rare reports on PANI-CNT composite disper-sions in polyblends with other bulk polymers [22]. Here, we report a facile method to prepare well-dispersed polyaniline and single-walled carbon nanotube (PANI-SWCNT) composites in a variety of organic solvent systems via simple ultrasonication. The PANI-SWCNT dispersions can be further mixed with other co-soluble polymers, such as PMMA at various ratios to obtain conductive polyblend solutions (see ESI† experimental section and Scheme S1 for details).

2. Results and discussion

In a typical synthesis, a desired loading of SWCNTs (relative to the content of PANI base) is added to a ~2% PANI/DBSA chloroform solution. The mixture is placed under ultrasonication overnight to obtain a dark homogeneous dispersion. The dispersion can be either centrifuged or filtered through glass wool to remove any

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possible minor insoluble solids. Actually, only the sample with 100% SWCNT loading showed an appreciable amount of precipitate when centrifuged at 4500 rpm for 10 min. The dispersion with 10% SWCNT loading is named PANI/0.1SWCNT and so forth.

The as-prepared PANI-SWCNT composites form very stable dispersions in chloroform (Fig. 1a). No visible precipitate shows up for months in dispersions with up to 50% SWCNT loading. The composite with 100% SWCNT loading, however, begins to precipitate within days, which indicates that the SWCNTs are not fully wrapped by the PANI chains (Fig. 1b). Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) images Fig. 1c and d reveal that SWCNTs in the composites are well dispersed with an average diameter of 20—30 nm for each bundle. The SWCNTs form well-connected conductive pathways throughout the composite. Metal catalysts from the synthesis of the SWCNTs are also observed as randomly distributed nanoparticles. Interestingly, it is difficult to observe the SWCNTs in the spin-coated films under SEM at first glance because they are so well hidden in the polymer matrix. As the same sample area is exposed to the electron beam for an extended time, the polymer is gradually burned away, revealing the SWCNT network underneath (see SEI† Fig. S1).

UV-vis spectra were collected for dilute PANI and PANI-SWCNT dispersions (see ESI† Fig. S2). Due to the high doping level, the π to π^* transition at ~360 nm and the polaron to π^* transition at ~430 nm are combined into one single distorted peak [23]. The peak observed at ~800 nm corresponds to the π to polaron transition [24]. As the SWCNT loading increases, the spectra gradually approach that of pure carbon nanotubes.

FT-IR spectra of all PANI and PANI-SWCNT samples show characteristic peaks for pristine polyaniline (see ESI† Fig. S3). The peaks at 1560 cm^{-1}, 1485 cm^{-1}, 1307 cm^{-1}, 1226 cm^{-1}, and 1147 cm^{-1} are assigned to PANI's quinoid C=C stretching, benzenoid C=C stretching, C-N stretching of secondary aromatic amines on the PANI backbone, the C-N$^+$ stretching vibration in the polaron structure, and the vibrational mode of the -NH$^+$ = structure (electronic-like band), respectively [25]. In contrast to some PANI-CNT composites fabricated by *in situ* polymerization [11,14,15], the quinoid/benzoid ratio (I_{1560}/I_{1485}) does not show a significant change as the loading of SWCNTs increase.

The PANI-SWCNT composite dispersions were spin-coated into transparent thin films (see ESI† Fig. S5). Not surprisingly, the presence of SWCNTs greatly enhances the conductivities of the composites, while maintaining relatively high transmittances (see ESI† Table S1). The films with 0%, 10%, 25%, 50% and 100% SWCNT loadings have conductivities of 1.0 S/cm, 7.2 S/cm, 19.2 S/cm, 33.4 S/cm and 36.9 S/cm, respectively. At the same time the corrected transmittance at 580 nm only decreases from 88.5% to 79.9%. The transmittance was measured at 580 nm, and corrected to that of a 100 nm thick film. The conductivity increases sharply even with a 10% loading, indicating the formation of a well-connected conductive SWCNT network in the composite film.

The PANI-SWCNT composite dispersions can be further mixed with PMMA dissolved in chloroform to create homogeneous poly-blend solutions without any visible particles. Highly transparent thin films are fabricated out of the polyblend solutions by spin-coating (Fig. 2a). The microscopic images (Fig. 2b and c) show that the existence of SWCNTs effectively reinforces the film due to its excellent mechanical strength, therefore the number of cracks in the film caused by the surface tension upon drying is reduced. The SEM image (Fig. 2d) also reveals that SWCNTs are randomly dispersed and well bridged in the polymer matrix. Due to the high aspect ratio of the SWCNTs [26], the conductivity percolation threshold of the polyblends is exceeded at a loading of less than 5 wt% PANI-SWCNT (Fig. 2e, ESI† Table S2), while the resistance of the film without SWCNTs goes beyond the instrument's limit even at higher loading percentages.
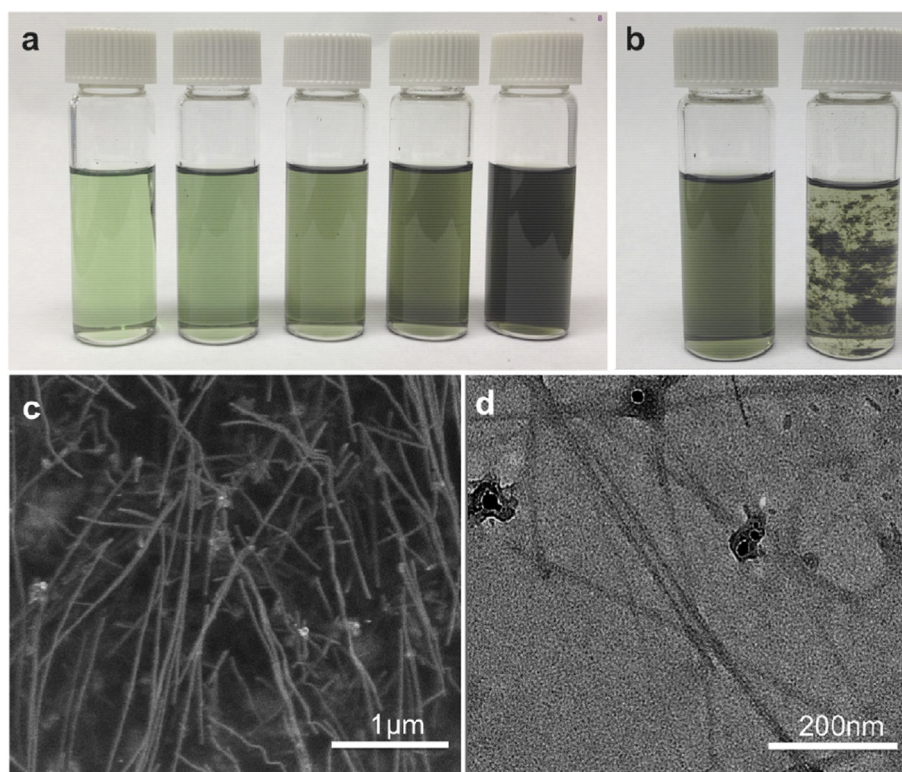
Fig. 1. (a) From left to right: diluted PANI/DBSA chloroform solutions with 0%, 10%, 25%, 50% and 100% SWCNT loadings, respectively; (b) PANI/0.5SWCNT dispersion (left) and PANI/1.0SWCNT dispersion (right) after one month; (c) SEM and (d) TEM images of diluted PANI/0.5SWCNT dispersion from the DBSA/CHCl₃ system.