Carbon black instead of multiwall carbon nanotubes for achieving comparable high electrical conductivities in polyurethane-based coatings

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ABSTRACT

In this work, we present a simple, reproducible and efficient method for the preparation of uniform and compact highly conductive coatings obtained from surfactant-free water-based mixtures of micro-beads made of cross-linked polyurethane (PU) with either carbon black (CB) or multiwall carbon nanotubes (MWNTs). Low percolation thresholds, 2.9 wt.% with CB and 0.8 wt.% with MWNTs, and high saturated conductivities, 200 S/cm for PU/CB and 500 S/cm for PU/MWNT, were achieved. This finding shows that, firstly, highly conductive carbon-based nanocomposite coatings can be made in water without surfactants using N-methylpyrrolidinone (NMP) as dispersing aid, and, secondly, carbon black can be used in place of multiwall carbon nanotubes for making cheaper coatings without sacrificing the electrical performance.

1. Introduction

The conductive coatings market is forecast to reach a value of $14.8 billion by 2017 [1] and carbon nanomaterial-based coatings will account for a valuable portion of it [2]. Nanomaterials, including metals and metal oxides, are predicted in fact to account for about 10% of sales by the same year [1]. The business and technological opportunities of developing highly conductive coatings using cheaper and more environmental friendly raw materials are therefore evident. Limiting the use of organic solvents in the development of environmentally friendly conductive coatings often requires the addition of surfactants in order to realize good aqueous dispersions of conductive fillers. However, surfactants have detrimental effects on the performance of the coatings since they are electrically insulating and often are not environmentally friendly.

In general, the solvent or mixture of solvents, referred to as the volatile component, serves as a medium capable of both dissolving the polymer and dispersing/debundling the filler, termed the nonvolatile component. The polymer usually fulfills the function of binder, imparting structural integrity to the conductive coating, while the filler is responsible for the electron transport throughout the film. Technical

and economical requirements are always considered in selecting these components, but toxicology and environmental protection are also of foremost importance in the development of coatings nowadays [3]. In order to dissolve the polymer, the volatile component is usually an organic solvent which often poses toxicological and environmental issues during processing. For this reason, attempts to either change or reduce the amount of solvent used in the formulation are regarded as paramount. Water is generally considered the solvent of choice for a greener industry and water-based coatings, paints and varnishes are commonly sold, for example, in home improvement and construction retail chains. On the other hand, water is a very poor solvent for the vast majority of polymers found in conductive coatings, as it is for carbon fillers like carbon nanotubes and graphene. A reason for this general 'insolubility' originates from the molecular nature of the components which are either too bulky to be held in solution by their polar/hydrogen bonding groups, such as for polyacrylates and polyurethanes, or because of their intrinsic hydrophobicity, as for carbon nanotubes and graphene. A way to overcome these limitations is to use water-based polymer emulsions and aqueous filler suspensions in which both materials are kept in solution by surfactants.

In the literature, there are few studies relating to the development of conductive composites made from water-based polyurethane (PU) emulsions and water dispersions of multiwall carbon nanotubes (MWNTs). In one of the most recent, a composite of PU

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and MWNTs dispersed with sodium dodecyl sulfate surfactant showed good percolation threshold, 0.5 wt.%, but very low saturated conductivities, 10^{-7} S/cm [4]. This is a common consequence of using electrically non-conducting surfactants which form an insulating layer around the conductive filler while stabilizing it in solution. A traditional, simple and efficient method employed to prepare polymer/carbon filler conductive coatings is solution casting processing [5]. A polymer, e.g., polyethylene, polyacrylate or polycarbonate, and a filler, e.g., carbon black, carbon nanotubes or graphene, are mixed together in a suitable solvent so to generate a homogeneous dispersion. This is then cast and let dry on a surface to produce a solid conductive film. Following the same method in our laboratory, highly conductive coatings from polycarbonate and multiwall carbon nanotubes using dichloromethane as a solvent have been prepared. Unprecedented conductivities as high as 1600 S/cm were recorded [6], and also broadband antenna and strain gauge transducer were fabricated using such conductive coatings [7]. Many other formulations and applications can be found in the literature using this and other methods [8–16].

We present in this paper a simple, reproducible and efficient method for the preparation of uniform and compact water-based coatings of hard micro-beads of cross-linked PU and carbon black (CB) or MWNTs dispersed without using surfactants. This is possible because of the intrinsic carboxylic defects present on the nanotubes and because of the addition of N-methylpyrrolidone, one of the best solvents for carbon nanotube dispersion [17–19], that promotes dispersion and improves the conductivity of the composites compared with those prepared previously using aqueous surfactant dispersions. We show that low percolation thresholds and high saturated conductivities can be achieved with this method using either of the fillers. The coatings so developed can potentially be applied in the fields of electromagnetic interference shielding [20–22], broadband receiver/transducer antennas [7], and sensors [21,23].

2. Experimental

2.1. Materials and chemicals

Polyurethane powder, under the trade name Decosphaera T, and carbon black Vulcan XC-72 were kindly supplied by Supercolori SPA and Cabot Corporation, respectively. Standard multiwall carbon nanotubes 10–30 nm diameter and 0.5–40 μm length (95%) were supplied by Helix Material Solutions. Polyethylenimine branched M_w ~ 25,000, N-methylpyrrolidone (≥99%), dichloromethane (≥99.5%), 0.1 N NaOH and 0.1 N HCl standards were supplied by Sigma-Aldrich. Camphorsulfonic acid (98%) was supplied by Spectrum Chemicals. Water ASTM type II was supplied by BDH. All materials were use as received.

2.2. Preparation of coatings

0.1 g of PU powder was weighed and transferred to a 5 ml clean glass vial. A corresponding amount of conductive filler, e.g., 0.005 g of MWNTs or CB for the 5 per hundred resin (phr) loadings, was added as is to the powder. These were then suspended in 1.5 ml of water and 0.5 ml of N-methylpyrrolidone (NMP), H_2O/NMP = 3/1 v/v, to which a 100 μl aliquot of a 1% polyethylenimine (PEI) aqueous solution was also added. The mixture was bath sonicated at room temperature for 5 min at 45 W using a VWR Synphony ultrasonic cleaner filled with water (1.9 l) and by keeping each vial directly immersed in the water and in the focal point of the ultrasonic waves, and intensively stirred for 15 min using a magnetic bar. Homogeneous and stable dispersions were obtained. The dispersions were drop-cast at room temperature and let dry on clean glass slides placed on a hotplate set at 70 °C. Visually uniform coatings were obtained within 1 h. The coatings were compact and hard, withstanding repeated scratching with the tip of a spatula.

2.3. Instrumentation and characterizations

PU particle size distributions were recorded with an Aerosizer DSP 3225 Powder Sizer (TSI Incorporated, Shoreview, MN) with wide geometric diameter range from 0.2 to 700 μm. The maximum shear force was 2.6 psi with normal deagglomeration. A density of 1.05 g/cm³ for the PU powder, as per supplier specifications, was set for the mass-to-volume conversion. Scanning differential thermograms were taken with a TA-DSC 2920 (TA Instruments) in aluminum crucibles at a heating rate of 10 °C/min in air. Raman spectra were obtained using a LabRAM HR800 Raman spectrometer (Horiba Jobin Yvon) equipped with a confocal microscope system. Raman spectra of raw materials and coatings were collected using a 100× objective (Olympus, Japan) in the range of 200–3400 cm^{-1} at laser wavelengths of 660 nm for PU, MWNTs and their coatings, and at 474 nm for CB and its coatings. The laser power at the sample was kept between 5 and 10 mW in order to avoid thermal decomposition of the coatings. The spectrometer was calibrated using the Raman band of silicon (520.7 cm^{-1}). The dispersion was of 1.5 cm^{-1} per pixel using a 300 g/mm grating. Raman samples were prepared by drop-casting the coating mixtures onto clean glass slides. The current–potential characteristics and conductivities of the coatings were recorded with a Keithley Picoammeter 6485 (Keithley Instruments) using a two-point probe setup and gold finger electrodes vacuum deposited on clean glass slides to an average thickness of 50 nm. The amount of carboxylic groups present in the MWNT and CB was determined by titration. To obtain the fully protonated dry MWNT (or CB), 1 g of MWNT (or CB) and 2.3 g of camphorsulfonic acid were placed in a 250 ml round-bottomed flask to which 200 ml of CH_2Cl_2 was added. After short sonication, the mixture was left stirring overnight and then centrifuged at 10,000 rpm for 30 min. After disposing of the supernatant, the solid was re-dispersed using a sonicator in 50 ml aliquots of fresh CH_2Cl_2 for five times in order to remove all camphorsulfonic acid. The solid was then collected and dried in a vacuum at 80 °C for 1 h. A known volume of 0.02 M NaOH (prepared from 1.0 N NaOH standard) was added to a known amount of this material which was then sonicated and left stirring overnight. This mixture was then centrifuged at 10,000 rpm for 30 min. The supernatant was back-titrated with 0.02 M HCl standard (prepared from 1.0 N HCl standard). The difference between the number of moles of NaOH originally added and titrated with HCl corresponds to the moles of – COOH groups present in the known amount of MWNT (or CB) used.

3. Results and discussion

Micro-beads made of cross-linked PU were dispersed using a sonicator in water-based solvent mixture (H_2O/NMP = 3/1 v/v) following an approach different to the vast majority of the cases in which PU emulsions are used as obtained just after polymerization. In this way, a fine and homogeneous dispersion of the beads was produced. The dispersion was reasonably stable with a visible solid–liquid phase separation observable only after several hours. In order to collect some information on the PU micro-beads, their particle size-distributions and thermal characteristics were taken as in Figs. 1 and 2, respectively.

The number-average diameter D_n of the PU micro-beads is found to be 4.9 μm with a polydispersity D_v/D_n of 2.8. As shown in Fig. 1, the numeric and volumetric size-distributions show a shoulder on the small diameter side, indicating a bias of the distribution towards smaller particle size compared to the mean. Considering in first approximation a random packing of bidispersed large (radius R) and small (radius r) hard spheres with $\rho = R/r \approx 3$ and a volume fraction of large spheres $f_R = 0.4$ (given the presence of a left shoulder on both distributions), one can estimate a packing porosity about 10% smaller that that expected for monodispersed distributions [24]. Accordingly, in the present case, a smaller amount of conductive filler should be needed in order to fill up the interstices among micro-beads in comparison to coatings