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Transparent, conductive polymer blend coatings from latex-based dispersions

Jiakuan Sun*, William W. Gerberich, Lorraine F. Francis[1]

Department of Chemical Engineering and Materials Science, University of Minnesota,
151 Amundson Hall, 421 Washington Avenue SE, Minneapolis, MN 55455, USA

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Abstract

Flexible, transparent and conductive polymer blend coatings were prepared from aqueous dispersions of poly(3,4-ethylenedixoythiophene)/poly(styrenesulfonate) [PEDOT/PSS] gel particles (∼80 nm) and latex (∼300 nm). The stable dispersions were deposited as wet coatings onto poly(ethylene terephthalate) substrates and dried at 80 °C. Microstructure studies using tapping mode atomic force microscopy (TMAFM) indicate that a network-like microstructure formed during drying at 0.03 volume fraction PEDOT/PSS loading. In this network-like structure, the PEDOT/PSS phase was forced into the boundary regions between latex. In addition, migration of the PEDOT/PSS particles towards coating surface is likely during drying of the aqueous dispersions. The addition of a small amount of dimethyl sulfoxide (DMSO) in dispersions altered the distribution of the PEDOT/PSS phase. As PEDOT/PSS concentration increases to 0.15 volume fraction, the coating surface is dominated by the PEDOT/PSS phase. The effect of DMSO on microstructure becomes less apparent as PEDOT/PSS concentration increases. The conductivity of the polymer blend coatings increases in a percolation-like fashion with a threshold of ∼0.02 volume fraction PEDOT/PSS. The addition of DMSO in dispersions enhanced the coating conductivity beyond the threshold by more than two orders of magnitude. The highest conductivity, ∼3 S/cm, occurs at 0.20 volume fraction PEDOT/PSS concentration. The polymer blend coatings have good transparency with only a weak dependence of transparency on wavelength due to the small refractive index difference between filler and matrix.

Keywords: Transparent and conductive coatings; Polymer blend; Electrical conductivity; Optical transparency; Microstructure; Percolation

1. Introduction

Transparent and conductive coatings have many applications, often serving as transparent electrodes. Currently, most transparent electrodes are based on coatings of conductive oxides, such as indium tin oxide (ITO) and antimony-doped tin oxide (ATO). These coatings are often produced at elevated temperature and lack mechanical flexibility, both of which limits their application on flexible substrates. Intrinsically conductive polymers are an alternative; however, they are not stable or are expensive. Another route to transparent and conductive coatings is to use polymeric nanocomposite coatings.

Flexible, transparent and conductive polymer nanocomposite coatings were prepared from stable aqueous dispersions of latex (∼300 nm) and nanosized ATO particles (∼15 nm) [1] by forming a segregated microstructure [1–4]. Since electrical conductivity is achieved at relatively low filler content and the size of ATO nanoparticles is much smaller than the wavelength of visible light, the nanocomposite coatings are optically transparent as well [1]. The above-mentioned ATO/latex system has three limitations: (1) relatively low achievable conductivity on the order of 10^{-2} S/cm [1] primarily attributed to the low intrinsic conductivity of the ATO nanoparticles [1] and the intrusion of polymer into the interstices between ATO particles and clusters [1,5]; (2) strong transparency dependence on wavelength [1]; (3) low mechanical flexibility of the resulting composite coatings [6]. In an attempt to overcome these limitations, this paper explores the use of intrinsically conductive nanoparticles in place of ATO.

Improving the conductivity of nanocomposite coatings requires attention to the properties of the conductive filler and matrix, as well as the microstructure and interface structure.

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* Corresponding author. Present address: Rohm and Haas (China) Holding Co., LTD. 1077 Zhang Heng Road, Zhang Jiang Hi Tech Park, Shanghai, China 201203. Tel.: +86 21 39628577; fax: +86 21 5895 9865.

E-mail addresses: jiakuansun@rohmhaas.com (J. Sun), lfrancis@umn.edu (L.F. Francis).

[1] Tel.: +1 612 625 0559; fax: +1 612 626 7246.

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The conductivity of polymer composites loaded with conductive fillers beyond percolation is increased by using fillers with lower intrinsic resistivity and by taking steps to decrease the resistance between fillers [5]. The resistance between conductive filler particles (R_c) consists of two contributions: constriction resistance and tunneling resistance [5]:

$$R_c = \frac{\rho_i}{d}(\text{constriction}) + \frac{\rho_t}{a}(\text{tunneling}) \qquad (1)$$

where ρ_i the intrinsic filler resistivity, d the diameter of the contact spot, ρ_t the tunneling resistivity, and a is the area of the contact spot. From Eq. (1), R_c is lowered by using fillers with lower intrinsic resistivity, by increasing the dimensions of the contact between particles, and by avoiding the intrusion of insulating polymer between conductive filler particle, which would increase the tunneling resistivity. Genetti et al. [7] demonstrated the importance of limiting the contact resistance; they enhanced the conductivity of Ni particle/polyethylene (PE) composites by nearly three orders of magnitude by synthesizing a layer of conductive polypyrrole (PPy) on Ni particle surfaces. The PPy layer on particle surface likely reduces the tunneling resistance and increases the contact area between Ni particles. One expects that deformable, conductive particles will have an even greater chance of forming composites with low contact resistance.

The transparency of conductive polymer composites is determined by the transparencies of the matrix and filler, the optical scattering at the interface between the two phases, and the composite thickness. Optical scattering decreases as the refractive index difference between matrix and filler, filler dimension, and filler concentration decrease for a given coating thickness [8]. The refractive index difference between ATO and matrix polymer (PVAc-*co*-acrylic) is ~0.5 [9,10]. Since polymer conductive fillers have nearly matching refractive index with matrix polymer, improvements on transparency are expected.

This paper explores the potential of using intrinsically conductive polymer particles as the filler in a latex-based coating. Poly(3,4-ethylenedioxythiophene)/poly(styrenesulfonate) (PEDOT/PSS) gel particles [11] were chosen for this study. In addition to exploring the effect of filler loading on microstructure, conductivity and transparency, the effect of polar solvents on the morphology and conductivity of PEDOT/latex composites was also investigated.

2. Experimental

2.1. Materials

An aqueous dispersion of PEDOT/PSS gel particles, commercially called Baytron P, was provided by the Bayer Company. Baytron P is an aqueous dispersion of PEDOT and PSS blend gel particles with an average size of ~80 nm, as specified by the manufacturer. The PEDOT/PSS gel particles consist of ~95 vol.% water and ~5 vol.% polymer, as specified by the manufacturer. PEDOT is a p-type semiconductor due to doping with $-SO_3^-$ groups.

Flexbond 325 (Air Products) is an aqueous dispersion (55 wt% solids) of PVAc-*co*-acylic polymer particles. The size distribution of latex particles, determined by a light scattering particle size analyzer (Coulter), ranges from 50 to 600 nm with a volume average particle size of 333 nm. The glass transition temperature (T_g) of the PVC-*co*-acrylic copolymer is 19 °C as specified by the manufacturer.

2.2. Preparation of coatings

In this paper, polymer composites composed of PEDOT/PSS filler in a PVAc-*co*-acrylic matrix are referred to as PEDOT/PVAc-*co*-acrylic. Two steps were used to fabricate the PEDOT/PVAc-*co*-acrylic coatings: (1) preparation of an aqueous dispersion containing latex, conductive filler, and other additives; and (2) deposition of the dispersion on the substrate and drying. To produce the PEDOT/PVAc-*co*-acrylic dispersions, the PEDOT/PSS dispersion was diluted in deionized water and stirred on a magnetic stir plate for 10 min; the latex was then added, the pH was adjusted to 5.5 using NH_4OH solution, and the mixture was stirred for 2 h. Dispersions were prepared to provide coatings with a range of filler loadings from 0.05 to 0.50 volume fraction (dry polymer) in the dried coating. Each dispersion contained 2 vol.% solids. The pH of the dispersions was adjusted to ~5.5 to achieve colloidal stability (see Section 3.1). The composite dispersions were coated onto polyethylene terepthalate (PET) substrates by a wire-wound rod with the coating rate manually controlled to be ~2 cm/s. The wet coating was then transferred into an oven and dried at 80 °C for 10 min. Two sets of coatings were prepared for each dispersion composition to verify experimental reproducibility.

A Dupont Zonyl FSO surfactant (0.1 vol.% relative to dispersion volume) was added to all the aqueous composite dispersions prepared here as a wetting agent. Zonyl FSO is a nonionic and fluorocarbon-based surfactant, which aids in spreading. To study the effect of polar solvents on the microstructure and conductivity of PEDOT/latex coatings, a small amount of DMSO (~1 vol.% relative to total dispersion volume) was added into the aqueous dispersions of PEDOT/PVAc-*co*-acrylic latex before coating process.

2.3. Characterization of microstructure and properties

Several instruments were used to characterize the thickness, microstructure, conductivity, and transparency of the polymer composite coatings. Coating thickness was measured by a Tencor P-10 profilometer. A DI multimode Nanoscope IIIa tapping mode AFM (TMAFM) was used to investigate the surface morphology of the composite coatings in air at room temperature. UV–vis transmission and absorbance spectra of the composite coatings were obtained using a Varian Cary 5-E UV–vis–NIR spectrometer. During the measurements, the PET substrate was scanned as a blank sample first, and then its spectrum was subtracted from the data.

For the measurement of coating conductivity, a four-point probe apparatus comprised of a Keithley 220 current source, a K&S four-point probe and a Keithley 6517A electrometer was used. The current was applied between two outer probes of four-point probe and the voltage across the two inner probes was