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Synthetic Metals 153 (2005) 129–132

SYNTHETIC METALS

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Effect of organoclay content on physical characteristics of poly(o-ethoxyaniline) nanocomposites

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Abstract

In order to improve the processibility of polyaniline (PANI), poly(o-ethoxyaniline) (PEOA) is grafted with ethoxy group on the PANI backbone and synthesized via an emulsion polymerization. The electric conductivity of PEOA is lower than that of PANI due to the interference of ethoxy side group in the electronic conjugation of polymer backbone. However, PEOA has better solubility than PANI in common organic solvents. PEOA/organically modified montmorillonite (OMMT) nanocomposites were thereby prepared via a solvent intercalation method, using an OMMT. The electrical conductivity of PEOA/OMMT nanocomposites was controlled via OMMT contents. The internal structures, electrical properties, and thermal properties of these nanocomposites were examined via wide angle X-ray diffraction (WAXD), transmission electron microscope (TEM), scanning electron microscope (SEM), two probe conductivity measurement, and thermogravimetric analyzer (TGA). The intercalated nanostructures analysed via WAXD and TEM were correlated with the electrical and thermal properties change originated from the nanoscale interaction between OMMT and PEOA.

Keywords: Conducting polymer; Poly(o-ethoxyaniline); Nanocomposite; OMMT

1. Introduction

Much attention has been paid to conjugated polymers [1] as novel electrically conducting materials. Among these, polyaniline (PANI) has attracted a special attention due to its superior electrical properties and environmental stability [2,3]. Although PANI is a promising conducting polymer, its engineering application has been hampered due to its poor processibility. In order to improve its processibility, much effort [4] has been paid on the synthesis of PANI, which is soluble in common organic solvents. As a consequence, the processibility of PANI has been improved by introducing some substituents (e.q., alkyl groups and sulfonic acid groups [2,4,5]) onto the backbone of PANI.

PANI mixed with other polymers or inorganic materials with controlled conductivity is used in many commercial products such as the electrodes of light emitting diodes, Li ion rechargeable batteries, corrosion protection, and microwave absorber [6,7]. Since the polymer intercalation into clay generates resistance to the conducting polymer [8-10], conductiving polymer/clay nanocomposites are introduced as a new alternative to control the electrical conductivity. Furthermore, a conducting polymer/clay nanocomposite system shows superior physical and mechanical properties such as solvent resistance, ionic conductivity, optical properties, heat resistance, decreased gas permeability, and flammability [11,12] as compared to pure conducting polymers, resulted from nanoscale polymer-clay interaction.

In this study, we synthesized nanocomposites with PEOA and OMMT via the solution intercalation method, using chloroform ($CHCl_3$) as a cosolvent. Later, we examined the characteristics of PEOA/OMMT nanocomposites by correlating the intercalated nanostructures with electrical and thermal properties.

2. Experimental

The PEOA particles were synthesized as a soluble conducting polymer in organic solvents. A 0.6 mol ethoxyaniline monomer (Aldrich, USA) in 400 mℓ 1M HCl was stirred for 2 h, and the polymerization was initiated at 25°C by a solution of 0.36 mol ammonium peroxysulfate in 240 mℓ 1M HCl. Products were dried at 25°C for 2 days using a vacuum oven. To control the electrical conductivity, the pH of the particles was adjusted to be 6 using 1M NaOH aq. solution. Later, the PEOA particles were dissolved in chloroform for 1 day to prepare nanocompsites. The OMMT (Cloisite 25A, Southern Clay Products, USA) was swollen in the same organic solvent for 1 day. Both PEOA and OMMT dispersed in chloroform were then

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doi:10.1016/j.synthmet.2005.07.137

mixed together, and stirred for 1 day to ensure the complete intercalation of PEOA chains into the multi-layered silicate of OMMT. Finally, the mixed solutions were filtered and dried to prepare PEOA/OMMT nanocomposites. These nanocomposites were designated as PEOA25, PEOA50, and PEOA75. Here, two digits represent the content in weight of OMMT in polymer matrix.

To confirm the nanostructures of the synthesized nanocomposites, X-ray diffraction (XRD) measurements were performed using the Rigaku DMAX 2500 (the wavelength of 0.154 nm) diffractometer. The nanostructures were also verified via transmission electron microscope (TEM, CM200, EDS DX-4, Phillips) and the microscale morphologies were investigated using scanning electron microscope (SEM, Hitach S-4300, Japan). The thermal properties were examined using a thermogravimetric analyzer (TGA, TA instrument Q50, USA).

The electrical conductivity of PEOA particles and its nanocomposites were measured using a two probe conductivity measurement (Keithley model 487, Cleveland, USA) with a pressed pellet sample.

3. Results and discussion

Fig. 1 shows the XRD patterns of two different PEOA/OMMT nanocomposites and pure OMMT. The maximum intensities for diffraction peaks of nanocomposites are shifted to a lower angle compared to that of the pure OMMT. It can be demonstrated using the Bragg formula that the basal spacing of layered silicates (d_{001}) increased due to the intercalation of polymers into the OMMT galleries. Furthermore, we found that the diffraction peak of PEOA25 is shifted to lower angle compared to that of PEOA75. It can, therefore, be conjectured that the crystalline order of the silicate layers gets much higher as the clay content increases [13, 14].

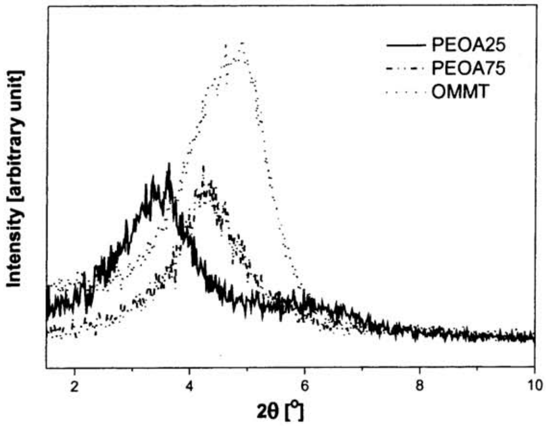

Fig. 1. XRD patterns of pure OMMT and two PEOA/OMMT nanocomposites.

In addition to XRD analysis, the internal structures of the nanocomposites in the nanometer scale were also examined via TEM, which generally provides a qualitative understanding of the internal structures through direct visualization, and exhibits the dispersity of silicate layers in the polymer matrix. Fig. 2 shows the results of TEM bright field images: (a) PEOA25 and (b) PEOA75. As indicated in X-ray diffractograms, we observed that organo-silicate layers in PEOA25 exhibited better dispersion due to the stronger interaction with PEOA. Therefore, we conclude that the internal structures of nanocomposites are determined by clay contents. In other words, the clay contents significantly affect properties of finished nanocomposites.

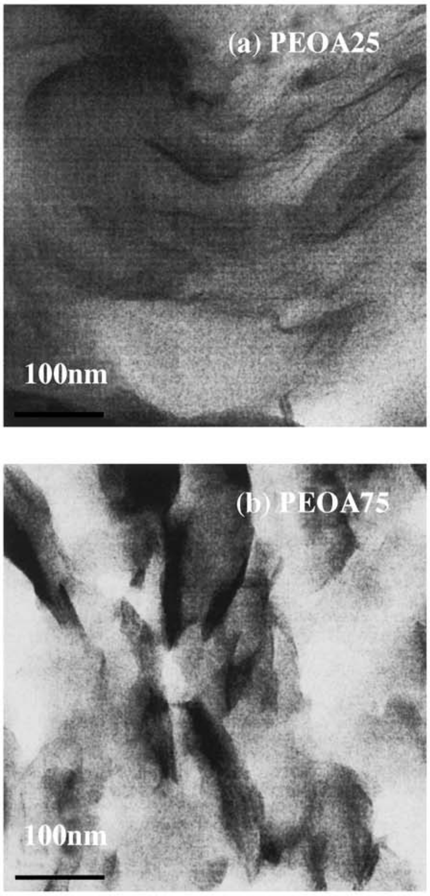

Fig. 2. TEM images of PEOA/OMMT nanocomposites. (a) PEOA25 and (b) PEOA75.

SEM micrographs of PEOA25 and pure OMMT are illustrated in Fig. 3. It is apparent that PEOA/OMMT nanocomposites form a partially-fused grain type morphology. It is evident that the incorporation of PEOA into the OMMT induces the morphological changes, which is in agreement with the results of XRD patterns. Furthermore, the SEM micrographs also show the existence of the two characteristic morphologies of round shape of PEOA and plate-like organoclay in PEOA/OMMT nanocomposites. This means that the dissolved PEOA not only intercalates into the intergallery of OMMT, but also adsorbes on the surface of isolated plates of OMMT.

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