



Macromolecular Nanotechnology

Synthesis and properties of conducting organic/inorganic polyurethane hybrids

Tzong-Liu Wang^{a,*}, Chien-Hsin Yang^a, Yeong-Tarng Shieh^a, An-Chi Yeh^b^a Department of Chemical and Materials Engineering, National University of Kaohsiung, No. 700, Kaohsiung University Road, Nan-Tzu District, Kaohsiung 811, Taiwan, ROC^b Department of Chemical and Materials Engineering, Cheng Shiu University, Kaohsiung County 833, Taiwan, ROC

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ABSTRACT

A series of polyurethane/polyaniline/silica organic/inorganic hybrids were synthesized via the conventional polyurethane (PU) prepolymer technique. Amine-encapped polyaniline (PANI) with low molecular weight and higher solubility was firstly synthesized. This PANI oligomer was then used together with nano-silica bearing silanol groups as chain extenders to prepare the conducting polyurethane hybrids. The polyurethane hybrids were designated as PU-*x*PANI-*y*SiO₂ (*x* + *y* = 1). For comparison, the urethane-aniline block copolymer and the PU/silica hybrid were designated as PU-PANI and PU-SiO₂, respectively.

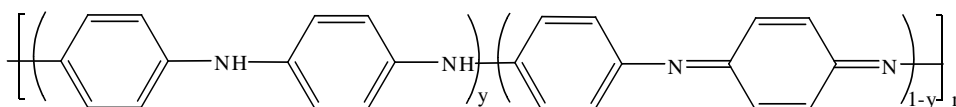
The structures of PU-PANI, PU-SiO₂ and conducting polyurethane hybrids were confirmed by FT-IR, solid-state ¹³C, and ²⁹Si NMR spectra. In nano-silica containing organic/inorganic conducting polyurethane hybrids, UV-vis spectra revealed the maximum absorption bands similar to that of PU-PANI. X-ray diffraction patterns indicated that these samples are typical of semicrystalline/amorphous materials. SEM image of PU-0.5PANI-0.5SiO₂ showed that PANI was dispersed homogeneously and interconnected continuously in the insulating PU-silica matrix. TGA results of the polymer hybrids exhibited higher thermal stabilities and lower decomposition rates than that of PU-PANI both in nitrogen and air. Differential scanning calorimetry (DSC) studies indicated that the polyurethane hybrids had higher glass-transition temperatures (*T*_g) with the increase of PANI, but lower than that of PU-PANI. Stress-strain curves for all of the polyurethane hybrids showed the elastomeric behavior of typical polyurethanes. The surface resistivity values of all hybrids were about 10⁸ ~ 10¹⁰ Ω/sq. and might meet the requirement of the anti-electrostatic materials.

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1. Introduction

Polyaniline (PANI) is a conducting polymer which has been extensively studied due to its relatively high conduc-

tivity and potential application in electronic devices [1,2]. The general formula for ideal PANI materials in their base forms consists in three (–C₆H₄–NH–) benzenoid units and one (–N=C₆H₄=N–) quinoid unit [1].



The *y* value accounts for the oxidation state of the polymer. Leucoemeraldine base (LEB), emeraldine base (EB) and pernigraniline base (PNB) correspond to the

* Corresponding author. Tel.: +886 7 5919278; fax: +886 7 5919277.
E-mail address: tlwang@nuk.edu.tw (T.-L. Wang).

completely reduced ($y = 1$), half oxidized ($y = 0.5$) and completely oxidized ($y = 0$) states, respectively. Whereas the three bases are insulating materials, base protonation leads to the corresponding salts. Emeraldine salt (ES) is the only one exhibiting high electric conductivity and has consequently received considerable interest. The increase in electronic conductivity that occurs after the transition emeraldine base (EB) to emeraldine salt (ES), involves a doping mechanism different from those commonly observed with conducting polymers [3–5].

Unfortunately, the poor processability of PANI and its inadequate mechanical properties limit its commercial applications. In order to overcome these problems, numerous methods have been studied [6,7]. A conducting polymer blend with PANI and conventional polymer can exhibit good mechanical properties associated with interesting electrical properties [8–14]. However, blending has very little effect on the environmental stability of the conducting polymer itself. One of the major limitations of the blending is that it almost always produces a highly heterogeneous two-phase morphology. Therefore, it may be more effective to prepare a conducting polymer with improved processability and mechanical property by the chemical synthesis approach. The combination of PANI segments with blocks of another polymer has been recently reported, such as the grafting of polyethylene glycol [15] or polyacrylic acid [16] onto a PANI backbone, and a block copolymer consisting of polyurethane and PANI oligomer [17,18], etc.

The use of a thermoplastic elastomer with conducting polymers is very attractive due to the combination of mechanical properties and a processability which does not require vulcanization. Thermoplastic polyurethane (PU) elastomer is one of the most versatile products in the group of engineering thermoplastics with excellent physical properties, chemical resistance, abrasion resistance as well as its ease of processing. Typically, thermoplastic PU elastomers (i.e., segmented copolyurethanes) are block copolymers of the $(A-B)_n$ type, consisting of alternating soft and hard-segments. The soft-segment is typically a long chain polyol which is a polyester-, polyether-, or polyalkyl-diol with a molecular weight between 500 and 5000. The hard-segment generally consists of an aromatic diisocyanate chain extended with a low molecular weight diol or diamine (i.e., chain extender). The unusual properties of these copolymers are directly related to their two-phase structures. The two-phase feature of the original reaction mixture is due to thermodynamic incompatibility of the different block polymer segments.

On the other hand, conductive composites of PANI and inorganic compounds have been synthesized in order to get new materials with modified properties [19–21]. Among those inorganic materials, silica (SiO_2) has received great attention because of its unique properties and wide applications [22,23]. Recently, a conductive hybrid composed of PANI dispersed in a polyurethane-silica matrix via the sol-gel process was also reported [24].

In past several years, polyurethane-related composites have been extensively studied in our laboratory; herein we present a simple methodology to synthesize a kind of elastomeric PU/PANI/silica conductive hybrids using the conventional polyurethane prepolymer technique. To meet the

above-mentioned requirements, both amine-encapped PANI and nano-silica bearing silanol groups were used as chain extenders. Hence, this kind of conductive hybrid consists of one type of urethane-aniline block copolymer homogeneously dispersed in the matrix of urethane-silica polymer network. In this work, a series of elastomeric polyurethane hybrids with different mole ratios of PANI and silica were synthesized and their properties were also investigated.

2. Experimental

2.1. Materials

4,4'-Methylene bis(4-phenyl isocyanate) (MDI, Aldrich), 1-methyl-2-pyrrolidinone (NMP, FERAK), aniline (ANI, TCI), *p*-phenylenediamine (*p*-PDA, TCI) were distilled under reduced pressure. Ammonium persulfate (APS), dodecylbenzene sulfonic acid (DBSA), hydrochloric acid (HCl) and ammonia solution were all from Union Chemical Works Ltd. and used without further purification. The silica nanoparticles ($M_w = 60.09$ g/mol) bearing surface silanol groups (18.7 mmol OH/g) were purchased from Desunano Co., Ltd.; the purity is higher than 99% and the polydispersity is 1.20. The surface area and particle size are 640 m^2/g and 10 nm, respectively. Polytetramethylene ether glycol (PTMG, Aldrich) with molecular weight ($\overline{M}_n = 1000$) was degassed under vacuum at 55 °C at 600 Pa (4.5 mm Hg) for 3 h to remove any absorbed water.

2.2. Preparation of amine-encapped polyaniline (PANI) chain extender

The polymerization of aniline was carried out as follows. Ammonia persulfate (APS) and aniline, mixed with 1 M HCl aqueous solution respectively, were individually kept in a refrigerator overnight. To control the molar mass, a suitable *p*-phenylene diamine (*p*-PDA) was mixed with the aniline solution. To the aniline solution, APS aqueous solution was added dropwise and the mixture was kept at 0 ~ 5 °C for 2 h with continuous stirring. The resulting polyaniline was isolated by filtration and dedoped by stirring in 0.1 M aqueous solution of ammonia for 24 h followed by filtration. The filtered cake was dried in a vacuum oven for 3 days and ground into powder by mortar and pestle. The yield was about 78.5%. Number average molecular weight (\overline{M}_n) determined by gel permeation chromatography (GPC) was found to be 1849 g/mol.

2.3. Synthesis of the polyurethane prepolymer

Isocyanate terminated PU prepolymer was prepared by reacting 0.02 mol of MDI and 0.01 mol of PTMG in 70 ml NMP at 80–85 °C for 3 h. This solution was then chain extended with 0.01 mol of chain extender solution in the following step.

2.4. Preparation of PU/PANI/silica conductive hybrids by sequential chain extension reaction

Two chain extender solutions were prepared by mixing x mole fraction of amine-encapped PANI and y mole

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