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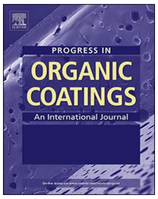

A novel antistatic polyurethane hybrid based on nanoscale ionic material

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ABSTRACT

A novel liquid-like nanoscale ionic material (NSiF-Hs) at ambient temperature was synthetized. NSiF-Hs, as supramolecular cross-linking agents, can react with prepolymer (polytetramethylene ether glycol and 4,4′-diphenyl methane diisocyanate) to prepare a novel polyurethane hybrid (PU/NSiF-Hs). The tensile strength and the elongation at break of PU/NSiF-Hs hybrids both increased with augmented proportion of NSiF-Hs when it was less than 4 wt%. Especially, NSiF-Hs endowed PU hybrid with permanent antistatic property duo to ionic bond and hygroscopicity of residual hydroxyl groups on NSiF-Hs. The surface resistivity of PU hybrid with 8 wt% NSiF-Hs reached 7.35×10^7 Ω/sq.

1. Introduction

Large accumulation of static electricity in insulating materials can lead to equipment failure, such as distortion of precision instruments, damage to electronic components etc. Recently, the severe fire hazard and explosion accident in petrochemical enterprise duo to the accumulation of static electricity make us be more alert to static electricity disasters. Due to its high electrical conductivity and fast electrostatic charge eliminating capacity, the antistatic coatings have been widely used in industrial fields such as aerospace petroleum storage, electronic/electrical products and chemical engineering. Generally, antistatic coatings can be divided into intrinsic antistatic coatings and composite antistatic coatings [1–7]. The conductive polymers with conjugated π bond are used as materials for intrinsic antistatic coatings, like polyacetylene, polyaniline, polypyrrole, polyphenylene, polythiophene [1,2]. The researches on intrinsic antistatic coatings are focused on diversified preparation methods. Composite antistatic coatings refers to general polymer insulation materials combined with antistatic agent or conductive fillers(carbonaceous filler, metal carbonaceous filler or metal oxide fillers) through dispersion or deposition methods [3–6]. But the poor dispersibility of carbonaceous filler and unstable metal filler are major problems. Ultrasonic dispersion and surface modification for nanofiller are main solutions. Shen [3] et al. prepared MWCNTs reinforced epoxy hybrid coatings with high electrical conductivity and corrosion resistance via electrostatic spraying. The electrical resistivity was decreased to 7.6×10^{-2} Ωm by the addition of 2 wt% MWCNTs (nine orders of magnitude higher than that of pure epoxy resin). Wang [7] et al. investigated a facile approach for fabricating antistatic and thermally conductive epoxy matrix nanocomposites. It has been carried out by mixing terephthalic acid-doped MWCNTs with a silver nanoparticle decorated polypyrrole functional coating (MWCNTs@Ag-PPy@COOH). Ag nanoparticles could work as a bridge between conductivity PPy and MWCNTs to increase the electron transport properties of the polymer matrix. The functional carboxyl group helped the dispersion of MWCNTs in the matrix to build up an electrostatic discharge channel. The percolation surface resistivity was decreased to 1.3×10^8 Ωsp^{-1} at 0.5 wt% MWCNTs@Ag-PPy@COOH concentration. Above all, new approaches should be developed to get permanent, efficient and multifunctional antistatic coatings. In this paper, a novel approach and conductive mechanism has been proposed. Nanoscale ionic materials with —OH groups were synthesized and used as crosslinking reagent in PU system. Finally, PU hybrid with permanent antistatic property and improved mechanical properties was got.

Supramolecular liquid has recently been introduced as a third-generation liquid materials after solvent liquids and ionic liquids [8]. Nanoscale ionic materials (NIMs), as a member of supramolecular liquid, have been accelerating the evolution of nanotechnology. The properties, such as solvent-free fluidity, nonvolatile, good thermal and tunable properties, provide significantly scientific and technological opportunities [9–14]. In 2005, Giannelis initially synthesized liquid-like nanosilica based NIMs at ambient temperature [15]. Afterwards, categories of NIMs have been diversified rapidly, either by manipulating the core (SiO_2 [16–19], γ-Fe_2O_3 [20,21], ZnO [22,23], quantum dots [24–28], proteins [29–31], carbon nanotubes [32–35], fullerene [36,37] etc.) or by changing corona and canopy [9–14,19,38,39] (cation and anion respectively). But few studies are about practical applications, so a must is needed [8]. The inorganic/organic core-shell

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structure bestows NIMs excellent dispersibility in and compatibility with polymer matrix, so it is potential to prepare novel organic/inorganic hybrids. Yang et al. produced liquid-like amino MWCNTs [40]. The liquid-like MWCNTs can be homogeneously dispersed and chemically embedded in an epoxy matrix by solvent-free processing. The molecular level coupling between MWCNTs and epoxy provided significant improvements in mechanical properties. Texter [41] et al. initially prepared a novel acrylate nanofluid. Acrylate nanofluid can polymerize with tetrahydroxyethyl pentaerythritol tetraacrylate by UV curing to give a nanocomposite. The nanofluids in resin resulted in softening rather than the conventional hardening upon forming nanocomposites using nanofillers. Texter [42] also prepared an isothiocyanate nanofluid by grafting the same fluid-inducing groups imparting fluidity and isothiocyanate groups to impart reactivity. The nanofluid was used to prepare a hybrid film. This humidity-cure films exhibited excellent physical properties, including adhesion, abrasion resistance, thermal stability, hardness, chemical and solvent resistance, and high humidity tolerance.

Generally, NIMs are obtained by grafting an oligomer shell to inorganic nanoparticle cores. Ionic liquids, polyethylene glycol, or siloxane are often employed as soft organic shell [9–14,16–32], in which electrostatic interaction, hydrogen bonding and ligand exchange play key roles [27]. Herein, we report a novel liquid-like NIM (name as NSiF-Hs, Fig. 1a) at ambient temperature and its polyurethane hybrid. Hydroxyl groups were introduced in NSiF-Hs through the amination of epoxy group. It is one of alternative routes to synthesize NIMs due to the plentiful choices of modifier. Different from the other NIMs reported before [40–42], NSiF-Hs can be used as supramolecular crosslinking agents to prepare organic-inorganic hybrid because of abundant hydroxyl groups on the grafted organic chains. NSiF-Hs exhibited excellent solubility and can be well dissolved in many solvents such as water, THF, DMF, $CHCl_3$ and small molecule alcohol, which made it potential to be used as a special reactant in hybrids. A whole new method is opened up to synthesize novel NIMs and to functionalize NIMs as well as to broaden its application. Our method to modify polyurethane is different from the conventional methods [10,14,43–45]. In our study, NSiF-Hs was directly used as reagent to prepare a novel antistatic polyurethane hybrid, it functioned as well-dispersed nanofiller and antistatic agent as well. It is versatile and applicable in potential fields for its unique properties, such as electron, medical and automobile [46,47]. It is a new method for functional NIMs and its polyurethane hybrids.

2. Experimental section

2.1. Materials

Ludox SM-30 colloidal silica aqueous (Ludox-SM, 30 wt.%, mean particle diameter: 7 nm), poly (ethylene glycol) 4-nonylphenyl 3-sulfopropyl ether potassium salt (C_9H_{19}-$(OCH_2CH_2)_{10}$-O $(CH_2)_3SO_3K$, PEG-SO_3K) were purchased from Sigma-Aldrich. 3-glycidyloxypropyl-trimethoxysilane (GPTMS, 97%) and tri-*n*-butylamine (99.5%), polytetramethylene ether glycol (PTMEG 1000), 4,4′-diphenyl methane diisocyanate (98%) were purchased from Aladdin. Other chemicals were used as received.

2.2. Preparation of NSiF-Hs

Typically, 1.67 g Ludox colloidal silica was diluted with 50 ml deionized water and sonicated at 30 °C for 1 h. Then 0.60 g GPTMS was slowly added into the above dispersion with 50 ml ethanol. The mixture was continually reacted at 70 °C for 24 h. Subsequently, 0.51 g tri-*n*-butylamine and 0.27 g hydrochloric acid were added and the mixture reacted at 70 °C for another 24 h. 3.53 g PEG-functionalized sulfonate was added and stirred at 70 °C for 24 h. The solution was removed solvent in rotary evaporator and dried in vacuum at 80 °C for 24 h. 50 ml THF was added and filtered to remove KCl precipitate. The product was dialyzed in a cellulose dialysis membrane bag (trapped molecular weight: 12000) and dried at 80 °C for 24 h.

2.3. Preparation of PU/NSiF-Hs hybrids

5.0 g PTMEG, 2.5 g MDI and 50 ml *N,N*-dimethylformamide were added into a 250 ml three-necked round bottom flask equipped with mechanical stirrer, nitrogen gas inlet and reflux condenser. The mixture reacted at 90 °C for 3 h under nitrogen atmosphere. After it cooled to the room temperature, 0.28 g ethylene glycol and different weight percentage of NSiF-Hs with 10 ml *N*, *N*-dimethylformamide were added and reacted for another 3 h. The viscous solution was casted on a glass plate and dried under vacuum at 60 °C for 12 h and 80 °C for 12 h. A transparent membrane was obtained at last.

2.4. Characterization

FT-IR spectra of all samples were collected in a FTIR spectrometer (Perkin Elmer FT-IR) in the wavenumber range 400–4000 cm^{-1} at a resolution of 1 cm^{-1} using KCl pellet. ^1H NMR spectra were measured by a Brucker 300 MHz NMR spectrophotometer at ambient temperature, $CDCl_3$ was used as solvent and TMS as internal standard. TEM was

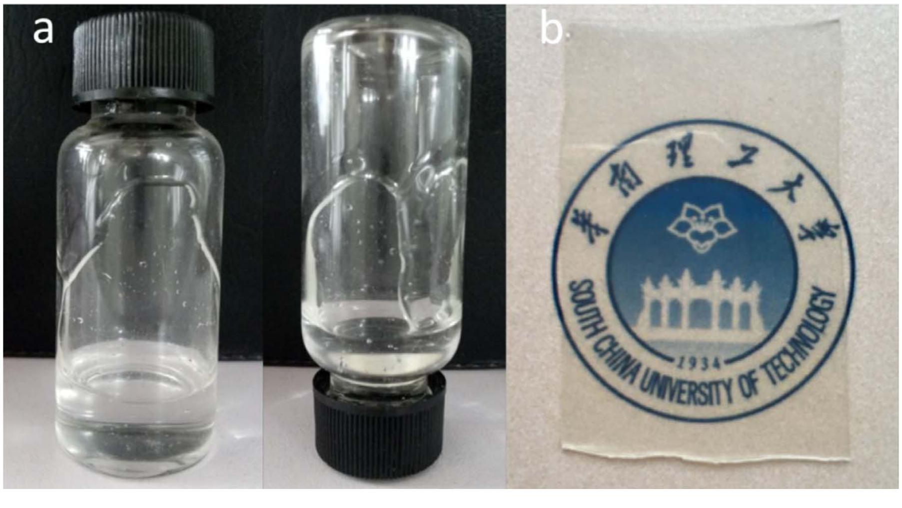

Fig. 1. (a) Macro physical state of NSiF-Hs. (b) Photograph of PU/NSiF-Hs hybrids.