



Mechanical enhancement of self-healing waterborne polyurethane by graphene oxide

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ABSTRACT

Waterborne polyurethane has been widely used in coatings and adhesives for its more environmentally friendly feature as compared with traditional solvent based polyurethanes. It is important to develop strategies to design and construct powerful waterborne polyurethane with outstanding thermal, mechanical and self-healing properties. Herein, a series of self-healing waterborne polyurethane/graphene oxide nanocomposites were prepared by solution blending method. The waterborne polyurethane/graphene oxide nanocomposites exhibited excellent dispersion stability and better thermo stability. Meanwhile, tensile strengths of the nanocomposites were 22–47% higher than that of neat waterborne polyurethane. Thus, the above results forward the synthesized waterborne polyurethane/graphene oxide nanocomposites as an eco-friendly and self-healing polymeric material with good thermal stability and mechanical property.

1. Introduction

Nowadays, waterborne polyurethane (WPU) has found wide applications in coating, adhesive, primer, paint additive, associate thickener, textiles, pigment paste, biomaterial, etc [1–4]. With the widespread application of WPU, ways to make WPU materials safer, more reliable and durable, as well as easier to maintain, have become an important topic. The incorporation of extrinsic healing agents in polymers is an effective way to extend the lifespan of materials and reduce the maintenance and replacement costs [5,6]. However, these healable agents could negatively affect the physical properties of the final product and the healing mechanism is not repeatable [7].

Work on intrinsic self-healing WPU (SHWPU) is a hot spot of research in the scientific fields. The intrinsic SHWPU have better compatibility with the bulk materials and the healing behavior is repeatable. WPU is a kind of polymer that has typical hard/soft segmental dual-component structure. The hard segment acts as a physical cross-linking point, while the soft segment provides elasticity for WPU. If the soft segment is able to significantly alter its stiffness by glass transition or melting, the polyurethane could be capable of exhibiting thermal responsive effect, which assists the self-healing behavior. Seyed et al. [8] synthesized a SHWPU that could be healed after infrared irradiation for 150 s. The healing behavior was attributed to the interplay among viscoelastic recovery response, surface-tension-driven viscoelastic restoration, and polymer diffusion. Aguirresarobe et al. [9] reported a

kind of organic-inorganic hybrid SHWPU that healed itself at room temperature. The drawback of this SHWPU was the healing procedure must be performed immediately after the film was cut off because the generated broken surface was easy to be passivated. Ye et al. [10] developed a WPU containing two types of reversible crosslinks that could reorganize after heating and finally heal the cracked WPU. But the healing temperature was high and the healing time was long. Recently, we [11] synthesized a new SHWPU containing disulfide bonds in the main chain. Disulfide bonds can undergo bond scission at elevated temperatures [12,13]. The self-healing mechanism was triggered by the chain exchange reaction of disulfide bonds and assisted by the shape memory effect to bring the crack on SHWPU surfaces in spatial proximity. The self-healing behavior of WPU could occur on a mild healing condition of 65 °C in 10 min. However, the mechanical property of the SHWPU was poor, which severely limited their possible applications in many cases.

Since the discovery of graphene, polymer/graphene nanocomposite have attracted tremendous attention [14–16]. Introduction of graphene into polymers can result in significant mechanical reinforcement owing to the exceptionally high aspect ratio and intrinsic strength of graphene. However, graphene tends to restack, aggregate and can't be dissolved in aqueous media or any other organic solvents, which make it difficult to disperse in polymer matrix and limit the application of graphene in polymer/graphene nanocomposites [17]. At present, using graphene oxide (GO) is the most adopting approach to producing

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graphene-based nanocomposites, because of its great scalability, versatility, and easy to use [18,19]. GO is a strongly oxygenated, highly hydrophilic layered material that contains multiple reactive oxygen groups, which renders it a good candidate for use in many applications, such as polymer composites, energy related materials, sensors, 'paper'-like materials, field-effect transistors and biomedical materials, due to its excellent mechanical and thermal properties [20–22]. As a two-dimensional nanomaterial, GO has been developed to design self-healing materials to enhance the mechanical property and expand the versatility of polymers [23–26]. Incorporation of GO enabled the composite with good mechanical strength, while the hydrogen bonding networks within the polymer chains provide self-healing capability [23]. These properties promote us to believe that integrating GO with SHWPU might generate new composite that have not only enhanced mechanical properties but also better self-healing property.

Herein, a series of SHWPU/GO nanocomposites were prepared. Effects of GO on the emulsion stability, mechanical, thermal and self-healing properties were investigated. This research is driven by the possibility of mechanical enhancement of the self-healing WPU, which may be the key requirement for applications in fields, such as construction, automotive and airplane wings [27].

2. Experimental

2.1. Materials

GO was provided by Chengdu Organic Chemicals Co. Ltd., Chinese Academy of Sciences. Poly(ϵ -caprolactone) glycol (PCL) ($M_n = 2000$) and Isophorone diisocyanate (IPDI) were purchased from Perstorp and Aldrich Chemical Corp, respectively. 2-bis(hydroxymethyl) propionic acid (DMPA) and 2-hydroxyethyl disulfide (HEDS) were supplied by Sigma-Aldrich. Dibutyltin dilaurate (DBTDL), triethylamine (TEA), 1-methyl-2-pyrrolidone (NMP), butanone, ethylene diamine (EDA) were obtained from Sinopharm Chemical Reagent. All reagents were used as received without further purification.

2.2. Sample preparation

The synthesis procedure of SHWPU was mentioned in our earlier publication [11]. In this work, PCL2000, IPDI and DMPA were reacted at 80 °C to form prepolymer. Then HEDS was used as chain extender at 50 °C (the mol ratio of DMPA and HEDS was 1:1). Afterwards, TEA was added to neutralize the $-COOH$ groups in DMPA, and then the polymer was emulsified by adding distilled water and stirred at a speed of 2000 r/min. The solid content of synthesized SHWPU dispersion was 26%. The number average (M_n) molecular weight of SHWPU was 42k and the polydispersity was 1.8. Aqueous GO dispersion was obtained by adding the GO powder into deionized water (the GO concentration in water was 1 mg/ml) and treating under ultrasonic for 1 h at 30 °C. Composite

dispersions were prepared by adding GO dispersion into synthesized SHWPU emulsion dropwise and stirred at a speed of 250 r/min for 3 h at 40 °C. SHWPU/GO nanocomposite films with 4 different GO contents (0.5 wt%, 1 wt%, 2 wt% and 4 wt%) were obtained by casting prepared blending dispersions on glass plates and dried in vacuum at 50 °C.

2.3. Characterization

Fourier transform infrared spectra (FTIR) of composite films were taken with a Nicolet 8700 infrared at room temperature. The spectra were recorded by averaging 32 scans at a resolution of 2 cm^{-1} from 4000 to 500 cm^{-1} . Raman spectra of composite films were conducted on a RenishawInVia Reflex confocal Raman spectrophotometer with a laser excitation wavelength of 532 nm.

Particle sizes (D_p) and Zeta potentials of the composite dispersions were measured using a Nano ZS from Malvern Instruments at room temperature.

The morphologies of the composites fracture surface were carried out on a SU8010 field emission scanning electron microscope (FE-SEM). Films were fractured under liquid nitrogen.

Tensile tests were performed on an Instron 5969 at room temperature with a cross-head speed of 200 mm/min. The size of the samples was $50\text{ mm} \times 5\text{ mm} \times 0.5\text{ mm}$. Five parallel measurements were carried out and the average value was taken.

Differential scanning calorimetry (DSC) was performed on a DSC204F1 instrument. The film samples were put into oven at around 50 °C for about 5 min to eliminate the thermal history. Then samples were frozen to -100 °C by liquid nitrogen. The measurement was scanned from -100 to 100 °C with a heating rate of 10 °C/min .

The dynamic mechanical analysis (DMA) measurements of samples were tested on a TA Q800 instrument. A rectangular sample ($25 \times 5\text{ mm}^2$) was cut from the thoroughly dried film and quenched from room temperature to -100 °C using liquid nitrogen and thereafter subjected to a heating scan at 5 °C/min under a dry nitrogen blanket to 50 °C.

Thermogravimetric (TG) analysis of sample was performed on a Discovery TGA instrument from 40 °C to 600 °C with a heating rate of 10 °C/min . Samples were heated in nitrogen atmosphere with the gas flow rate of $10\text{ cm}^3/\text{min}$.

The gap closure behavior of composite films was recorded on a BX51 polarizing microscope equipped with a heating device. Samples were scratched with a razor blade to an approximate 50% thickness and heated at 70 °C for 10 min. For more precise test, surfaces analysis tests of composite films were performed on a Veeco NT9100 Optical Profiler.

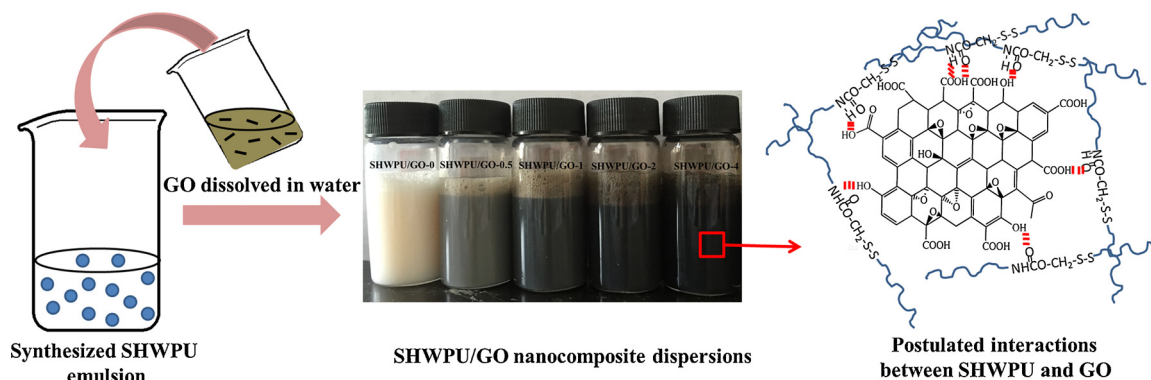


Fig. 1. Schematic illustration for the preparation of SHWPU/GO nanocomposite films.

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