



Preparation and properties of amino-functional reduced graphene oxide/waterborne polyurethane hybrid emulsions



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ABSTRACT

In this study, we provided a novel method to prepare amino-functional reduced graphene oxide/waterborne polyurethane (rGO/WPU) hybrid emulsions. Firstly, the silane-functionalized reduced graphene oxide (A-rGO) with free amine groups on its surface was prepared via the modification of GO with 3-aminopropyltriethoxysilane (APTES) and the reduction by diethanol amine (DEA). Then, the obtained A-rGO sheets were incorporated into polyurethane by in situ polymerization to prepare A-rGO/WPU hybrid emulsions. The results from Fourier transform infrared spectroscopy (FTIR), X-Ray Diffraction (XRD), thermal gravity analysis (TGA), and Raman spectra clearly indicated that APTES was grafted on the surface of GO, and GO was reduced by DEA. With the increase of A-rGO content, the glass transition temperature, mechanical property, storage modulus, and thermal stability of A-rGO/WPU films increased gradually due to the homogeneous dispersion of A-rGO sheets in the WPU matrix and the strong covalent interaction between A-rGO sheets and WPU matrix. When the content of A-rGO sheets was 0.5 wt%, the A-rGO sheets could homogeneously dispersed in the WPU matrix, and the A-rGO/WPU films exhibited excellent overall performance.

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1. Introduction

As the versatile environmentally friendly materials, waterborne polyurethanes (WPU) have gained increasing interest in a broad range of applications owing to their excellent elasticity, abrasion resistance, flexibility, and broad substrate suitability [1–4]. For instance, WPUs have been widely used as coatings, adhesives and inks. In the field of the flexible packaging printing ink, the WPU as a binder can offer an efficient alternative to the solvent-based polyurethane binder, which is still widely used in the market.

However, most WPUs are linear thermoplastic polymers and some properties of WPUs, such as water resistance, thermostability and mechanical property, are inferior to that of solvent-based polyurethanes [5,6]. In recent years, some approaches have been given to improve the properties of WPUs. The common method is to synthesize crosslinkable WPUs [7], waterborne polyurethane-acrylate (PUA) dispersions [8,9], organic silicone-modified WPUs

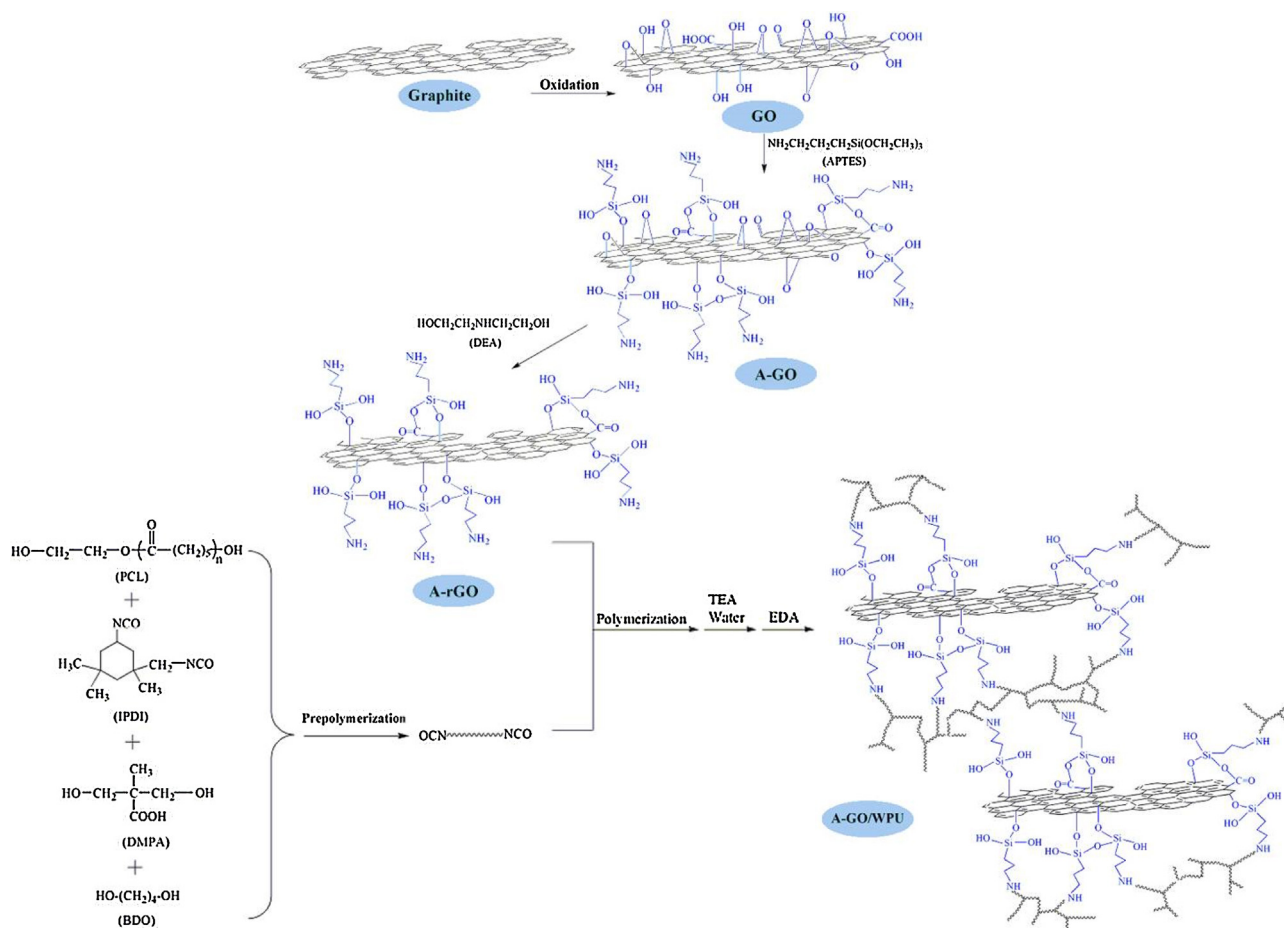
[10–12], organic fluorine-modified WPUs [13], and inorganic nanoparticles/WPU composites [14–16], etc.

Graphene, a single layer of sp^2 -bonded carbon atoms in a two-dimensional honeycomb lattice, has high stiffness, electrical conductivity, and thermal stability. The use of graphene as fillers in the preparation of graphene/polymer composites has attracted an increasing interest owing to their excellent mechanical property and thermostability, etc. The properties of graphene/polymer composites depend greatly on the dispersion level of graphene and the interfacial interaction between graphene and the polymer matrix [17]. However, the dispersibility of pristine graphene in most polymers is poor. In order to solve this issue, various methods have been used to modify the surface properties of graphene to improve the dispersibility of graphene and the interfacial interaction between graphene and polymer matrix, includes covalent and non-covalent bonding functionalization. Compared with the non-covalent functionalization, the covalent functionalization is usually more effective, because the modified graphene is stable and the produced strong interfacial bond is necessary for efficient load transfer from polymer matrix to graphene.

The surface of graphene oxide (GO) sheet has a large number of reactive groups, such as hydroxyl, carboxyl, epoxide and carbonyl, etc. The graphene is usually functionalized by the

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Scheme 1. Schematic illustration of the synthesis process of A-rGO and A-rGO/WPU emulsions.

functionalization and reduction of graphene oxide (GO). Organic amines [18], isocyanates [19], azide compounds [20], and organosilane compounds [21–23] have been used for the covalent modification of graphene oxide. Then the resulting modified graphene oxide is reduced by reducing agents such as hydrazine hydrate [24], sodium borohydride [25], hydroquinone [26], hydroiodic acid [27], potassium hydroxide [28], etc.

Recently, many researchers have engaged in the preparation and characterization of graphene/waterborne polyurethane composites. Lee et al. [29] prepared the functionalized graphene sheets (FGS)/waterborne polyurethane (WPU) composites by an in situ method, and the modulus improvement of composites was more evident than that of composites prepared by a physical mixing method. Wang et al. [16] used 3-aminopropyltriethoxysilane (APTES) to covalently modify GO using *N,N'*-dicyclohexylcarbodiimide (DCC) as a catalyst under 70 °C for 24 h, and obtained APTES-functionalized graphene (f-GNS) with free alkoxy groups, which was then mixed with APTES-terminated polyurethane prepolymer to obtain f-GNS/WPU composites by the sol-gel method. The tensile strength and Young's modulus of WPU with 2.0 wt% functionalized graphene increased by 71% and 86%, respectively, because of the homogeneous dispersion of functionalized graphene in the polymer matrix and strong interfacial interactions between the two components.

In this work, we provided a novel method to prepare reduced graphene oxide/waterborne polyurethane (rGO/WPU) hybrid emulsions. Firstly, we prepared graphene oxide (GO) by the modified Hummers method, and then functionalized the GO with 3-aminopropyltriethoxysilane (APTES) to prepare the GO with free

amine groups (A-GO) via the condensation between the hydroxyl on the surface of GO and the Si–OH groups produced by the hydrolysis of APTES. The A-GO was subsequently reduced by the reducing agent diethanolamine (DEA) and thereby the reduced graphene oxide (A-rGO) containing free amine groups was obtained. At last, A-rGO was covalently incorporated into the PU via the reaction between the free amine groups of A-rGO and the isocyanate groups of PU prepolymer to prepare the A-rGO/WPU hybrid emulsions by in situ polymerization. The A-rGO sheets with free amine groups could act as a multifunctional crosslinker and a traditional reinforcing filler. Various analytical techniques, such as, Raman spectra, XRD, DSC, SEM, DMA, TGA, and mechanical test were used to characterize the A-rGO sheets and A-rGO/WPU hybrid emulsions. The effects of the A-rGO content on the thermal stability and mechanical properties of A-rGO/WPU films were also investigated.

2. Experimental

2.1. Materials

Polycaprolactone diol (PCL, 2000 g/mol, Daicel, Japan) was dried at 120 °C under vacuum for 2 h to remove residual water. 2,2-Dimethylolpropionic acid (DMPA, Nippon Kasei Chemical Co.) was dried at 50 °C for 48 h in a vacuum oven. Isophorone diisocyanate (IPDI, Bayer) was used as received. 1-methyl-2-pyrrolidinone (NMP, Fuchen, Tianjin), triethylamine (TEA, Lingfeng, Shanghai), 1,4-butanediol (BDO, Kermel, Tianjin), ethylene diamine (EDA, Lingfeng, Shanghai) and diethanol amine (DEA, Lingfeng, Shanghai) were dried over a 4A molecular sieve before use.

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