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The utilization of carbon nitride to reinforce the mechanical and thermal properties of UV-curable waterborne polyurethane acrylate coatings

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ABSTRACT

The waterborne polyurethane-acrylate (WPUA and Wsi-PUA) oligomers were prepared by anionic self-emulsifying method, using isophorone diisocyanate (IPDI), polyethylene glycol (PEG), dimethylol propionic acid (DMPA), vinyl hydroxyl silicone oil (VHSO) and hydroxyethyl methyl acrylate (HEMA) as raw materials. Then, a series of UV-curable waterborne Wsi-PUA–C_3N_4 composites containing different content of g-C_3N_4 were obtained with oligomer and photoinitiator Darocur 1173. FTIR, XRD, TEM, SEM, and TGA were employed to investigate the structure, morphology and thermal property of the Wsi-PUA–C_3N_4 composite films. The effect of g-C_3N_4 content on the performance was also investigated. The mechanical performance, water resistance and gel content of UV-PUA films were measured. It was found that with g-C_3N_4 particle was introduced into Wsi-PUA oligomer, the hardness, tensile strength, gel content, water resistance and thermal stability of composite films were significantly augmented. Moreover, when the content of g-C_3N_4 was 1.0 wt.%, the UV-curable film had the best mechanical property. The obtained composite is promising for a number of applications, e.g., for protecting the surfaces of metal and wood.

1. Introduction

In recent years, waterborne coatings using ultraviolet (UV)-curing technology have gained increasing interest due to the advantages of their environmental safety, high cure speed, high efficiency, solvent-free formulation, low energy consumption and enhanced performance [1–4]. Waterborne polyurethane-acrylate (WPUA), a unique kind of polymer, can obtain various properties and enhanced performance resulted from its specific segmented structure. And it can be satisfactorily applied in coatings for wood, automobiles, leather, printing inks and so on [5,6]. However, the poor thermal stability and low tensile strength of UV-cured PUA coating probably limit its engineering applications in some fields. It is thereby essential to fabricate modified PUA composite with enhanced thermal and mechanical properties to broaden its applications.

Hybrid materials with inorganic and organic components attract more and more attention because of their improved properties. To reinforce the polymer with nanosized inorganic particle is an effective way to improve the property of polymer [7]. Such composite materials display outstanding properties and can be widely applied in systems ranging from electronic devices to biosensors and medicine. Therefore, the field of polymer-based nanocomposite materials has attracted great attention. In recent years, varies of nanoparticles, including silica nanoparticles [8–10], alumina particles [11], clay [12], montmorillonites [13], boehmites [14,15], layered silicate [16], ZnO [17], TiO_2 [18] and layered double hydroxide [19], have been studied and introduced into the UV-curing system and the composites consequently display improved properties. Also, most studies have been based on how to enhance the chemical and physical interaction between organic polymer and inorganic material. Graphitic carbon nitride (g-C_3N_4), a class of two-dimensional layered material, has attracted considerable

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attention because of its chemical inertness, excellent thermal stability, abrasive resistance and high hardness, which is a promising candidate to complement amorphous carbon and graphite carbon in material applications. In recent years, g-C_3N_4 has been widely used as carrier in many catalytic areas, especially for oxygen reduction reaction [20–22], however, g-C_3N_4 is stable and shows negligible photocatalytic activity [20–22]. In addition, to the best of our knowledge, no published reports are available regarding the effect of g-C_3N_4 on the mechanical and thermal properties of WPUA.

In this study, the WPUA and Wsi-PUA oligomer were prepared by anionic self-emulsifying method, using isophorone diisocyanate (IPDI), polyethylene glycol (PEG), dimethylol propionic acid (DMPA), hydroxyethyl methyl acrylate (HEMA) and vinyl hydroxyl silicone oil as raw materials. Subsequently, g-C_3N_4 particles were introduced into the chains of amorphous Wsi-PUA to prepare Wsi-PUA–C_3N_4 composite coatings. The g-C_3N_4 particles were expected to be multifunctional cross-links as well as reinforcing fillers, and the effect of g-C_3N_4 content on performance had been examined in various ways.

2. Experimental

2.1. Materials

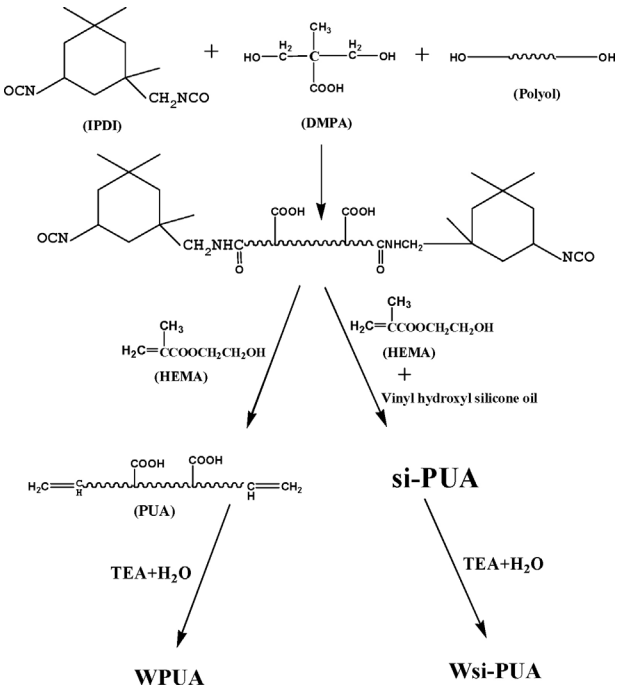
Isophorone diisocyanate (IPDI), 2-hydroxyethyl acrylate (HEA), polyethylene glycol (PEG), dimethylol propionic acid (DMPA), hydroxyethyl methyl acrylate (HEMA), 1,6-hexanediol diacrylate (HDDA) and vinyl hydroxyl silicone oil (VHSO) were purchased from ChengDu XiYa Chemical Co. Ltd. Acetone, anhydrous ethanol and *N*,*N*-dimethylformamide (DMF) were purchased from Guangzhou Chemical Company in China; triethylamine (TEA), benzophenone (BP) and 2-hydroxy-2methylpropiophenone (Darocur-1173) were purchased from Aladdin in China.

2.2. Preparation of g-C_3N_4

The g-C_3N_4 was synthesized by simple calcination of melamine powder [23,24]. First, a certain amount of the melamine power was put into a semi-closed alumina crucible with a cover. The crucible was heated to 250 °C for 1 h, 350 for 2 h and 550 °C for 2 h, successively, at a heating rate of 2 °C min^{-1}. After cooling to room temperature, the obtained yellow sample was grinded into powder and dried at 85 °C for 48 h, and then was gathered with 300 mesh sieve. The g-C_3N_4 was obtained.

2.3. Preparation of Wsi-PUA and Wsi-PUA–C_3N_4 composite coatings

The basic formulation and preparation procedure were given in Table 1 and Scheme 1, respectively. 15.5 g IPDI was charged into a 250 mL round-bottom four-necked flask with a mechanical stirrer, thermometer, condenser and nitrogen in/outlet. 10.5 g PEG 600, 2.85 g hydrophilic monomer (DMPA) and 4 drops of DBTDL were added dropwise and reacted at 70 °C for 3.5 h. The isocyanate (NCO) content was monitored during the reaction using the standard dibutylamine back-titration method. Upon reaching the theoretical NCO value, 2.5 g HEMA, 0.5 g vinyl hydroxyl silicone oil (VHSO) and 0.6 g of the inhibitor hydroquinone were added to react at 75 °C for 2.5 h. After the reaction mixture was cooled to room temperature, 2.15 g TEA was added into the reactor for 1 h thorough mixing to secure 100% neutralization. Then, deionized water was fed and reacted with prepolymer at 40 °C for 1 h. Finally, acetone in the Wsi-PUA dispersion was removed through distillation by



Scheme 1. Synthesis routes of the WPUA and Wsi-PUA samples.

pressure reduction at 50 °C. The resulting Wsi-PUA product was obtained.

Different amounts of g-C_3N_4 (0.25 to 2.0 wt.%) were introduced into the liquid monomer Wsi-PUA and dispersed by ultrasound for 8 h at room temperature.

3.0 wt.% of the photoinitiator was added into the obtained mixture and the composite was coated onto tinplate substrates. The coatings were then exposed to a medium pressure mercury lamp (1 kW, Fusion UV systems, USA) with the band conveyer speed of 2.0 m·min^{-1}. The resulting UV-curable Wsi-PUA–C_3N_4 composite coatings were obtained (Fig. 1).

2.4. Characterization

Fourier transform infrared spectrometer (FTIR) spectra between 500 and 4000 cm^{-1} were obtained on a Nicolet 6700 spectrometer (USA). X-ray diffraction (XRD) patterns were recorded on a D/max-1200 diffractometer (China) using graphite monochromatic Cu K_α radiation (λ = 0.1541 nm) at a generator voltage of 40 kV and a current of 40 mA; measurements were conducted within a 2θ range of 5.0–70.0° at a scanning rate of 6°/min. Scanning electronic microscope (SEM) was performed on JSM-6330F (Germany) scanning electron microscope with an accelerating voltage of 20.0 kV; the fracture surfaces of samples were coated with a thin layer of gold before analysis. The thermogravimetric analysis (TGA) was performed on a Netzsch TG 209 thermoanalyzer (Germany); the temperature range of the measurement was 50–800 °C and the heating rate was 10 °C min^{-1}.

The tension properties were inspected by using a tensile tester (LLOYD LR100K, China) at a cross-head speed of 500 mm min^{-1} and a temperature of 25 °C. The hybrid films were painted on the tinplate substrates for pencil hardness test by using a QHQ-A pencil hardness apparatus (Tianjin Instrument Co., China). Five samples of each category were tested and their average values were reported.

The composite films were cut into 2 cm × 2 cm to determine their weight (W_0). Then, the sample was put into a solvent (xylene)