



Bio-based waterborne polyurethane/carbon dot nanocomposite as a surface coating material



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ABSTRACT

Waterborne surface coating materials with low volatile organic compounds (VOCs) are environmentally friendly and hence the most desired materials for the modern society. The present study reports *in situ* fabricated thermosetting hyperbranched waterborne polyurethane (WPU)/carbon dot (CD) nanocomposites as surface coating materials. CD was used as a nanoreinforcing agent (at 0.25, 0.5 and 1.0 weight percentages) in the nanocomposites. The structures of the waterborne polyurethane and its fabricated thermosetting nanocomposites were analyzed by using different spectroscopic and analytical tools like Fourier transform infrared spectroscopy, nuclear magnetic resonance spectroscopy, UV–visible spectroscopy and X-ray diffractometry. The mechanical properties of the pristine thermosetting WPU were significantly improved after incorporation of CD (tensile strength from 4.5 to 8.5 MPa, elongation at break value from 96 to 136%, scratch hardness from 3 to 9 kg, impact strength from 70 to 100 cm). The thermal stability of WPU also enhanced from 250 to 280 °C after incorporation of CD in the matrix. Interestingly, the fabricated nanocomposites demonstrated an excitation wavelength and concentration dependent photoluminescence behavior as well as exhibited good transparency. Thus, the fabricated WPU nanocomposites show great potential as low VOC containing environment friendly transparent surface coating material.

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1. Introduction

Amongst all the polymers, polyurethane (PU) is one of the most important and versatile polymers. It is obtained by the rearrangement reaction between di/poly isocyanates and di/polyol compounds [1,2]. The promising feature of PU is that its properties can be tailor-made by varying its compositions, structures of raw materials and NCO/OH ratio [3,4]. In this context, hyperbranched polyurethane (HPU) is attracted much attention due to its several advantages such as low viscosity, high solubility *etc.* As a result, its processing is much easier than its linear counterpart [5]. However, such conventional solvent based PU possesses some serious problems such as high volatile organic compound content (VOC), flammability, toxicity *etc.* These problems can be effectively addressed by waterborne PUs (WPUs) which are binary colloidal system where stabilizing group containing PU particles dispersed in water medium. Generally, WPUs are prepared by reacting less reactive diisocyanate, polyol and ion generating dihydroxy acid such as 2, 2-bis(hydroxymethyl)propionic acid [6]. WPUs exhibit

some advantages other than the above mentioned issues such as cost effectiveness and eco-friendly nature [7,8]. In spite of aforementioned advantages, WPUs also associate with some serious short comings like inferior mechanical property due to the presence of hydrophilic ionic groups or water soluble segments [9]. They are also moisture and other chemical environments sensitive. This causes inferior mechanical properties, thermal stability and poor chemical resistance as compared to solvent borne counterpart.

However, modifications like blending, creating a cross linking reaction or forming an interpenetrating network could be an option to improve the material properties of WPUs [10]. In addition to this, nanotechnology based strategy in the form of polymeric nanocomposite can effectively tackle the problem associate with WPUs. A numerous WPU nanocomposites are found in literature that exhibit dramatic enhancement in mechanical properties after incorporation of minute amount of nanofillers [11–16]. Different types of nano fillers like graphene oxides, zinc oxide, silver nanoparticles, nanoclay, functionalized carbon nanotubes, *etc.* are used for the fabrication of nanocomposites [17–20]. Various bio-nanofillers have also been utilized in this endeavor [13,21,22]. The improvement in properties of nanocomposites relies on the facts such as optimized dispersion, interfacial interactions and nanoscale morphology [23]. Among the genre of nanofillers,

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carbon based nanomaterial are engraved a distinct niche due to their high aspect ratio, high mechanical and thermal properties [14–16]. Even though this kind of carbon nanomaterials possesses such excellent properties, but they also suffer from some inadequacy such as agglomeration particularly at high dose level due to lack of proper functionality and inherent inertness. In this context, carbon dot (CD) is attracted the interest of material scientists in recent times due to its high aqueous solubility, facile modification, tunable fluorescence emissions, cheap production and excellent biological properties like good biocompatibility etc. [24–26]. Thus, fabrication of WPU/CD nanocomposite is a good choice for this purpose. Therefore, current study reports preparation of thermosetting WPU/CD nanocomposites by incorporating different weight% of CD following an *in situ* polymerization technique. A glycerol based polyester polyol has been utilized successfully for the development of hyperbranched polyurethane architecture. Thermosetting version of the polyurethane was obtained by curing with diglycidyl ether based epoxy and fatty acid based poly(amido amine). The mechanical, thermal and optical properties of the thermosetting nanocomposites were delved into for its utility as environmentally friendly low VOC surface coating material. Use of glycerol based polymer, fatty acid based poly(amido amine) and bio-based nanomaterial to fabricate a novel polymeric nanocomposite also justifies its bio-based attribute.

2. Experimental

2.1. Materials

Isophorone diisocyanate (IPDI, Aldrich, Germany), triethylamine (TEA, Merck, India) and quinine sulfate (Sigma-Aldrich, Germany) were used as received. Poly(ethylene glycol) with $M_n = 600$ and $M_n = 200$ (PEG-600, and PEG-200 Merck, India), butane diol (BD, Merck, India), 2,2-bis(hydroxymethyl)propionic acid (BMPA, Aldrich, Germany), glycerol (Merck, India) and maleic anhydride (MA, Merck, India) were kept in a vacuum oven at 60 °C for 6 h prior to use. Then it was kept in a vacuum desiccator for overnight. Banana (*Musa acuminata*) was purchased from local market of Tezpur, Assam, India. Epoxy resin like Araldite (Petro Araldite Pvt Ltd, India) and hardener like poly(amido amine) (PAA, Aradur of Petro Araldite Pvt Ltd, India) were also used as received. Epoxy resin and PAA were used for curing of WPU. Tetrahydrofuran (THF, Merck, India,) was used after distillation.

2.2. Preparation of CD

CD was prepared from banana juice by following the procedure described elsewhere [24]. Briefly, pulp free banana juice was heated at 150 °C for 4 h with ethanol. The dark brown product obtained was filtered and the filtrate was centrifuged with ethanol to separate the large particles. CD was obtained in a semi solid form after drying under reduced pressure.

2.3. Fabrication of WPU/CD nanocomposite

WPU/CD nanocomposites were prepared by using an *in situ* pre-polymer process. In the first step required amount of IPDI (4.44 g), PEG 600 (4.8 g) and BMPA (0.7102 g) (—NCO to —OH ratio is 1.5) were taken into a three neck 100 mL round bottom flask equipped with a nitrogen inlet, a mechanical stirrer and a thermometer. The reaction was carried out at 80–85 °C for 2 h under constant mechanical agitation under nitrogen atmosphere. The reaction mass became highly viscous and white in color. It was cooled down to room temperature. Then 0.5 g of the polyol and 0.2 g of BD were dissolved in 15 mL of THF and this solution was added into the reaction (NCO/OH ratio was equal to one) mixture.

The reaction was carried out at 65–70 °C for another 3.5 h. In the last step, CD was introduced into the reaction and it was further heated at the same temperature for another 1.5 h. TEA was then added drop wise to neutralize —COOH groups at room temperature followed by addition of water slowly. THF was recovered under reduced pressure. WPU nanocomposite was mixed with epoxy (30 wt%) and PAA (15 wt%) by using mechanical stirring. Then the mixture was ultrasonicated to obtain a uniform homogeneous dispersion. This was cured at 100 °C for 45 min after degassing under vacuum to obtain the desired thermosetting nanocomposite. CD was incorporated into WPU matrix in 0.25, 0.5 and 1.0 wt% separately by following the same procedure and coded as PNC0.25, PNC0.5, PNC1.0, respectively. A pristine thermosetting WPU was also prepared by the same method without using CD.

2.4. Instruments and methods

FTIR spectra were recorded in a Nicolet FTIR spectrophotometer (Impact-410 Madison, USA) using KBr pellet. The ^1H NMR spectrum of WPU was recorded with 400 MHz, Joel, Japan NMR spectrometer by using d_8 -THF as the solvent and trimethyl silane as the internal standard. UV visible spectra were recorded at room temperature (25 °C) using a Hitachi spectrophotometer (U2001, Japan). Photoluminescence (PL) behavior was studied by using a PerkinElmer fluorescence spectrometer. The scratch hardness was carried out by scratch hardness tester (Sheen Instrument Ltd, UK) and impact strength by impact tester (S.C. Dey Co., Kolkata) of the cured film. Universal testing machine (UTM, Zwick Z010, Germany) equipped with a 500 N load cell operated at a crosshead speed of 50 mm/min was used to measure the tensile strength and elongation at break value. Gloss of the films was measured by mini gloss meter (Sheen Instruments Ltd, UK) at an incident angle 60°. The thermal degradation behavior of WPU and nanocomposite films was studied by thermo gravimetric analysis (TGA) in a PerkinElmer, TGA-4000 thermal instrument using nitrogen flow rate of 30 mL/min and at the heat rate of 10 °C/min from room temperature to 700 °C. The crystallinity pattern was studied by X-ray diffraction technique (XRD) at room temperature on a Rigaku X-ray diffractometer (Miniflex, UK) in the range of 2–70°.

3. Results and discussion

3.1. Synthesis of polyester polyol

Polyester polyol was prepared by a two steps process. In the first step PEG 200 and MA (1:2 molar ratio) were reacted at 150 °C for 2.5 h in a three necked glass reactor equipped with a mechanical stirrer. In the second step, glycerol is added and reaction was carried out for 3 h at 160 °C. *p*-Toluene sulphonic acid was used as catalyst. The synthesized polyester polyol was characterized by FTIR and ^1H NMR spectroscopy.

FTIR data (cm^{-1}): 3400 (O—H stretching frequency), 2950 (—C—H stretching frequency), 1719 (—C=O stretching frequency), 1604 (C=C stretching frequency), 1172 (C—O stretching frequency).

^1H NMR data (ppm): δ 6.6–6.8 (H—C=C—H olefinic protons), δ 7.8 (—O—H hydroxyl proton), δ 4.3 (—CH₂—O—C=O), δ 3.4 (—CH₂—O—H), 1.3–2.5 (—CH₂—).

3.2. Preparation of WPU/CD nanocomposites

CD was prepared by heating pulp free banana juice at 150 °C for 4 h with ethanol. CD was obtained in a semisolid form. TEM image depicted in Fig. 1a reveals pseudo spherical morphology having dimension in between 4.15 and 6.60 nm range. Thermosetting WPU/CD nanocomposites were fabricated by *in situ* polymerization technique by using CD as shown in Scheme 1. CD contains various

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