



Dual-functional photoinitiators and photo-grafting of cotton cellulose nanowhiskers



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ABSTRACT

Novel dual-functional photoinitiators (DFP) of cotton cellulose nanowhiskers (CNW) were prepared and photo-grafted onto macromolecular networks by photolysis and photopolymerization. DFP were prepared with incorporating a fragmental photoinitiator, 2-hydroxyl-2-methyl-1-phenyl-1-propanone, onto isophorone diisocyanate modified CNW. Characterizations were conducted to verify the feasibility of the synthesis by Fourier transform infrared spectroscopy, X-ray photoelectron spectroscopy, nuclear magnetic resonance spectroscopy, and X-ray powder diffraction, respectively. Thermal stability was investigated by thermogravimetric analysis. The photopolymerization kinetics of DFP in polyurethane acrylate (PUA) oligomers were investigated by real time Fourier transform infrared and UV–vis spectroscopy. Scanning electron microscope was performed to study the fracture surfaces of UV-cured PUA films. The mechanical properties of PUA/DFP films were studied, exhibiting that 5 wt.% DFP significantly reinforced elongation at break of PUA matrix by 80%. It was found that DFP could simultaneously effectively initiate the photopolymerization and photo-graft CNW onto UV-cured PUA networks.

1. Introduction

Cellulose is the most important and abundant biopolymer in nature from plants, bacteria, marine animals etc. Cellulose nanowhiskers (CNW) with highly ordered crystalline regions can be obtained from natural cellulose (Bondeson et al., 2006; Moon et al., 2011), which have features of high aspect ratio, good aqueous stability, high specific strength and stiffness, environmental sustainability, and biodegradability etc. (Bondeson et al., 2006; Ye and Yang, 2015). Meanwhile, sufficient surface –OH groups facilitate a chemical grafting feature to achieve excellent structures and functions of CNW derivatives. Therefore, it is theoretically feasible to connect cellulose with photoinitiator to be a macrophotoinitiator by the –OH groups. In fact, cellulose has been investigated to be a raw material for macrophotoinitiators (Mezger and Cantow, 1984; Mezger and Cantow, 1983).

The technology of UV-curing or photopolymerization has expanded rapidly resulting from its excellent features: quick curing, energy efficiency and generally cost-effectiveness etc. (Lalevée and Fouassier, 2015; Nakamura, 2014; Tiwari and Polykarpov, 2015). It has found pervasive applications for UV-curable chemicals and oligomers used in coatings, printing inks, adhesives, composite materials, dental restora-

tive formulations, 3D-printing raw materials etc. (Chen et al., 2016; Lalevée and Fouassier, 2015; Nakamura, 2014; Tiwari and Polykarpov, 2015). Among them, the photoinitiator is one of the most important components of UV-curing formulations (Fouassier and Lalevée, 2012). For the free radicals of photoinitiators (type I) after the photolysis cleavage (Fouassier and Lalevée, 2012), generally, these photolysis fragments are supposed to be three portions. The first portion of the trapped radicals is surrounded by immobile polymer chains and unable to react furtherly (Anseth et al., 1996; Kurdikar and Peppas, 1994). The second portion of the radicals is attached onto cross-linked polymer chains (Decker, 1996). The third portion of the free radicals is not attached onto the UV-cured network. However, both photoinitiators and the fragments of photolysis lead to chemical odor and migration, which are dangerous to both environment and people. Then, macrophotoinitiators are synthesized and investigated to reduce these problems of low molecular photoinitiators (Corrales et al., 2003). Therefore, this investigation intended to combine cellulose nanowhiskers and a fragmental photoinitiator to be a novel macrophotoinitiator.

UV-curing polymeric nanocomposites are desired to obtain extra functional properties (Decker et al., 2005; Sangermano et al., 2007). Sylvain Galland et al. study a photopolymerizable hyperbranched

Abbreviations: 1173, 2-hydroxyl-2-methyl-1-phenyl-1-propanone; CNW, cellulose nanowhiskers; DBTDL, dibutyltin dilaurate; DFP, dual-functional photoinitiators; IPDI, isophorone diisocyanate; PUA, polyurethane acrylate

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acrylate matrix with an additive of 10–60 vol.% cellulose nanofibers (Galland et al., 2014), leading to an improvement in oxygen barrier and thermomechanical properties. Alireza Kaboorani et al. investigate the UV-curable wood coatings with cellulose nanocrystal modified by a cationic surfactant (Kaboorani et al., 2016), with which the barrier and optical properties of the UV-cured nanocomposite coatings are improved.

Instead of physical adding cellulose nanofiber or nanocrystals into the UV-curing polymeric matrix (Galland et al., 2014; Kaboorani et al., 2016; Vardanyan et al., 2014), a novel method was investigated with chemical grafting CNW onto UV-cured macromolecules by photolysis of dual-functional photoinitiators (DFP), which were functioned simultaneously as a photoinitiator and a nanocomposite additive. The CNW were photo-grafted onto the UV-cured polymeric films with the photolysis radicals.

2. Material and methods

2.1. Main materials

Absorbent cotton (95% cellulose content and a degree of polymerization of 1300 or so), chemically pure 98% concentrated sulfuric acid, dibutyltin dilaurate (DBTDL), phosphotungstic acid, sodium hydroxide and anhydrous acetone were bought from Tianjin Kermel chemical reagent Co. Ltd. Industrially pure isophorone diisocyanate (IPDI) and 2-hydroxy-2-methylpropiop-henone (Darocur 1173) of were obtained from BASF SE (Germany). The waterborne polyurethane acrylate (PUA) oligomers were synthesized in our lab according to the acetone procedure (Deng and Ye, 2016).

2.2. Synthesis of CNW grafted 1173

CNW suspension (1.4 wt.%) was prepared by the acid-catalyzed hydrolysis of cotton cellulose following a published procedure (Oliveira et al., 2016; Rahbar Shamskar et al., 2016; Wu et al., 2013; Ye and Yang, 2015). The viscosity-average molecular weight of CNW was measured via the Ubbelohde viscosity method to be 128, which was calculated from the formulation $[\eta] = K[M]^\alpha$ (Ye and Farriol, 2005). About 20 g suspension of CNW was freeze-dried to obtain pure CNW. 20 ml acetone was added into the pure CNW. Then, they were transferred into a 100-ml conical flask with a stopper to be eventually sonicated and dispersed with an ultrasound machine for 30 min at room temperature. Two grams IPDI and 0.02 g DBTDL as the catalyst were added into the CNW's acetone suspension, reacted under water-bathing thermostatic shaker at 40 °C for 3 h. Then 1.5 g photoinitiators 1173 were added into them and reacted at 60 °C for 4 h. After the last reaction was finished, those unreacted materials and some by-product were washed out with acetone and centrifuged for several times at 6000 rpm till there was no 1173 absorption peak at 245 nm in the effluent characterized by a UV-vis spectrophotometer. The purified products, DFP, were white solid powders after drying in a vacuum drying oven at 60 °C for 24 h.

The physical adsorption experiment was carried out with 1173 and CNW using the same temperatures and reaction time as those of preparing DFP in order to obtain CNW/1173 adsorbates.

2.3. Preparation of PUA films

UV-cured PUA oligomers were synthesized in our lab (Deng and Ye, 2016), which were consisted of IPDI in the hard segment and polyethylene glycol 1000 (PEG 1000) in the soft segment. The isocyanate end groups of the PU oligomers, –NCO, were reacted with 2-hydroxyethyl acrylate (HEA) to provide two acrylate functional groups at the ends of the PUA macromolecules. The UV-cured PUA films were prepared by blending PUA mentioned above with DFP in the respective concentration of 1 wt%, 3 wt% and 5 wt%. While serving as

reference, pure PUA film was prepared by mixing 3 wt% 1173 with PUA, and PUA/CNW film was obtained by mixing 3 wt% 1173 and 1 wt % CNW with PUA. Then, these mixed coatings of different formulations were coated on substrate with the film thickness of 40 μm and UV-cured under a high-pressure mercury lamp (1000 W; BLTUV, Dongguan Ergu Optoelectronics Technology Co. Ltd., China).

2.4. Photopolymerization

2.4.1. Real time FT-IR measurement

The free radical photopolymerization of DFP in UV-curable PUA oligomers was conducted in real-time infrared spectroscopy by monitoring the decrease upon UV irradiation of the peak at 810 cm⁻¹ of the acrylate double bond. UV irradiation was provided from LT-UVA UV-LED curing instrument (365 nm, Zhuozhou Lantian Co., China). In one set of experiments, the formulations were coated onto KBr plates in the usual way. The infrared spectrum of the non-irradiated material was recorded and then the wet film subjected to UV irradiation. After UV-curing, the IR spectra of the films were obtained. The percentage of conversions and the polymerization rates can be calculated by the following Eqs. (1) and (2) (Aguirre-Soto et al., 2015; Decker and Moussa, 1989). Thus, conversion-time curves were plotted for photopolymerization reactions occurring within seconds.

$$\alpha = \frac{A_0 - A_t}{A_0} \quad (1)$$

$$R_p = \frac{A_0 - A_t}{A_0 \Delta t} \quad (2)$$

Where A_0 and A_t represent the original FT-IR 810 cm⁻¹ C=C double bond peak area at time zero and at time t , respectively, Δt represents the accumulated UV irradiation time, α is the conversion, and R_p is the rate of photopolymerization (Decker, 2002; Decker and Moussa, 1988; Decker and Moussa, 1989).

2.4.2. Steady state photolysis measurement

The acetonitrile suspension of DFP was put into a 1 cm quartz cuvette with a cover slip to prevent evaporation. Subsequently, the irradiation was carried out under UV-LED irradiation of 365 nm with an intensity of 80 mW/cm². The light exposure time intervals were set at appropriate ranges for different samples, depending on the rate of photolysis. Then, the UV spectra of different exposure time were recorded by spectrophotometer. The photolysis reaction order can be evaluated through the profile of absorption versus exposure time. Therefore, photolysis reaction order can be defined as follows:

$$\frac{d[\text{DFP}]}{dt} = k_p [\text{DFP}]^n \quad (3)$$

Where $[\text{DFP}]$ is the concentration of DFP, k_p is photolysis reaction constant, n is the photolysis reaction order.

2.5. Characterization

Fourier transform infrared spectroscopy (FT-IR) spectra were recorded on a VERTEX 33 spectrophotometer (Bruker Instrument Co., Germany) with 64 scans and signal-averaged resolution of 2 cm⁻¹ at room temperature. Samples were prepared by dispersing the sample powders in KBr powders and compressed the mixtures to form disks.

X-ray photoelectron spectroscopy (XPS) measurements were conducted with the instrument Axis Ultra DLD apparatus (Kratos Ltd. Co., UK) equipped with a nonmonochromated Al K α X-ray source (1486.6 eV) and operated at 15 kV under a current of 5 mA. Samples were placed in an ultrahigh vacuum chamber (5×10^{-9} torr) with electron collection by a hemispherical analyzer at the angle of 90°.

X-ray diffraction (XRD) measurements were performed at room temperature with Cu K α X-rays with D8 Advance (Germany, Bruker) to

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