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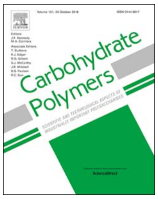

Fabrication of UV-absorbent cellulose-rosin based thermoplastic elastomer via “graft from” ATRP

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ABSTRACT

Cellulose-rosin based thermoplastic elastomers with UV absorption properties were fabricated by a combination of rosin, poly(butyl acrylate) (PBA) and ethyl cellulose (EC) via “graft from” ATRP with the aid of EC-rosin macroinitiator (EC-*g*-(DA)-Br) prepared by a simple esterification reaction between EC, dehydroabietic acid (DA, one of rosin’s resin acids) and 2-bromoisobutylryl bromide. The introduction of rosin affords these elastomers with UV absorption property. And the glass transition temperature of these EC-rosin grafted copolymers could be tuned by changing the content of PBA. Moreover, the introduction of PBA to EC endowed EC-*g*-(DA)-*g*-PBA with a good film-forming property and excellent thermoplastic elastomer behavior. All of these EC-rosin grafted copolymers showed an excellent UV absorption performance, and maintained outstanding UV absorption capability after continuous UV-irradiation or being heated to 115 °C for 1 h. As a result, these EC-rosin grafted copolymers have a potential application in coating materials with UV absorption property.

1. Introduction

Recently, extensive research has focused on the preparation of novel polymeric materials from renewable resources due to their potential as alternatives to petroleum-based plastics (Makhado, Pandey, Nomngongo, & Ramontja, 2017; Pandey, 2016, 2017; Pandey & Ramontja, 2016; Vandana et al., 2015; Wang, Yuan, & Tang, 2017). Cellulose, as the largest natural polymer with the character of inexpensive and biodegradable, has been widely used as an alternative polymer materials in the various fields, to replace the counterparts derived from fossil fuel (Lu et al., 2016; Nechyporchuk, Belgacem, & Bras, 2016; Osong, Norgren, & Engstrand, 2016). Most recently from sustainable point of view, renewable chemicals obtained from plant or crop raw material resources were widely employed to modify the cellulose by living/controlled polymerization (Dong et al., 2008; Liu, Wang et al., 2014; Liu, Yao et al., 2014; Yu et al., 2014).

Rosin is an important renewable natural product obtained from pine tree. Rosin mainly consists of resin acids (about 85 wt%), which commonly bears a hydrophenanthrene rings and a carboxyl group (Ganewatta et al., 2015; Maiti, Ray, & Kundu, 1989; Tang, Wang, Decho, & Chen, 2014; Wang, Liu et al., 2017; Zheng et al., 2010). Most recently, rosin as well as its derivatives were reported to be used to modify cellulose and it derivatives. Hussain and co-workers conducted a first combination of rosin and cellulose by esterification for the preparation a nanoparticle used for drug delivery (Hussain, 2010). In our previous work, we also combined rosin with cellulose for synthesizing a class of novel sustainable copolymers including cellulose-rosin copolymer (EC-DA), cellulose-*g*-poly(*n*-butyl acrylate-*co*-dehydroabietic ethyl methacrylate) and cellulose-*g*-poly(lauryl methacrylate-*co*-dehydroabietic ethyl methacrylate) (Liu, Wang et al., 2014; Liu, Yao et al., 2014; Yu et al., 2014). Niu et al. developed a functionalized cellulose modified by rosin, which was used as a filler to reinforce polylactic acid (PLA) and chitosan (Niu, Liu, Song, Han, & Pan, 2017). Daniele and co-workers developed a class of antibacterial cellulose-based nanomaterials by grafting nontoxic rosin acids on the surface of CNCs via esterification (Castro, Bras, Gandini, & Belgacem, 2016). Duan et al. prepared a series of chitosan grafted rosin copolymers under microwave irradiation to act as drug carrier (Duan, Chen, Jiang, & Li, 2008; Duan, Shen, Fang, & Li, 2009). In summary, the intrinsic and unique properties of rosin, including hydrophobicity, rigidity, UV absorption and so on were imparted to cellulose-rosin copolymers. These cellulose-rosin copolymers were found to have a potential application in drug carrier or UV-absorbent coating materials. However, due to the intrinsic rigidity of both rosin and cellulose, the flexibility of these cellulose-rosin copolymers should be tailored before their further application.

Thermoplastic elastomers (TPEs) that featured with thermoplastic

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and elastomeric properties are a class of engineering polymer with hard and soft segments (Legge, 1987). In general, TPEs were classified into to two types according to their architecture. The first class is a hard and soft segment-separated triblock copolymer with linear or star structures, (e.g.,polystyrene-*b*-polybutadiene-*b*-polystyrene (SBS) and polystyrene-*b*-polyisoprene-*b*-polystyrene (SIS) triblock copolymers). The second class of TPEs is a multi-graft copolymer with comb or brush structures. Duan and coworkers prepared a tetra-functional multigraft copolymer (PS-*g*-PI) used for a TPEs, in which the backbone is a rubbery polymer chains with multiple glassy chains fixed at each junction point (Duan, Thunga et al., 2009). In contrast, brush polymers with rigid polystyrene backbones and soft PA-amide brushes were also designed as TPEs (Chen, Kushner, Williams, & Guan, 2012). Inspired by the second class of TPEs, the next generation TPEs that utilized the cellulose as rigid backbone and grafted soft side chains from this backbone as a soft matrix, were developed (Reulier, Perrin, & Avérous, 2016; Wang et al., 2016; Yu et al., 2017).

Jiang and coworkers first developed a cellulose based TPEs, in which rigid cellulose acted as backbone and soft poly(*n*-butyl acrylate-co-methacrylate) acted as side chain (Jiang, Wang, Qiao, Wang, & Tang, 2013). Similarly, we integrated cellulose, rosin and fatty acid for synthesizing a class of novel cellulose derived TPEs, by which cellulose and rosin derived polymer formed a hard phase and fatty acid derived polymer formed a soft phase. Due to the presence of conjugated double bonds, rosin and its derivatives possess an excellent UV absorption property in UV region (200–400 nm) and could endow the UV-absorbent property to the polymer integrated. In this work, we tentatively evaluated the UV absorption properties of these rosin-cellulose composites (Liu, Wang et al., 2014; Liu, Yao et al., 2014; Yu et al., 2014).

TPEs with UV absorption property have been attracting more and more attentions. Yu and co-workers prepared a UV-absorbent lignin-based TPEs which having excellent UV absorption and mechanical properties (Yu et al., 2015). However, the TPEs with UV absorption properties were frequently prepared by using lignin as feedstock (Kai et al., 2016; Qian et al., 2015; Wang & Venditti, 2015; Yu et al., 2015). The reports on cellulose based TPEs with UV adsorption property were rare, which leaves much room to investigate UV-absorbent cellulose-based TPEs.

Herein we report a strategy to prepare a series of cellulose-rosin based copolymers thermoplastic elastomers (TPEs) with UV absorption property. Different from the synthetic strategy of cellulose-rosin copolymer in our previous work (Liu, Wang et al., 2014; Liu, Yao et al., 2014; Yu et al., 2014), dehydroabietic acid (DA, one of rosin's resin acids) and ATRP initiating sites (2-bromoisobutyryl groups) were both introduced into the backbone of ethyl cellulose (EC) at the same time to fabricate the ATRP macroinitiator (EC-*g*-(DA)-Br) by esterification reaction, by which the UV absorption property of rosin was imparted to cellulose derived ATRP macroinitiator. Next, butyl acrylate (BA) with different molar ratios to EC-*g*-(DA)-Br was utilized to perform "graft from" ATRP and achieved the grafted copolymers EC-rosin-graft-poly (butyl acrylate) (EC-*g*-(DA)-*g*-PBA) (Scheme 1). Compared with the EC-*g*-(DA)-Br, EC-*g*-(DA)-*g*-PBA is flexible, and has an improved film-forming property as well as a good mechanical property. In addition, UV absorption property that inherits from rosin would be imparted to EC-*g*-(DA)-*g*-PBA which could be potentially used in coating materials with UV absorption property.

2. Experimental

2.1. Materials

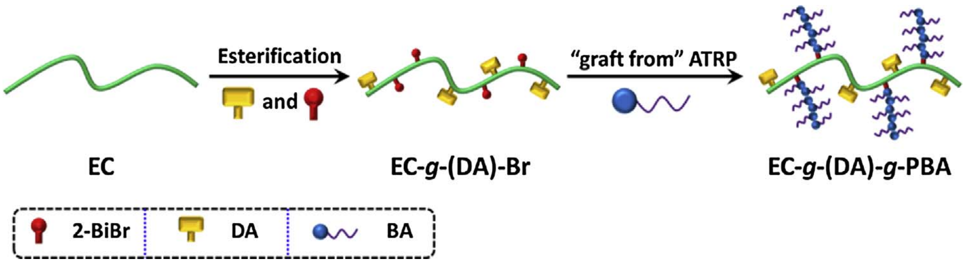
Dehydroabietic acid (DA, ~98%) was obtained from Wuzhou Chemicals, China and used as received. Ethyl cellulose (EC, 270–330 mPa·S), *N,N,N′,N″,N″*-pentamethyl-diethylenetriamine (PMDETA, 99%), CuBr (99.9999%), dimethylaminopyridine (DMAP, 99%), *N,N*-dimethylformamide (DMF), *p*-nitrobenzaldehyde (> 97%) oxalyl chloride (99%), and 2-bromoisobutylryl bromide (2-BiBr) (98%) were purchased from Aladdin Industrial Inc., and used as received. Butyl acrylate (BA) was purchased from Aladdin Industrial Inc., and used after the remove of inhibitor by aluminium oxide. Tetrahydrofuran (THF) and petroleum ether (boiling point ranges from 30 °C to 60 °C) was purchased from Nanjing Reagent Chemical Co., Ltd. THF was dried over 4A molecular sieves, followed by the distillation before use. *p*-nitrobenzaldehyde (> 99%) was purchased from Aldrich and used as received. All the other reagents were all analytical grades and purchased from Nanjing Reagent Chemical Co., Ltd and used as received.

2.2. Preparation of ethyl cellulose-rosin macroinitiator

According to our previous work (Liu, Wang et al., 2014; Liu, Yao et al., 2014; Yu et al., 2014), the procedure for the synthesis of ethyl cellulose-rosin macroinitiator (EC-*g*-(DA)-Br) was divided into two steps (Scheme 2). In the first step, DA (5 g, 15.7 mmol) and dichloromethane (30 mL) were charged in a round-bottomed flask set in an ice-water bath under stirring. Oxalyl chloride (2.40 g, 18.9 mmol) was added drop-wise to flask within 30 min at 0 °C, and stirred at 25 °C for 5 h. Excessive oxalyl chloride and dichloromethane were removed by evaporation. Dehydroabietic acyl chloride (DA-Cl) was then obtained. In the second step, DA-Cl (1.37 g, 4.1 mmol) and 2-BiBr (2.2 g, 9.6 mmol) were dissolved in THF and added drop-wise to a flask containing a solution of EC (1 g, 4.57 mmol) and DMAP (1.67 g, 13.67 mmol). The reaction was run at 25 °C for 24 h, and the solution was precipitated with petroleum ether. ATRP macroinitiator EC-*g*-(DA)-Br was obtained after filtration, followed by drying at 40 °C until constant weight. ^{1}H NMR was used to determine the contents of initiating sites (2-bromoisobutyryl ester group) and DA in macroinitiator EC-*g*-(DA)-Br by using *p*-nitrobenzaldehyde as an internal standard (Jiang et al., 2013; Yu et al., 2014; Yu et al., 2015).

2.3. Preparation of cellulose-rosin grafted copolymers via "graft from" ATRP

As shown in Scheme 2, the preparation of EC-*g*-(DA)-*g*-PBA5 was used as example (Table 1, entry 1). BA (0.40 g, 3.15 mmol), PMDETA (54.6 mg, 0.315 mmol), THF 5 mL, DMF 0.2 mL and EC-*g*-(DA)-Br (0.84 g, 0.63 mmol Br) were added into a flask, followed by three freeze-pump-thaw cycles. This solution was then transferred into the Schlenk flask containing CuBr (45.2 mg, 0.315 mmol). Next, this



Scheme 1. Preparation of cellulose-rosin grafted copolymers by ATRP.