

A two step method for the preparation of carbamate cross-linked cellulose films using an ionic liquid and their water retention properties



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ABSTRACT

Carbamate cross-linked cellulose films can be prepared in a two step method using cellulose dissolved in 1-*n*-butyl-3-methylimidazolium chloride ionic liquid. The new technique involves casting the film from cellulose ionic liquid solution onto a glass surface and application of alkyl/aryl diisocyanate in dry dimethylsulfoxide solution onto the cellulose – ionic liquid coating on glass and allowing the cross-linking reaction to occur on the pre-formed cellulose coating. The carbamate cross-linked cellulose films formed were characterized by FT-IR, and TG-DTA. The water retention values of the films are shown to decrease with the increase in hydrophobicity of the alkyl/aryl group linker in the carbamate bridges.

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1. Introduction

Fabrication of cellulose into films has attracted attention in recent years due to interests in renewable biomass based biodegradable packaging materials as well as numerous possible applications of these materials. Some of the potential applications of cellulose films include: enzyme immobilization (Turner, Spear, Holbrey, & Rogers, 2004), anion exchange (Schmitt, Granet, Sarrazin, Mackenzie, & Krausz, 2011), separation membranes, microfiltration (Grainger & Hägg, 2007) (Liu, Zeng, Tao, & Zhang, 2010), metal ion absorption (Tian et al., 2011), (Chen et al., 2009), thermoresponsive materials (Geissler, Bonaccorso, Heim, Heinze, & Zhang, 2014), and controlled drug release (Bodhibukkana et al., 2006). Since the 2004 report by Rogers and co-workers on casting cellulose films via regeneration from ionic liquid solutions and preparation of active laccase enzyme-encapsulated films, a number of researchers have used this technique for the preparation of various types of cellulose films (Turner, Spear, Holbrey, & Rogers, 2004). The ionic liquid based methods are especially useful in the preparation of modified films and composite films with other natural polymers such as chitosan (Niroomand, Khosravani, & Younesi, 2016), natural hair, collagen (Zhang, Ding, Chen, & Huang, 2013),

as well as silicates (Wu, Dong, He, Yu, & Zhang, 2016) and graphite (Chen, Xu, Wang, Qian, & Sun, 2015). In another cellulose modification example Qiu et al. has recently reported the alteration of microcrystalline cellulose by cross-linking with toluene diisocyanate under homogeneous phase in *N,N*-dimethylacetamide/LiCl solvent system (Qiu, Tao, Ren, & Hu, 2012). During these experiments modified cellulose films were prepared by solution casting method and their hydrophobicity, thermal stability, permeability, and degradability were studied; improvements in hydrophobicity and thermal stability were also reported (Qiu, Tao, Ren, & Hu, 2012). In addition, Qiu and co-workers observed a rapid drop in urea permeation rate due to cross-linking of microcrystalline cellulose with toluene diisocyanate (Qiu et al., 2012).

In our earlier work we have shown that cellulose carbamate silica hybrid materials can be prepared in good yields by using the homogeneous phase reaction of 3-(triethoxysilyl)propyl isocyanate with cellulose dissolved in 1-*n*-butyl-3-methylimidazolium chloride ionic liquid and then using NH₄OH catalyzed hydrolysis of triethoxysilyl groups and the sol-gel process (Amarasekara & Owereh, 2009). However, in this technique diisocyanates reacts rapidly with cellulose –OH groups in cellulose – ionic liquid solution forming a gel, making this type of preparations not suitable for casting onto a thin coating on a glass plate. In an attempt to circumvent this problem, we have now developed a simple two step technique involving casting the film from cellulose ionic liquid solution and then application of

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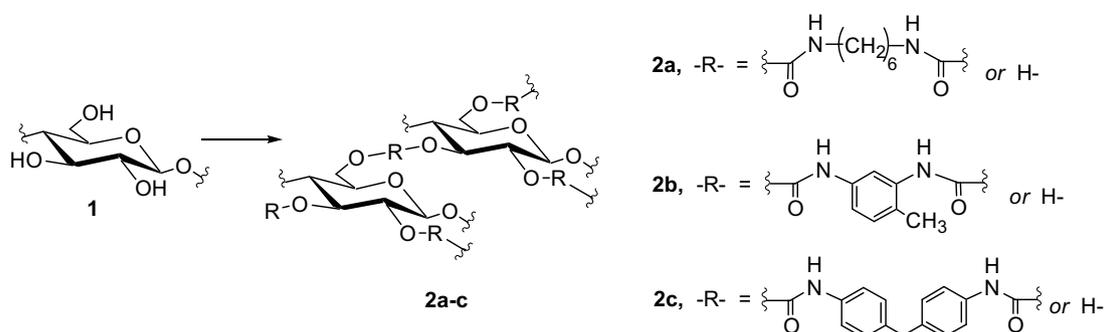


Fig. 1. Conversion of cellulose (1) to carbamate cross-linked cellulose (2a–c) in the films.

diisocyanate onto the cellulose – ionic liquid coating on the glass and allowing the cross-linking reaction to occur on the pre-formed cellulose coating. In this communication we report the preparation of three different carbamate cross-linked cellulose films by the new technique as shown in Fig. 1 and comparison of their water retention properties with a pure cellulose film regenerated from 1-*n*-butyl-3-methylimidazolium chloride ionic liquid.

2. Experimental methods

2.1. Materials and instruments

Sigmacell cellulose – type 101 (DP~450, from cotton linters), 1-*n*-butyl-3-methylimidazolium chloride (>98%) hexamethylene diisocyanate, toluene 2,4-diisocyanate, and 4,4'-methylenebis (phenyl isocyanate) were purchased from Aldrich Chemical Co. 4.5 × 4.5 × 0.2 cm Glass plates were used to cast cellulose films and these plates were thoroughly washed using soap, rinsed with deionized water and dried in an oven at 90 °C, before use. Attenuated total reflection infrared (ATR-IR) spectra of cellulose films were recorded in the 650–4000 cm⁻¹ range on a Smiths IdentifyIR spectrometer with a diamond ATR (Danbury, CT, USA). Thermogravimetric analysis was carried out in air using TA instruments TGA 2050 system. The mass of the thin film piece used for a TG scan was approximately 10 mg, and platinum crucibles were used in all experiments. The TG curves were recorded in the 25–800 °C temperature range using a scanning rate of 20 °C/min. The oven was kept at 800 °C for at least one hour to burn leftovers from the previous run. Temperatures reported from TG data are onset temperatures (T_{onset}), as determined by the step tangent method (Ngo, LeCompte, Hargens, & McEwen, 2000). The derivative thermogravimetric analysis (DTG) data peaks in the derivative of the weight% curve correspond to weight loss steps in the TG curve. Film thickness was measured using a Pittsburgh instruments digital micrometer model 895.

2.2. General experimental procedure for the preparation of carbamate cross-linked cellulose (2a–c) films

Cellulose (DP~450) (0.250 g) was mixed with 1-*n*-butyl-3-methylimidazolium chloride (2.75 g) and heated at 80 °C for 3.0 h to give a pale yellow viscous solution. A 0.60 g portion of the cellulose – ionic liquid solution (50 mg of cellulose, 0.309 mmol glucose equiv.) was evenly coated on the cleaned glass plate using a glass rod, covering a 3.0 × 3.0 cm area. Then diisocyanate (0.463 mmol in 0.30 mL of dry DMSO, 1.5 equiv.) was carefully added on to the film and evenly spread with a glass rod. The film was left in a desiccator at room temperature for 24 h for cross-linking and then repeatedly washed with distilled water to remove 1-*n*-butyl-3-methylimidazolium chloride and excess reagents. The film was dried at room temperature for 2 days, peeled off from the glass

Table 1

Thermal decomposition onset temperature (T_{onset}) and derivative thermogravimetric analysis (DTG) peaks data for cellulose thin film and carbamate cross-linked thin films 2a, 2b and 2c.

Cellulose film	$T_{\text{onset}}/^{\circ}\text{C}$	DTG/ $^{\circ}\text{C}$
Pure cellulose	284	310, 362, 588
2a	285	333, 544
2b	278	296, 563
2c	280	316, 576

plate, transferred to a desiccator for further drying and storage. The carbamate cross-linked cellulose films 2a, 2b and 2c were prepared using hexamethylene diisocyanate, toluene 2,4-diisocyanate, and 4,4'-methylenebis (phenyl isocyanate) respectively. The photographs, ATR-IR spectra, TG-DTG data of films 2a–c are shown in Figs. 2 and 3 and Table 1 respectively.

2.3. Experimental procedure for the preparation of pure cellulose film

A pure cellulose film was prepared using the procedure 2.2., without adding the diisocyanate. The cellulose film, ATR-IR spectrum and TG-DTG data of the film are shown in Figs. 2 and 3, and Table 1 respectively.

2.4. Water retention value (WRV)

Carbamate cross-linked cellulose and pure cellulose films were cut into small pieces with approximately equal size, weighed and then soaked in deionized water for 24 h. The surface water was carefully wiped out with filter paper before the films were subjected to second weighing. All the procedures were carried out at room temperature.

WRV was calculated as the amount of absorbed water related to dry film mass as follows: (Qiu, Tao, Ren, & Hu, 2012).

$$\text{WRV}(\%) = \frac{W_s - W_0}{W_0} \times 100\%$$

W_0 is the dry weight of film before soaking and W_s is the weight of film after soaking for 24 h. The average WRVs of triplicate experiments are shown in Table 2.

3. Results and discussion

In this study we have developed a two step technique for the preparation of carbamate cross-linked cellulose films, involving casting the film from cellulose ionic liquid solution followed by application of diisocyanate onto the cellulose coating and allowing the cross-linking reaction to occur on the pre-formed cellulose film. In all experiments 1.5 equivalents of diisocyanate per glucose unit

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