European Polymer Journal 69 (2015) 328–340

Contents lists available at ScienceDirect

European Polymer Journal

journal homepage: www.elsevier.com/locate/europolj

Macromolecular Nanotechnology

Ductile nanocellulose-based films with high stretchability and tear resistance

Steven Spoljaric, Arto Salminen, Nguyen Dang Luong, Jukka Seppälä *

Polymer Technology, Department of Biotechnology and Chemical Technology, Aalto University School of Chemical Technology, P.O. Box 16100, 00076 Aalto, Finland

ARTICLE INFO

Article history:
Received 18 February 2015
Received in revised form 5 June 2015
Accepted 16 June 2015
Available online 17 June 2015

Keywords:
Nanofibrillated cellulose
Hydroxyethylcellulose
Ductility
Tear strength

ABSTRACT

Hybrid composite films of nanofibrillated cellulose (NFC), cationic hydroxyethylcellulose (CHEC) and glycerol were prepared via solution blending. NFC adopted a fibrillar structure, being coated with the CHEC moieties. Ionic interactions between NFC and CHEC were present, as confirmed by FTIR, leading to enhanced strength, moduli and work-to-break values. Simultaneously, segments of non-cationic HEC worked in tandem with glycerol to lubricate the cellulose nanofibrils, yielding maximum strain-at-break values of 141%. The NFC–CHEC–glycerol films were subsequently coated with a 4.5–6 μm layer of poly(propylene carbonate) (PPC), microscopy confirming effective coating of NFC at the composite-coating layer boundary. The hydrophobic nature of PPC enhanced water stability for acute time periods and increased contact angle values. Film strength and toughness was also enhanced by PPC, indicative of its reinforcing ability. The hybrid composites highlight the ability to prepare extremely ductile cellulose-based films, with the aforementioned materials being amongst the most ductile cellulose-based and/or cellulose-majority films documented.

1. Introduction

Lignocellulosic materials have rapidly become a popular material and research field, driven by their many benefits including renewability, sustainability, recyclability, low cost and biodegradability [1]. Within this class of natural materials, nanofibrillated cellulose (NFC) is among the most studied and most promising. NFC is a nanomaterial derived from wood, prepared from the fragmentation of cellulose within wood pulp. The process yields cellulose nanofibrils with a high aspect ratio (4–20 nm wide, 500–2000 nm in length), high stiffness and mechanical properties and a low percolation threshold. This combination of favourable characteristics and nanoscale dimensions has encouraged the use of NFC-reinforcement in polymer nanocomposites, with composites displaying enhanced mechanical [2] and thermal [3] behaviour compared to materials filled with traditional wood-pulp. The nanoscale dimensions of the fibrils allow property enhancement to occur without compromising optical properties. The interest in NFC as a composite component is further fuelled by the ongoing focus on environmentally friendly and 'green' composites and materials.

Despite its many advantages, the utilisation of NFC presents several drawbacks and limitations. Most notably, NFC films are extremely brittle and possess poor ductility and tear strength. Films prepared from pure NFC seldom reach strain at break values of 10% [4,5]. The most common methods of enhancing ductility within cellulose films involve the incorporation of plasticisers such as glycerol, sorbitol and poly(ethylene glycol) [6]. More recently, processing techniques including multi-layer formation and over-pressure filtration and hot pressing [7] have been utilised to increase elongation. Sehaqui

* Corresponding author.
E-mail address: jukka.seppala@aalto.fi (J. Seppälä).

http://dx.doi.org/10.1016/j.eurpolymj.2015.06.019
0014-3057/

et al. [8,9] demonstrated how the ductility of NFC can be increased by blending with hydroxyethylcellulose (HEC), reaching maximum strain values of 55%. Furthermore, blending with HEC has increased ductility in other naturally-derived materials, including bacterial cellulose [10] and chitosan [11]. Thus, there is great potential in determining the limits of ductility and elasticity enhancement in natural composites and blends via the incorporation of HEC.

As is quite often the case with polymer composites, increased ductility and elasticity comes at the expense of strength and toughness. In order to retain some of the initial mechanical characteristics, chemical modification of the cellulosic materials can be performed to facilitate superior interaction and adhesion. NFC has the advantage of possessing a slight negative charge. Therefore, its polyelectrolytic nature can be taken advantage of via the introduction of cationic groups. HEC can be readily cationised using simple and safe methods [12,13]. Compounding cationised-HEC (CHEC) with NFC can lead to enhanced strength and toughness due to ionic complexation between both cellulosic components. Since several hydroxyl groups that constitute HEC would not be cationised, segments of HEC can also interact with NFC via hydrogen bonding and coat the nanofibrils [9,10]. The primary mechanism influencing film ductility arises from this interaction, as HEC-coated NFC fibrils experience slippage and alignment instead of fracturing under applied load. Thus, a synergy between the strength obtained from ionic bonding and the lubrication effect of HEC coating the cellulose nanofibrils is necessary. To the best of the authors' knowledge, the bulk of research concerning HEC-cellulose blends focus on physical interactions (hydrogen bonding, etc.) between the components rather than polyelectrolytic complexation.

One disadvantage of utilising electrostatic interactions is that potential enhancements in strength and modulus may be at the expense of film ductility. A possible method of overcoming this is to incorporate a compound, such as glycerol, into the cellulosic composite. Glycerol may effectively lubricate NFC and CHEC segments, allowing for slippage during the application of load and subsequently enhancing material ductility. This provides prospects to determine the limits of ductile and elastic behaviour within composites containing maximal cellulose loadings.

Despite its potential to enhance ductility within nanocellulose films, glycerol possesses a tendency of migration and leaching from cellulose films. Due to its polar nature, glycerol readily adsorbs to water molecules. In order to prevent glycerol migration and avoid any deterioration in mechanical properties over time, cellulose films may be coated with a hydrophobic polymer, thus preventing glycerol from leaching and water from penetrating the film. One potential candidate for coating cellulose-based films is poly(propylene carbonate) (PPC), a biodegradable aliphatic polyester synthesised from carbon dioxide and propylene oxide. A great deal of industrial and research interest has been directed towards PPC, due to the potential of its synthesis process in reducing greenhouse gas emissions and saving fossil-fuel consumption. Furthermore, its precursor propylene oxide can also potentially be synthesised from renewable sources [14]. Apart from its environmental attributes, PPC is inexpensive to produce and displays superior barrier properties and ductility. Within recent years, limited attention has been given to PPC-cellulose derivative nanocomposites, including cellulose nanocrystals [15], cellulose acetate butyrate [16] and NFC [17]. The aforementioned nanocomposites displayed enhanced mechanical properties, thermal stability and good transparency, thus demonstrating a need to further characterise, optimise and exploit these hybrid materials.

Herein, the preparation and characterisation of poly(propylene carbonate)-coated NFC–CHEC–glycerol composite films is presented. A physical blending method in aqueous media was utilised to prepare composite films that possessed enhanced ductility and work-to-break, while containing as-high-as-possible concentrations of cellulosic constituents. HEC was cationised prior to blending with NFC and glycerol in order to encourage ionic complexation with the anionic cellulose nanofibrils. Given the multi-component nature of these composite films, there are several key factors that are addressed, namely:

(a) The influence of NFC:CHEC ratio on material properties.
(b) The influence of glycerol concentration on material properties.
(c) The effectiveness of PPC coating on water resistance and mechanical properties.

2. Experimental

2.1. Materials

Nanofibrillated cellulose (NFC) was provided by UPM Corporation (Helsinki, Finland), under the product name UPM Fibril Cellulose. A nominal energy consumption of 0.3 kW h kg^{-1} was utilised to mechanically disintegrate bleached birch kraft pulp. The birch pulp was first pre-treated with a Masuko supermasscolloider (Masuko Sangyo Ltd., Japan) to a target SR number of 90-94. Subsequently, the material was fluidized by six passes through a M7115 fluidiser (Microfluidics Corp. Newton, MA, USA) with an operating pressure of 1850 bar. The solids content of the prepared dispersion was 1.61 wt% Hydroxyethylcellulose, glycidyltrimethylammonium chloride (GTMC), poly(propylene carbonate) (PPC, average $M_n \sim 50{,}000$), isopropanol, sodium hydroxide (NaOH), hydrochloric acid (HCl) and glycerol (anhydrous) were supplied by Sigma Aldrich, USA.

2.2. Materials preparation

2.2.1. Cationisation of HEC with GTMC

HEC was cationised with GTMC using a method based on Nakamura and Sato [18]. The procedure is summarised in Scheme 1. 13.08 g of HEC was dispersed in 100 g of an 89 wt% isopropanol solution in water at 25 °C, to which 5.23 g of