Composites Part B 156 (2019) 43–50

Contents lists available at ScienceDirect

Composites Part B

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

Adhesion properties of poly(ethylene oxide)-lignin blend for nanocellulose composites

Tippabattini Jayaramudu[a,b], Hyun-U. Ko[a], Hyun Chan Kim[a], Jung Woong Kim[a], Eun Sik Choi[a], Jaehwan Kim[a,*]

[a] Creative Research Center for Nanocellulose Future Composites, Department of Mechanical Engineering, Inha University, 100 Inha-Ro, Nam-Ku, Incheon, 22212, South Korea

[b] Laboratory of Material Sciences, Instituto de Quimica de Recursos Naturales, Universidad de Talca, 747, Talca, Chile

ARTICLE INFO

Keywords:
Lignin
Poly(ethylene oxide)
Blend
Cellulose
Adhesion

ABSTRACT

In this paper, poly(ethylene oxide)-lignin (PEO-L) blends were prepared for eco-friendly nanocellulose composites and the effect of lignin content on its adhesion property was studied by using single lap joint test. The PEO-L blends were prepared by blending method using 60% methanol. Cellulose nanofiber (CNF) film, chosen as an adherent material of eco-friendly nanocellulose composites, was prepared by casting CNF emulsion, followed by vacuum filtration and drying. The successful formation of PEO-L blends was confirmed from FTIR, DSC and XRD studies. The shear strength of PEO-L blend increased with the lignin content and the 30% lignin case (442 kPa) showed 189% larger shear strength than the pure PEO (835 kPa). This shear strength improvement is associated with enhanced hydrogen bonds between lignin/PEO and CNF film.

1. Introduction

The environmental impact of products along all stages of their life cycle from raw material extraction to waste management is an important concern of our society. Composite materials based on renewable resources have gained considerable interest from the industries because of environmental issues. Especially, eco-friendly and low-cost natural fibre reinforced polymer (NFRP) composites have been widely used in automotive and building industries [1]. There are various natural fibres such as cellulose, jute, … Among them, cellulose nanofiber (CNF), a natural fibre isolated from wood, cotton, algae and etc., has merits in terms of renewability, biocompatibility, high elastic modulus and mechanical strength, optical transparency, low thermal expansion coefficient and good thermal stability [2,3]. It is known to be a new building block of future materials [4]. CNF is a promising natural fibre candidate for NFRP composites [5]. To form eco-friendly and low-cost NFRP, not only fibres but also polymer matrix should be natural materials too.

Lignin, the second richest renewable material next to cellulose, is a waste-by-product natural material while producing pulp from wood. Thus, once lignin is developed as polymer matrix materials, then it will be beneficial for achieving eco-friendly and low-cost NFRP composites. Lignin is mainly used in the formulation of adhesives, surfactants, dispersants and a stabilizing agent for plastics and rubbers for advanced composites applications [6,7]. Fig. 1 shows chemical structure and crosslinks between the repeating units of lignin. Lignin consists of three hydroxycinnamyl alcohols precursors: p-coumaryl, coniferyl, and sinapyl alcohols. Each of these monolignols gives rise to different types of lignin units called p-hydroxyphenyl (H), guaiacyl (G), and syringyl (S) units, respectively, which are crosslinked together and form aromatic heterogeneous complex structures. Moreover, lignin has other functional groups (-OH, C=O, OCH_3 and CHO). Due to these functional groups, it can be easily blended with various monomers or polymers. However, the resulting material properties are not good for NFRP composites due to its brittleness, which is caused by globular structure of lignin fragments [8]. Recently, it has been reported that blending of polyether components to lignin can reduce its brittleness of lignin [9].

Natural fibre and polymer matrix interaction plays a crucial role in determining the properties of NFRP composites. It is known fact that natural fibres cannot effectively reinforce the composites once poor bonding interaction at the fibre–polymer interface is formed. Thus, it is necessary to develop a polymer matrix material that can have excellent bonding interaction with natural fibres, especially CNFs. Generally, blending method of two or more polymers has been considered to be one of the most promising methods to achieve new materials with good performance as compared with their chemical modification. Blending

* Corresponding author.
E-mail address: Jaehwan@inha.ac.kr (J. Kim).

https://doi.org/10.1016/j.compositesb.2018.08.063
Received 3 May 2018; Received in revised form 26 July 2018; Accepted 20 August 2018
Available online 21 August 2018
1359-8368/

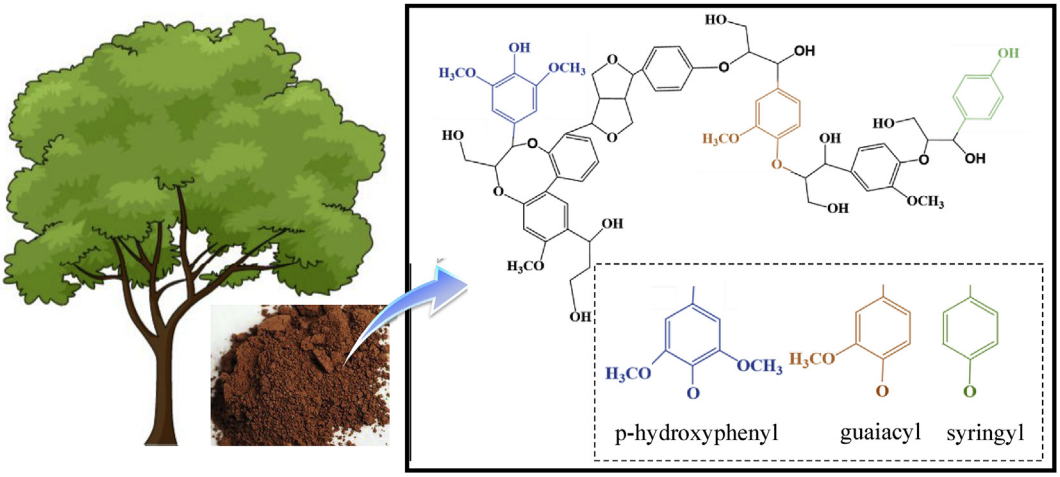

Fig. 1. Chemical structure and the crosslinks between the repeating units of lignin.

synthetic polymers with natural polymers provides ways to reduce costs and offers benefits from the combined properties so as to enhance interactions in NFRP composites. Recently, blending of poly(ethylene oxide) (PEO) and lignin has been studied for improving miscibility and hydrogen bond formation of the blends [10–13]. Various lignin materials were blended with PEO and PEO molecular weight effect was studied in terms of miscibility, thermal properties and chemical structure of blends. PEO-lignin (PEO-L) based materials have been widely utilized in advanced composite applications [14–16]. PEO, a semi-crystalline and thermoplastic material, is an outstanding synthetic polymer material, widely used in pharmaceutical and advanced scientific applications [17–19]. It is a low toxic, chain flexible, biocompatible and excellent water-soluble material. With the general formula of $X–(OCH_2CH_2)_n-Y$, main ether oxygen (-O-) and methylene ($-CH_2-$) are the main functional groups and hydroxyl (-OH) groups are the end groups. Owing to these properties, PEO has been widely used in food additives, pharmaceutical, tissue engineering and composite applications [14,20,21]. Combination of PEO with lignin materials is extensively used in composites due to the formation of miscibility and a strong hydrogen bond between the ether oxygen of PEO and lignin functional groups [22].

The main attention of this work is to investigate the feasibility of PEO-L blend for polymer matrix of nanocellulose composites. PEO-L blend was used to improve the adhesion at the interface between cellulose and PEO-L blend matrix in the nanocellulose composite. PEO-L was prepared by blending method and characterized by using Fourier transform infrared (FTIR) spectroscopy, differential scanning calorimetry (DSC) and X-ray diffraction (XRD) studies. The effect of lignin content on the thermal stability and mechanical properties of the PEO-L blends were studied by using thermogravimetric analysis (TGA) and universal tensile test. To test adhesion properties at interface of PEO-L blend and cellulose for NFRP composites, CNF film was used instead of single CNF because CNF is too small to test adhesion properties. Single lap joint (SLJ) test was performed by attaching CNF films with PEO-L blend.

2. Materials and methods

2.1. Materials

PEO (Mv = 50,00,000), alkali lignin with low sulfonate content and cellulose microcrystalline powder (~50 μm) were procured from Sigma–Aldrich Co. (St. Louis, MO, USA). Methanol was purchased from Daejung Chemicals & Metals Co. Ltd., Korea and used without any further purification to prepare the PEO-L blend. Deionized (DI) water was used throughout the experiment.

2.2. Preparation of poly(ethylene oxide)-lignin blend

PEO-L solution was prepared by blending PEO and lignin solutions with 60% methanol aqueous solution as solvent. Firstly, lignin was dried at 90 °C for 6 h and dissolved in 60% methanol solution with various amounts from 0.1 to 0.3 g using a magnetic stirrer. Then 0.7 g of PEO was added under the vigorous stirring and raised the temperature from room temperature to 65 °C, the melting temperature of PEO, by using a hot plate under stirring condition over a period of 4 h. After that, the reaction temperature was reduced to 50 °C with continuous stirring for 20 h. The obtained homogeneous PEO-L solution was stored at 4 °C for later use.

To test bonding behaviour between the prepared PEO-L blend and cellulose nanofiber, which are essential ingredients for nanocellulose composites, two CNF films were bonded using PEO-L blends. At first, to provide the CNF film, a CNF suspension was prepared by using aqueous counter collision method that uses high pressure water jet to extract CNFs from pulp without any chemical treatment [23,24]. In this process, cellulose microcrystalline (Sigma Aldrich) was defibrillated for 30 passes using an ACC machine (ACCNAC-100, CNNT, Korea). The CNF suspension was vacuum filtrated to form a film and dried at 60 °C until perfectly dried. Thickness of the prepared CNF films was 60 μm.

To characterize the prepared PEO-L blend, its film type specimens were prepared for FTIR, DSC, XRD and TGA analysis. The fully blended PEO-L solution was poured into a glass petri dish and allowed to store at room temperature to form a PEO-L film. For comparison purpose, the pure PEO specimen was also prepared by following the similar process. The PEO-L specimens were named according to the lignin contents as the pure PEO, 10% PEO-L, 20% PEO-L and 30% PEO-L, where the percent represents the lignin wt.%. Colour of the specimens gradually changed from bright white to dark yellow as the lignin content increased. Fig. 2 AB show the preparation process of PEO-L blend and schematic of its chemical bonding mechanism.

2.3. Characterization

2.3.1. FTIR analysis

FTIR analysis was conducted to study the formation of PEO-L blends. The PEO-L specimens were completely dried in a vacuum oven at 60 °C for 6 h and the spectra were recorded on an FTIR spectroscopy (Bruker Optics, Billerica, MA) ranging from 400 - 4000 cm^{-1} by using KBr disk pellet method with 16 average scans.

2.3.2. Thermal analysis

Glass transition temperature of the specimens were investigated by using a DSC instrument (DSC 200 F3, NETZSCH) at a heating rate of