



Advanced Green composites using liquid crystalline cellulose fibers and waxy maize starch based resin

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ABSTRACT

Advanced green composites have been fabricated by using modified liquid crystalline cellulose (M-LCC) fibers and micro-fibrillated cellulose (MFC) modified waxy maize starch (M-WMS) based resin. LCC fibers, as a reinforcement, were modified in terms of tensile properties by a combination of chemical and heat treatment, under a predetermined tension. The surface topography, crystallinity, molecular alignment, and mechanical properties of M-LCC fibers were investigated to determine the effects of combination modification process on the fibers. M-WMS, as a resin, was prepared by two steps. In the first step, an environment-friendly cross-linker, 1,2,3,4-butane tetracarboxylic acid (BTCA), was used to improve the water resistance and tensile properties of the resin. In the second step, 'MFC', as reinforcing agent, was dispersed in the cross-linked resin to obtain substantial improvements in its tensile properties. Unidirectional advanced green composites consisting of M-LCC fibers and M-WMS were fabricated using hand lay-up followed by a compression molding process. The results showed that the M-LCC fibers had strength close to 2 GPa and the composites had strength close to 800 MPa. These advanced green composites could be used in structural applications.

1. Introduction

Growing environmental problems and depletion of petroleum resources created by conventional non-biodegradable plastics and composites have generated keen interest in developing environment-friendly and biodegradable green polymers and composites. Consequently, inexpensive polysaccharides, such as cellulose and starch from yearly renewable crops have received much attention as environment-friendly and biodegradable polymers for developing fully green materials since they are abundantly available around the world [1,2]. Cellulose-based natural fibers from ramie, sisal, hemp, flax, jute, bamboo, pineapple, and other plants have already replaced some non-degradable synthetic fibers in composites that can be used for non-load bearing secondary structures [3,4]. Excellent specific mechanical properties of some of these fibers compared to fibers such as E-glass fibers have provided lighter and stronger eco-friendly structures [3]. On the resin front, commercially available starches, such as potato, corn, waxy maize, wheat, etc., have been shown to possess promising characteristics as biodegradable resins with good mechanical properties for composite materials [5]. So far, most of the fully green composites have been made using natural fibers and biodegradable resins for low load-bearing indoor applications, such as interiors of housing and

automobiles, furniture, cabinetry, etc. [4,6]. These composites show relatively moderate mechanical properties (tensile strength in the range of 50–200 MPa and Young's modulus in the range of 3–9 GPa) depending on the type of fibers used, their orientation and form (e.g., woven, nonwoven or knitted fabrics) as well as the volume fraction [4,7].

Since cellulose can form cholesteric liquid crystalline phases in specific solvents that dissolve them at substantially high concentrations, a new class of high-performance cellulose fiber termed as liquid crystalline cellulose (LCC) fiber has been developed using an air gap wet spinning technique [8]. The air gap wet spinning technique has been commonly used to produce highly oriented synthetic fibers, such as Kevlar[®], Twaron[®], and Zylon[®]. This specific spinning technique retains the high degree of molecular alignment present in the liquid crystalline cellulose solution during its transformation into fibers. This results in much higher strength (~1500 MPa) and Young's modulus (~48 GPa) compared to any natural cellulosic fiber [9]. Earlier, Netravali, et al. fabricated soy protein-based 'advanced green composites' with high strength (over 635 MPa) using only 40% LCC fiber content [10]. Their fracture toughness was found to be higher than those made with Kevlar[®] and glass fiber composites using the same soy protein-based resin [10]. These advanced green composites were thought to be suitable for some

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primary structural applications. Later, Kim and Netravali improved the crystallinity of LCC fibers by treating them with KOH solution [10]. Some KOH treatments were carried out under a predetermined tension. As a result of increased crystallinity after the KOH treatment, they observed significant increase in the tensile strength (about 18%) and Young's modulus (about 33%) of the LCC fibers. They combined the modified LCC fibers and cross-linked soy protein resin to fabricate advanced green composites with excellent strength and toughness [11]. The composites using the modified LCC fibers showed higher tensile properties compared to composites made using as-received fibers. However, significant opportunity still exists to further enhance the properties of LCC fibers and to obtain advanced green composites with even higher properties. It has been hypothesized that higher tensile properties of LCC fibers can be achieved by further enhancing the crystallinity or molecular alignment or both after their formation. In this paper, for the first time, an optimized treatment of LCC fibers to enhance both the crystallinity and molecular orientation along the fiber axis has been reported. The optimized treatment consists of a combination of chemical and heat treatment under a pre-determined tension.

It is universally understood that good fiber-resin interfacial interaction or high bond strength can enhance the tensile properties of composites. Based on that it should be further possible to obtain composites with even higher strength and stiffness. In the case of soy protein which contains 18 amino acids, only 8 have polar groups such as carboxyl, hydroxyl or amine that can form hydrogen bonds with cellulose. The other 10 amino acids do not contribute to the fiber-resin bond. It has been reported that starch-cellulose interfacial bond is better than protein-cellulose bond because of the chemical similarities between starch and cellulose, both of which are made of glucose monomers that can provide ample hydrogen bonding [12]. Out of many commercially-available starch varieties, waxy maize starch (WMS) was selected as the resin in this study. WMS is a genetically modified maize starch containing about 99% amylopectin. While some native starches are difficult to process to obtain homogeneous films due to substantial gelatinization resulting in semisolid viscosity, WMS has excellent ability to form a transparent, smooth, and homogeneous film [13].

In the present study, advanced green composites were fabricated using modified LCC (M-LCC) fibers as reinforcement and modified WMS (M-WMS) as the resin. Fiber modification was achieved using an optimum combination of both chemical and heat treatments carried out under pre-determined tension. WMS resin was cross-linked by an environment-friendly and water-soluble cross-linker, 1,2,3,4-butane tetracarboxylic acid (BTCA), to improve its strength as well as water resistance characteristics. In addition, the mechanical properties of the resin were significantly enhanced by dispersing micro-fibrillated cellulose (MFC) in it. After that, M-LCC fiber-reinforced M-WMS composites or advanced green composites were fabricated using a hand lay-up procedure followed by a compression molding curing process. The tensile properties of the unidirectional advanced green composites were investigated, and a comparative analysis with conventional composites has been reported.

2. Experimental details

2.1. Materials

Pharmaceutical grade WMS powder was purchased from Nutra Bio, Middlesex, NJ. MFC (KY-100G), in water at 10 wt%, was provided by Daicel Chemical Industries, Japan. LCC yarn was provided by Dr. H. Boerstael, Teijin Twaron BV, Arnhem, The Netherlands. Analytical grade BTCA, sodium hypophosphite ($\text{NaPO}_2\text{H}_2\cdot\text{H}_2\text{O}$), sodium bisulphite (NaHSO_3), and reagent grade sorbitol ($\geq 98\%$ purity) were purchased from Sigma-Aldrich Chemical Co., Allentown, PA.

2.2. Preparation of M-WMS resin

WMS powder (2 g) was added to 50 mL of water and mixed using a magnetic stirrer for about 15 min. The WMS mixture was heated at 90 °C for 30 min and stirred continuously to obtain gelatinized WMS. BTCA (15 wt% of starch) as a cross-linker and sodium hypophosphite (50 wt% of BTCA) as a catalyst were added to the gelatinized WMS. The solution was stirred further for 60 min at the same temperature of 90 °C to obtain a pre-cured WMS resin. M-WMS resin was prepared by incorporating uniformly dispersed MFC in pre-cured WMS resin. To uniformly disperse MFC: initially, as-received MFC was added to water at a ratio of 1:150 (w/w) and homogenized using a VWR 250 homogenizer (VWR International, PA, USA) for about 15 min at 20,000 rpm. Then, the homogenized mixture was stirred overnight using a high-speed magnetic stirring (~ 1000 rpm). The pre-cured WMS resin was added to the uniformly dispersed MFC suspension at a ratio of 70:30 (w/w) and stirred at 90 °C for 1 h. In this stage, the resin is termed as pre-cured M-WMS resin which was used for making LCC fiber-reinforced green composites.

2.3. Modification of LCC fibers

As-received LCC fibers were modified by a combination of chemical and heat treatment process under predetermined constant tension. Single LCC yarns were immersed in 5% NaHSO_3 solution with a tensile load of 2 kg/yarn for 1 h at room temperature (RT). One end of the yarn was fixed with a clamp while the other end was attached to a pre-determined load. The applied load calculated for each single fiber was around 7% of the single LCC fiber strength. After completing the immersion process, the yarns were taken out and rinsed several times with DI water to remove any residual NaHSO_3 . Then, the yarns were dried at 140 °C in an air circulatory oven for 1 h with the same tension (2 kg/yarn). Fibers treated as above are termed as modified LCC or M-LCC fibers. As-received and M-LCC fibers were conditioned at standard ASTM conditions of 21 °C and 65% RH for 24 h before testing.

2.4. Preparation of advanced green composites

LCC and M-LCC fiber-reinforced unidirectional composites were fabricated using simple hand lay-up and compression molding process. At first, LCC and M-LCC fibers, in a parallel array, were dipped into the pre-cured M-WMS resin, taken out and gently squeezed to remove excess resin. The soaking and squeezing steps of the fibers into M-WMS resin were repeated several times to ensure complete impregnation of all fibers. Wet fiber bundles were organized in a unidirectional array on a Teflon[®] coated metal mold to prevent any shrinkage or distortion, as much as possible and dried for 18 h in an air-circulating oven at 40 °C. Finally, the dried strips were cured using Carver Hydraulic hot press at 130 °C for 20 min under a pressure of 8 MPa to fabricate advanced green composites in sheet forms. All composite sheets were conditioned at 21 °C and 65% RH for 24 h before testing.

2.5. Characterization

The linear density and effective diameter of the fibers were measured by vibroscope method according to ASTM D1577-07 [14]. The vibroscope consisted of a system for applying an oscillatory force of known frequency to a single fiber under a known tension to determine the 1st order mechanical resonance under the specific oscillatory force. Surface morphology of the fibers was characterized using LEO 1550 field emission scanning electron microscope (FESEM) at 3 kV accelerating voltage. X-Ray diffraction (XRD) patterns of the fibers were recorded on an X-Ray diffractometer (Scintag theta-theta, Scintag Inc., Cupertino, CA) to determine their crystallinity. The diffractometer was equipped with $\text{CuK}\alpha$ radiation ($\lambda = 1.54 \text{ \AA}$) at 40 kV and 20 mA. The data were recorded in the range of 5°–40° Bragg angles (2 θ) at a scan

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