Facile Fabrication of Cellulosic Paper-based Composites with Temperature-controlled Hydrophobicity and Excellent Mechanical Strength

Tongtong Yun, Yilin Wang, Jie Lu, Yi Cheng*, Yanna Lyu, Haisong Wang*

School of Light Industry and Chemical Engineering, Dalian Polytechnic University, Dalian, Liaoning Province, 116034, China

Abstract: In this paper, we presented a novel strategy to employ a plant-derived carbohydrate polymer, i.e., cellulose, to prepare a hydrophobic composite. Cellulose was used as a scaffold, and ethylene-propylene side by side (ES) fiber was thermally melted and then coated on the cellulose surface to achieve hydrophobicity. Experimental results revealed that the thermo-coating ES fibers greatly increased the water contact angle of the cellulose scaffold from 25° to 153° while simultaneously enhanced the wet tensile strength of the composite approximately 6.7-fold (drying temperature of 170°C) compared with the pure cellulose paper. In particular, compared with other related research, the prepared cellulose-based composite possessed excellent hydrophobicity and superior mechanical strength, which introduces a new chemical engineering approach to prepare hydrophobic cellulose-based functional materials.

Keywords: cellulose; ES fiber; paper-based composites; hydrophobicity; mechanical strength
DOI: 10.12103/j.issn.2096-2355.2020.02.002

1 Introduction

Functional materials with hydrophobicity have extensive industrial applications due to their fascinating chemical and physical properties [1-5]. Generally, hydrophobic surfaces have been developed on a series of inorganic and organic materials [6-7], which can be characterized by low surface energy and surface roughness [8-9].

Received: 8 January 2020; accepted: 17 February 2020.
Nevertheless, the most traditional hydrophobic materials are not fabricated from renewable and biodegradable materials \(^{(16)}\). Cellulose is the main component of plant cell walls and plays a vital role in mechanical support for plants \(^{(11-12)}\). Cellulosic fiber-based products have been widely used as packaging materials due to their favorable properties, such as superior mechanical strength, low-cost, biodegradability, renewability, and environmental friendliness \(^{(13)}\). Cellulose-based hydrophobic composites could have great potential for use in microfluidic devices, oil/water separating membranes, packaging materials, and bioactive substrates \(^{(14-17)}\).

However, cellulose has numerous hydroxyl groups and a complex hydrogen bonding system, which gives cellulose superior hydrophilicity. Making hydrophilic cellulose hydrophobic while keeping its superior mechanical strength could therefore open up new pathways for practical applications of cellulose-based functional composites \(^{(9)}\). Traditional hydrophobic materials are normally fabricated on the substrates of silicon wafers \(^{(18)}\), glass slides \(^{(19)}\), polymeric materials \(^{(20-21)}\), and metal-oxide surfaces \(^{(22)}\). Using cellulose as the scaffold for preparing a hydrophobic composite is still under studied. Although cellulose-based hydrophobic composites have been developed using dip-coating \(^{(17)}\), doctor blade-coating \(^{(23)}\), spray-coating \(^{(14)}\), plasma processing \(^{(1,10)}\), layer-by-layer deposition \(^{(24)}\), and liquid flame spray \(^{(15)}\), most of these methods severely damage cellulose's chemical, physical, and thermal depolymerization \(^{(25-26)}\). Other pathways to give cellulose hydrophobicity include internal sizing, surface sizing, and conventional barrier coating layers, all of which can add hydrophobic layers to cellulose \(^{(9)}\). However, these methods are normally accompanied by high cost, deterioration of the mechanical strength and recyclability of the cellulose-based composite. Overall, a simple and effective way to prepare cellulose-based hydrophobic composites with superior mechanical properties is still required.

To address this challenge, we developed a novel, feasible, and effective approach to prepare hydrophobic cellulose-based composites by simply thermo-fusing ethylene-propylene side by side (ES) fiber to embed cellulose fibers. ES fiber is a new type of heat-bonding composite fiber that is inherently hydrophobic \(^{(27)}\). Meanwhile, its skin-core structure, with different melting points, is very likely to provide controllable hydrophobicity and mechanical properties via changing drying temperature. Additionally, non-woven fabric molded materials without a binder can be formed due to the hot-melted ES fibers acting as a binder between fibers \(^{(28)}\), which can be applied to prepare wet-strength materials, such as the functional wet wipes \(^{(28-30)}\). The experimental results demonstrated that the prepared hydrophobic cellulose-based composite possessed excellent mechanical strength given by cellulose as a scaffold, and the thermally melted ES fibers on the cellulose surface make the as-prepared composite hydrophobic. Therefore, the resultant cellulose/ES composite thus achieved temperature-controlled hydrophobicity and superior mechanical strength simultaneously, which gives it potential to be applied in the manufacturing of functional cellulose-based materials.

### 2 Experimental

#### 2.1 Materials

Softwood kraft pulp (average cellulose DP of 1190; cellulose, hemicellulose and lignin contents of 86.3%, 12.2% and 1.5%, respectively) was a product of the Asia Pacific Semper (Shandong) Pulp & Paper Co., Ltd. ES fiber was purchased from Liaoning Forest Wood Paper Co., Ltd. Calcium carbonate, talcum, and wollastonite were purchased from Sinopharm Chemical Reagent Co., Ltd.

#### 2.2 Pulp refining

Softwood kraft pulp was refined according to TAPPI standardized method T248 sp-08 \(^{(1)}\), in which dry fiber sheets were soaked in deionized water overnight and then loaded in a PFI (Pulp and Fiber Research Institute) refiner (Test Machines Inc.) and exposed to different levels of refining, as defined by the number of revolutions. The beating degrees of softwood kraft pulp

---

Vol.5, No.2, 2020 | 21
used in this experiment were 45°SR, 55°SR, and 65°SR. The refining of softwood kraft pulp was determined according to GB/T 3332—1982.

2.3 Fabrication of cellulose-based composite

The pulp after refining was diluted with water to a concentration of 0.2%~0.5% (pulp concentration for papermaking according to ISO 5269/2—1980). The ES fiber was mixed with the softwood fiber with different mass ratios of 2%~14% (drying temperature of 170°C, beating degree of 45°SR). The cellulose-based composites were formed following TAPPI standardized method T205 sp-02. The prepared composites were dried in two stages: drying in a hot press at 100°C and 1.1 MPa for 5 min and then on a hot plate for 20 min at temperatures of 135°C or 170°C to melt the ES fiber and form a coating on the cellulose surface.

2.4 Characterizations

The mechanical strength of the cellulose-based composite was tested after hanging overnight at (23±0.1)℃ and relative humidity of (50±0.2)%. The thickness and basic weight of the cellulose-based composite were measured before the mechanical properties test. The dry tensile strength (DTS) of the cellulose-based composite (machine direction) was determined using a horizontal tensile testing machine (Frank-PTI company, Germany). The specimens were cut to dimensions of 15 mm×150 mm with a span distance of 25 mm. To measure the wet tensile strength (WTS), the cellulose-based composite was dipped in distilled water for 1 h and then immediately subjected to tensile strength measurement. Nine samples were measured for each experiment to give an average result.

Water contact angles (WCA) were measured using optical tensiometer apparatus (Biolin Science Co., Ltd., Finland). The reported WCA are the averages of five measurements, which were carried out on different areas of each sample. The bouncing process of 5 μL de-ionized water droplets on the composite surface was recorded via a high-speed camera at 14 frames per second.

The morphologies of the cellulose-based composite surface were investigated by scanning electron microscopy (SEM; JEOL, JSM-7800F) operated at 25 kV. Gold-palladium (12 nm) was coated on the samples prior to the SEM test.

3 Results and discussion

3.1 Effect of ES fiber amount on WTS of cellulose/ES composite

As shown in Fig.1, our proposed method to fabricate a cellulose-based hydrophobic composite was to thermally melt the ES fibers to derive an ES-coated cellulose matrix, which was a relatively facile and implementable strategy.

The effect of ES fiber amount (%) on the wet tensile index of the cellulose-based composite (45°SR, 100°C) is shown in Fig. 2, the wet tensile index of pure cellulosic paper is 3.82 N/m/g. Moreover, the wet tensile index of the cellulose/ES composite is less than that of the pure cellulosic paper when ES fiber amount

Fig.1  Schematic illustration of the fabrication and structure of the proposed cellulose-based hydrophobic composite
was less than 7%. A possible reason for this is that the internal skeleton of the cellulose paper was destroyed by adding a small amount of ES fibers. The wet tensile index of the cellulose-based composite increased as the ES fiber amount increased and reached the maximum value (4.58 N·m/g) when the ES fiber amount was 10% (mass ratio of cellulose to ES fiber is 9:1). The ES fibers were melted after being heated, which could act as an adhesive between fibers in the composite and thus render the increase in the wet tensile index of the cellulose-based composite. When the ES fiber amount was more than 10%, it cannot be uniformly distributed in the cellulose matrix, resulting in a decrease in the wet tensile index. Nevertheless, the WTS of the cellulose/ES fiber augmented when the amount of ES fiber added to the cellulose increased, which could have been the result of a newly formed strong hydrogen bonding system between the cellulose and ES fibers [27]. Overall, the cellulose-based composite with the maximum WTS was prepared by adding 10% ES fiber. The amount of ES fiber was thereby set at 10% for the remaining experiments in this study.

3.2 Effect of cellulose refining on WTS of cellulose/ES composite

The pulp is usually dissociated prior to PFI refining so that the interwoven fiber bundles can be disintegrated into individual fibers by mechanical disintegration while maintaining the inherent state of the fibers. Refining involves treating the fibers in water with mechanical force to make the fibers swollen and finely fiberized. Refining can generally increase the specific surface area of the fibers and produce additional free hydroxyl groups on the surface of the fibers. Meanwhile, refining could also reduce the fiber length and increase the fines content. The effect of beating degree of softwood pulp on WTS of the cellulose-based composite is shown in Fig.3. The wet tensile index of the cellulose-based composite increased from 24.3 N·m/g to 25.3 N·m/g with beating degree rising from 45°SR to 55°SR. This is due to a deficiency in the fibrillation degree of the interior softwood fiber, which led to the number of hydrogen bonds between the softwood fibers being insufficient when the beating degree was lower (45°SR). Meanwhile, ES fibers after thermal dissolution cannot increase the strength of cellulose-based composite much by filling the holes formed between softwood cellulosic fibers for the number of which has been reduced. The cellulose-based composite (mass ratio of softwood fiber to ES fiber of 9:1) had the maximum wet strength when the beating degree of the softwood pulp was 55°SR. Furthermore, the wet tensile index of the cellulose-based composite decreased when the beating degree of softwood pulp was 65°SR, which could be attributed to the followings: (1) the hydrogen bonds between the softwood cellulosic fibers were enhanced and thus made it difficult for the melted ES fibers to enter the holes between the softwood cellulosic fibers [28] or (2)
the softwood cellulosic fiber was excessively cut off, which affected the WTS of the cellulose-based composite \(^{29}\). The wet tensile index of the cellulose-based composite reached its maximum value when the beating degree of softwood pulp was 55°SR, which could be attributed to the fact that the fiber length, length-width ratio, contact area between fibers, and hole sizes were well balanced \(^{30}\).

3.3 Hydrophobicity endowed from ES fibers during compositing

To investigate the effect of ES fibers on the hydrophobicity of the cellulose-based composite, the WCAs of composite at different drying temperatures were measured and are shown in Fig. 4. The WCA of the cellulose-based composite was much improved when the drying temperature increased. Meanwhile, the cellulose-based composite was changed from hydrophilic to hydrophobic. The improvements in the hydrophobicity of the cellulose-based composite was attributed to the ES fiber that mainly consists of hydrophobic polyethylene and polypropylene. When the drying temperature was 135°C, the polyethylene in the surface layer was thermally melted and partially filled the pores between the softwood cellulosic fibers, preventing the capillary pores from adsorbing water. When the drying temperature was 170°C, both the polyethylene and polypropylene in the surface and core layers were melted (Fig. 1), which could fill the pores between cellulosic fibers and cover the surface of the hydrophilic fibers. Therefore, the addition of the hot-melted ES fiber imparted the hydrophobic property on the cellulose-based composite surface and therefore greatly improved the WTS of the cellulose-based composite \(^{24}\).

3.4 Mechanical strength endowed from ES fibers during compositing

The effect of drying temperature on the wet tensile index of the cellulose-based composite is shown in Fig. 5. The wet tensile index of the cellulose-based composite increased from 5.1 N·m/g to 25.3 N·m/g when the drying temperature raised from 100°C to 170°C. This can be attributed to the inherent properties of ES fiber, which is a two-component sheath-core composite fiber. The skin layer in the ES fiber has a low melting point (approximately 130°C) and excellent flexibility, while the core layer has a high melting point (approximately 165°C) and possesses high mechanical strength.

![Fig. 4 Effect of drying temperature on the water contact angle of the cellulose-based composite](image)

![Fig. 5 Effect of drying temperature on the wet tensile index of the cellulose-based composite](image)

When the drying temperature was 100°C, the core layer of the ES fiber did not reach the melting point, and the ES fiber was thus unable to increase the WTS of the cellulose-based composite through pore filling effect \(^{31}\). Moreover, such addition of ES fibers can also hinder the formation of hydrogen bonds between softwood cellulosic fibers at lower drying temperature, which could further decrease the WTS of the resultant
cellulose-based composite compared with that dried at higher temperature \(^{[31]}\). When the drying temperature was 135\(^\circ\)C, the portion of the ES fiber with a lower melting point was thermally melted, which caused a fractional adhesion effect between the softwood pulp fibers, significantly improving the WTS of the cellulose-based composite. When the drying temperature reached 170\(^\circ\)C, both the skin and core layers of the ES fiber were melted, which filled the gap formed by the interlacing cellulose fibers and exerted a viscose effect between the fibers (Fig. 1). Thus, the WTS of the cellulose-based composite was further enhanced \(^{[32]}\). In addition, the composite dried at 170\(^\circ\)C had the highest WTS (wet tensile index=25.3 N-m/g), which is consistent with the result of drying temperature's effect on the hydrophobic properties. Therefore, 170\(^\circ\)C was selected as the optimal drying temperature in the subsequent experiments.

3.5 Surface morphology of cellulose/ES composite

An SEM image of the pure softwood cellulose paper at 100\(^\circ\)C is shown in Fig. 6(a). The softwood pulp fiber inside the pure cellulose paper was markedly fibrillated, and the surface was rough and had many pores. The SEM images of the cellulose-based composite dried at 100\(^\circ\)C, 135\(^\circ\)C, and 170\(^\circ\)C are shown in Fig.6(b)–Fig.6(d), respectively. It can be clearly seen that the ES fiber is smooth and not fibrillated when the drying temperature was 100\(^\circ\)C (Fig. 6(b)). The wet tensile index of the cellulose-based composite was only 5.1 N-m/g due to the smooth ES fiber being unable to generate an effective combination with the softwood pulp fiber. As shown in Fig. 6(c), when the drying temperature was 135\(^\circ\)C, the surface layer of the ES fiber was partially melted, which strengthened the adhesion effect between the ES fibers and cellulose fibers so that the WTS of the cellulose-based composite increased (Fig. 5). When the drying temperature was 170\(^\circ\)C, both the surface layer and core layer of the ES fiber were melted to a greater extent (Fig.1 and Fig. 6(d)), which formed a hydrophobic structure because the pore filling effect led to a smoother surface.

3.6 Comparisons of cellulose/ES composite with other hydrophobic materials

As shown in Fig.7, the obtained cellulose/ES composite was compared with other reported cellulose-based composites that focused on simultaneously improving the hydrophobicity and mechanical properties. In a previous study, Li et al. \(^{[29]}\) successfully fabricated hydrophobic cellulosic papers using layer-by-layer technology for depositing multilayer of TiO\(_2\) nanoparticles/sodium alginate (TiO\(_2\)/ALG)\(_{x,y}\) on a cellulose paper surface followed by adsorption of colloidal carnauba wax. The WCA of the paper reached up to 151\(^\circ\) along with a dry tensile index of 41.5 N-m/g (Fig. 7). Our proposed cellulose-based composite had significantly better dry tensile index (68.7 N-m/g) while simultaneously achieving comparable hydrophobicity (WCA=153\(^\circ\)). Moreover, minerals such as precipitated calcium carbonate (PCC), clay, and talc have been added to cellulose fiber to improve its hydrophobicity and mechanical properties \(^{[9]}\). As shown in Fig. 7, all these cellulose/mineral composites had slightly lower hydrophobicity but much lower mechanical strengths compared with cellulose-based composite prepared in this work. Furthermore, it should be noted that the preparation of all these cellulose/mineral composites used oxygen plasma and fluorocarbon deposition plasma, which are uneconomical and non-environmentally friendly compared with our simple thermal fusion method.
This work was supported by Natural Science Foundation of China (No. 31770624 and No. 21978029), National Key R&D Program of China (No. 2018YFD0400703), Natural Science Foundation of Liaoning (No. 20170540069), the Program for Liaoning Excellent Talents in University (LR2016058) and Liaoning Million Talents Program (201945).

4 Conclusions

In this work, the double-layer ethylene-propylene side by side (ES) fiber and softwood kraft pulp cellulose were thermally bonded to prepare a cellulose-based hydrophobic composite. The results showed that our as-prepared cellulose/ES composite perfectly achieved controllable hydrophobicity and mechanical strength by adjusting the drying temperature. The wet tensile index of the novel hydrophobic cellulose-based composite can reach as high as 25.3 N m/g (drying temperature of 170℃). Moreover, the water contact angle of the composite paper reached 153° when the drying temperature was 170℃. This research using thermally melted ES fibers thus presents a facile method to synchronously achieve hydrophobicity and mechanical strength of cellulose-based composite. More importantly, our cellulose/ES composite exceeded most previously reported cellulose-based hydrophobic materials in both hydrophobicity and mechanical strength. Therefore, by making a hydrophobic cellulose-based composite using a simple thermal fusion method, this research paves a new way to prepare cellulose functional products with excellent waterproofing property and wet strength.

Acknowledgments

This work was supported by Natural Science Foundation of China (No. 31770624 and No. 21978029), National Key R&D Program of China (No. 2018YFD0400703), Natural Science Foundation of Liaoning (No. 20170540069), the Program for Liaoning Excellent Talents in University (LR2016058) and Liaoning Million Talents Program (201945).

References


