Eco-friendly Modification for the Cellulose Nanofibers Derived from Pineapple Leaves for High-performance Nanocomposite

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Abstract. This study extracted cellulose nanofibers (NFC) from pineapple leaves, and then employed eco-friendly aqueous system to modify NFC with a layer of polystyrene (PS). The successful modification was confirmed by FTIR analysis, after acid-base treatment can effectively reduce the lignin content and better water transport, and the PS layer could lower NFC’s surface polarity for improving the interfacial compatibility in PS matrix. By introducing NFC into PS matrix, the PS-modified NFC showed better interfacial adhesion and uniform dispersion, and resulted nanocomposite with higher tensile strength, char yield and transparency. Therefore, the eco-friendly modification could help NFC reinforce nanocomposite for enhancing mechanical property, thermal resistance and transparent appearance.

1. Introduction

Traditional petroleum-based plastic has good plasticity, high strength and durability, and is widely used in commodity and industry. Regarding to the unpredictable petroleum price and supply, it becomes important to develop biomass materials for replacing part of petroleum and creating high-performance composite. Natural fibers are considered as ideal reinforcement candidate due to stiffness, abundant and sustainable sources, and biodegradability.[1]

Among natural fibers,[2] cellulose nanofibers (NFC) has attracted much attention because of light, excellent strength, high surface area, and high aspect ratio. However, cellulose surface is very hydrophilic and hard to be well-dispersed in polymer matrix. Generally, surface polarity of NFC can be adjusted by modification, which is usually based on organic solvent system.[3] For environmental protection and low cost, this study established extraction of NFC from pineapple leaves,[4][5] and aqueous-based modification to functionalize NFC with a layer of polystyrene (PS). The PS-modified NFC was also used to fabricate PS-based nanocomposite with high mechanical property, thermal resistance and transparency.[6]

2. Experiment

2.1. Preparation of NFC (named as OF)

The raw pineapple leaves were chopped, sun-dried, crushed, and further treated with a NaOH solution to remove lignin, hemicellulose and impurities. Subsequently, it was neutralized by HCl solution as shown in Scheme 1, washed by water, and then dried for obtaining pineapple leaves fiber (PLF). PLF
was further bleached in the acetate buffer solution containing NaClO2 at pH 4.8 and 60°C for 3 h. In the end, the bleached PLF was purified by water and stored at 4°C before further treatment. The bleached PLF (0.7 g) were suspended in a sodium phosphate buffer (90 mL, pH 6.8) containing TEMPO, NaClO2, and NaClO. The TEMPO-mediated oxidation was started and kept at 60°C by stirring at 500 rpm for 3.5 h. After washed by water, the TEMPO-mediated oxidation and purification were repeated again. In the end, PLF was nanofibrillated by homogenization at 6000 rpm, and the obtained NFC (named as OF) was stored after freeze-drying.

![Scheme 1. Chemical pretreatment of PLF.](image)

2.2. **Surface modification**
Dried OF, 0.6g of styrene monomer, 0.018g of initiator (AIBN), and 0.0124g of dispersant (PVA) were mixed in distilled water, and the solution was stirred continuously at 75°C for 6 h to execute suspension polymerization. The PS-modified NFC (named as PF) was obtained after filtration, washing by distilled water, and freeze-drying.

2.3. **Preparation of nanocomposite**
The PS pellets, NFC (PF or OF) were mixed according to the formulation shown in **Table 1**. The NFC (PF or OF) and PS pellets were blended at 160 °C in a counter-rotating internal mixer with a rotation speed of 50 rpm. After being well blended for 5 minutes, the PS nanocomposite was granulated by compression molding at 160°C.

| Sample       | PS (wt%) | PF (wt%) | OF (wt%) |
|--------------|----------|----------|----------|
| PS           | 100      | -        | -        |
| PONFC0.5     | 99.5     | -        | 0.5      |
| PONFC1.0     | 99.0     | -        | 1.0      |
| PONFC3.0     | 97.0     | -        | 3.0      |
| PSNFC0.5     | 99.5     | 0.5      | -        |
| PSNFC1.0     | 99.0     | 1.0      | -        |
| PSNFC3.0     | 97.0     | 3.0      | -        |

3. **Results and Discussion**

3.1. **FTIR**

The FTIR spectra of styrene, OF and PF are shown in **Figure 1**. Styrene monomer exhibits C-H peaks at 695 cm⁻¹ and 906 cm⁻¹, and C=C peaks at 1494 cm⁻¹ and 1630 cm⁻¹. OF and PF have a broad peak at 3400-3600 cm⁻¹, which is contributed by the OH stretch. In OF, the peak donated by lignin at 1735 cm⁻¹ disappears, indicating the acid/base chemical pretreatment and TEMPO-mediated oxidation successfully remove lignin and impurity from PLF. The existence of CH3 and CH2 peak
and C-O-C peak (1059 cm⁻¹) demonstrates the successful carboxylation of OF by TEMPO-mediated oxidation. In PF, the aromatic C-H vibration (696 cm⁻¹ and 900 cm⁻¹) and aromatic C=C (1492 cm⁻¹ and 1601 cm⁻¹) peaks explain the existence of polymerized styrene on NFC surface.

Figure 1. FTIR spectra of (1) styrene, (2) OF and (3) PF.

3.2. Contact angle

Surface polarity of NFC can be represented by surface hydrophilicity, and here the surface hydrophilicity is characterized in terms of contact angle, as shown in Figure 2. OF has low contact angle of 12.02°, indicating extremely high hydrophilicity and surface polarity. After PS-modification on PF surface, the contact angle increases to 114.49°. PF surface displays highly hydrophobic and low polarity, and that are helpful to improve compatibility between PF and PS matrix in nanocomposite.

Figure 2. Contact angle of water droplets on the surface of (a) OF and (b) PF.

3.3. Tensile strength

The tensile test of nanocomposites containing 0.5-3% NFC is shown in Table 2. Pristine PS performs tensile strength of 23.1 MPa, and all the nanocomposites containing OF or PF can improve tensile strength. At same NFC content, PF reinforces nanocomposite more significantly than OF does. NFC has high tensile strength, aspect ratio and surface area, so it can effectively strengthen nanocomposite. In PONFC nanocomposites, PONFC1.0 performs the highest improvement of 15.6%; in PSNFC nanocomposites, PSNFC exhibits the best improvement of 34.6%. By modifying with a PS layer on
the NFC surface, the interfacial compatibility and adhesion between PF and PS matrix are enhanced. As a result, PF can disperse homogeneously in nanocomposite and boost mechanical property.

**Table 2.** Physical properties of nanocomposites

| Sample       | Mechanical properties | Heat resistance | TGA analysis |
|--------------|-----------------------|-----------------|--------------|
|              | Tensile strength (MPa) | HDT (°C)        | Td5 (°C)     | Char yield at 550°C (%) |
| PS           | 23.1±0.5              | 90.3±0.60       | 389.3        | 0.38                      |
| PONFC0.5     | 24.6±0.7              | 92.9±0.70       | 378.9        | 0.43                      |
| PONFC1.0     | 26.7±1.1              | 92.7±0.70       | 373.9        | 0.74                      |
| PONFC3.0     | 25.2±1.1              | 92.6±0.89       | 338.7        | 1.70                      |
| PSNFC0.5     | 26.4±1.7              | 92.2±0.21       | 384.3        | 0.46                      |
| PSNFC1.0     | 31.1±2.0              | 92.8±0.74       | 329.8        | 2.41                      |
| PSNFC3.0     | 29.4±1.1              | 92.6±0.64       | 314.6        | 4.18                      |

3.4. Thermal properties

As shown in **Table 2**, pristine PS has HDT of 90.3°C, and OF and PF can slightly improve nanocomposites’ HDT about 2-3%. So, the increasing HDT means that nanocomposites perform better thermal resistance.

The TGA analysis is shown in **Figure 3**, and the decomposition temperatures at 5% weight-loss (Td5) and char yield are summarized in **Table 2**. Pristine PS has Td5 of 389.3°C and char yield of 0.38%. After introducing OF or PF into nanocomposite, the Td5 decreases and char yield gets higher. The Td5 decrement is proportional to the NFC amount. NFC, including OF and PF, has lower decomposition temperatures than PS, and results nanocomposites with lower Td5. In addition, NFC has high specific surface area, and that increases the heated area for early decomposition at lower temperature. Also, OF and PF decompose to form a carbon layer and elevate char yield, that can prevent PS matrix from further decomposition. Basically, more NFC amount generates higher char yield. For example, PSNFC3.0 has char yield of 4.18%.

![Figure 3. TGA analysis of nanocomposites.](image)

3.5. Transparency
It is observed in Figure 4 that PSNFC nanocomposites are more transparent than PONFC nanocomposites. OF has high surface polarity as confirmed in contact angle test, and it easily aggregates in PS matrix. As a result, the OF disperses heterogeneously and generates blurred appearance. On the other hand, PF is modified a PS layer on NFC surface, and successfully decreases surface polarity as confirmed in contact angle test. The low surface polarity improves the compatibility between PF and PS matrix, and therefore PF disperses homogeneously in nanocomposite. In consequence, the well-dispersed PF makes the PSNFC nanocomposite very transparent to the naked eye.

Figure 4. Nanocomposites’ appearance and transparency: (a) PONFC0.5, (b) PONFC1.0, (c) PSNFC0.5, and (d) PSNFC1.0

4. Conclusion
This study successfully used eco-friendly synthesis to modify NFC surface with a PS layer, as confirmed by the existence of aromatic functional groups in FTIR analysis. The modified NFC (PF) increased surface hydrophobicity, and the contact angle of water droplet reached 114.49°. The surface modification improved interfacial compatibility and adhesion between NFC and PS matrix, and made PF uniformly dispersed in nanocomposite. As a result, the PF-based nanocomposite performed transparency, high tensile reinforcement (34.6% improvement at 1% PF), and good thermal resistance.

5. References
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