Butane Tetracarboxylic Acid as Green Modifier for Tuned Hydrophilicity of Surface Modified Cellulose

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Abstract. This study proposes one straightforward way for butane tetracarboxylic acid modification of cellulose nanofibrils (CNF). Esterified cellulose nanofibrils (ECNF) were characterized using Fourier Transform Infrared Spectroscopy (FT-IR), scanning electron microscopy (SEM), transmission electron microscopy (TEM). The reaction mechanism between tetracarboxylic acid modification and CNF was discussed. The resultant ECNF exhibited improved hydrophobicity in water compared with pure CNF. These results confirmed how esterified (ECNF) biobased nanoparticles with tuned hydrophilicity, obtained by treatment with a low cost, sustainable and easily soluble cross-linker, have the potential for widespread applicability in the field polymeric based nanocomposites having different polarity.

1. Introduction
Nanocellulose is a general term for cellulose with one or more dimensions on the nanometer scale. Not only nanocellulose retains regenerative and biodegradable characteristics of natural cellulose, but it also has the advantages of large specific surface area, high strength (110-220 GPa), low density\textsuperscript{[1]} (1.6 g/cm\textsuperscript{3}) high aspect ratio, extensive chemical modification, and is excellent candidate materials as reinforcing fillers. The high aspect ratio enables excellent stress transfer between the filler and the matrix. However, nanocellulose is rich in abundant hydroxyl, resulting in incompatible hydrophobic thermoplastics and poor interfacial adhesion between the fillers and polymer matrix. This dramatically limits the utilization of nanocellulose fillers for reinforcement.

To enhance the interactions between the cellulose surface and polymers, thereby improving its dispersibility among the composite properties, chemical modifications such as acidification\textsuperscript{[2]}, etherification\textsuperscript{[3]}, urbanization, silane coupling,\textsuperscript{[4]} and polymer grafting through surface-initiated radical polymerization and ring-opening polymerization, have been performed. Meanwhile, hydrogen bonding, electrostatic interactions, and physisorption have also been used. However, the chemical modification of nanocellulose is mainly carried out in solvent system\textsuperscript{[5]}, which requires multiple solvent replacement, resulting in a complex modification process, longer treatment cycle, more waste liquid, and severe environmental pollution, which is not suitable for the large-scale and industrial preparation of nanocellulose reinforced polymer\textsuperscript{[6]}.

In this study, a combination of freeze-drying and chemical modification can be used to prepare large quantities of modified nano-cellulose powder. Specifically, the chemical modifier BTCA and nanocellulose were mixed uniformly in a water/tert-butanol system and then freeze-dried to obtain...
nanocellulose aerogel. Then, the aerogel was placed at 170℃ for 3 min to bring the surface esterification modified nanocellulose aerogel powder. BTCA is a polycarboxylic acid compound, which can be easily esterified with the hydroxyl group of nanocellulose. By controlling the addition amount of BTCA\(^\text{[7]}\), the degree of modification can be well controlled. In addition, the modification method is carried out in the dry state, which can reduce the use of a large number of organic solvents for the modification of conventional nanocellulose. The addition of tert-butyl alcohol can affect the growth of ice crystals and the aggregation of nanocellulose, which ensures that the nanocellulose aerogel powder has a suitable microstructure.

2. Experiment

2.1. Experimental material and setups

The nanocellulose was pretreated with inorganic acid and then homogenized under high pressure. 1,2,3,4-butane tetracarboxylic acid (BTCA, 99%) was purchased from Sigma-Aldrich Co. Sodium hypophosphite monohydrate (SHP, 98%) as a catalyst for the reaction of BTCA with CNF. All the reagents used are analytical grade and without further purification.

2.2. Preparation of CNF aerogels

The CNF aqueous suspensions (0.2 wt%) was mixed with t-BuOH and water at different mass ratios (5/5), as shown in Table 1. Then they were poured into a high-speed disperser (Ultra-Turrax, IKA) by vigorous stirring for 12 h to get the homogenous suspensions. And the amount of SHP was always the same as the BTCA. The mixed suspensions were poured into cylindrical or rectangular moulds and freeze-dried in a lyophilizer (TELSAR LYOBETA MINI, Spain) at a condenser temperature of −85 °C for three days. The crosslinking of aerogels were achieved by curing the freeze-dried samples containing the cross-linker in a vacuum oven at 170 °C for 3 min to perform sufficient covalent crosslinking. For comparison, neat CNF aerogels and BTCA crosslinked CNF aerogels were also fabricated according to similar procedures as mentioned above. The macroscopic morphologies of all the prepared aerogels were white with well-defined shapes, as shown in Figure 1.

| Sample | t-BuOH(ml) | Water(ml) | BTCA(g) | SHP(g) | CNF(g) |
|--------|------------|-----------|---------|--------|--------|
| 1      | 25         | 25        | 0.003   | 0.0015 | 1.5    |

Figure 1. Schematic illustration for the experimental process.

2.3. Characterizations

The nanocellulose suspension sample was diluted with deionized water to a mass fraction of 0.1% and ultrasonic for two minutes with a Sonics(VCX 1500HV) ultrasonic dispersion instrument. The sample
was dropped onto a TEM network and stained with uranium dioxide acetate. Shot by Tecnai G2 F20 S-TWIN (200KV).

Morphology of freeze-drying CNF aerogel was conducted under 2500 magnification using an SEM system (S-4800, Hitachi, Japan). All samples were sputter-coated with gold before testing.

The chemical compositions of the neat CNF aerogel and esterified crosslinking CNF aerogel were analyzed via Fourier transform infrared (FTIR) spectroscopy (Nicolet IS10, Madison, WI) in the range of 4000–500 cm⁻¹ with a resolution of 4 cm⁻¹. All tests were repeated three times.

3. Results and Discussions

3.1. cellulose nanofibrils structure analysis

Figure 2. (a)TEM figure of cellulose nanofibrils suspension (b)Diameter distribution of cellulose nanofibrils(c)(d)SEM figure of freeze-dried cellulose nanofibril aerogel.

**Fig2(a)** shows the morphology of the prepared cellulose nanofibrils, and the average length of cellulose nanofibrils is between 100nm and 250nm. The addition of tert-butyl alcohol effectively prevented the agglomeration and keratinization of nanocellulose, as shown in **Fig(c-d)**.

Similar to previous reports in the literature, the possible reasons for this phenomenon are tert-butyl alcohol can accelerate this drying rate due to its higher vapour pressure (4.1 KPa at 20 °C) and lower boiling point (82.2 °C) firstly, and reduce the shrinkage degree of nanocellulose during drying process because of its low surface tension. More critical, water/t-BuOH mixture can reduce interfibrillar contacts and adhesion by giving more interfibrillar connections and bonding due to larger molecular size than water.
3.2. cellulose nanofibrils structure analysis

Fig. 3(a) shows the FTIR spectra of the neat CNF aerogel and CNF/BTCA/SHP aerogel. The FTIR spectra of all of the samples exhibited broadband from 3100 to 3400 cm\(^{-1}\) and a strong peak at 2910 cm\(^{-1}\), which were assigned to the O-H and C-H stretching vibrations, respectively. The crosslinking reaction between the cellulose nanofibrils and BTCA occurs through transesterification reactions between the hydroxyl groups of cellulose and carboxylic acid groups of BTCA.

And the specific process, as shown in Fig. 3(b), is that Na\(^+\) react with carboxylic acid groups and transform them into corresponding carboxylates with the catalyst SHP. The strong hydrogen bonding is weakened because of the polar groups such as C=O and O-H\[^{9}\]. With the temperature increasing, cyclic anhydrides gradually form from free carboxylate and carboxylic acid groups. They immediately undergo esterification with O-H groups in cellulose and achieve crosslinking.

The aerogel prepared by the modified crosslinking method has certain hydrophobicity and can maintain its shape in the water.

4. Conclusions
In summary, we successfully prepared a nanocellulose and changed its hydrophilicity by BTCA esterification and crosslinking. FTIR shows that we have successfully modified the aerogel and retains its shape in water rather than dispersed out. Compared with other modification methods, our one-step modification method does not use organic solvents, and the process is simple, environmentally friendly and suitable for industrial production.

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