Surface Modification of the Cellulose Nanofiber Extracted from Wood Powder

Shinichiro CHIKU, Kentaro Abe*, Fumiaki Nakatsubo* and Hiroyuki Yano*
Murata Manufacturing Co., Ltd., 1-10-1 Higashi-Kotari, Nagaokakyo 617-8555 Kyoto, Japan
Fax: 81-45-939-7157, e-mail: tiku@murata.co.jp
*Research Institute for Sustainable Humanosphere, Kyoto University, Gokasho, Uji 611-0011 Kyoto, Japan

Wood powder, after chemical removal of lignin and hemicellulose, was mechanically disintegrated into cellulose nanofiber. Focused on piezoelectricity, polarized optics and other applications with isotropic media, we attempted two different modifications (cyanoethylation and cyanoethylated dihydroxypropylation) of the nanofiber surfaces to decrease interfibrillar hydrogen bonds to enable uniaxial elongation and isotropic film orientation. Synthesized surface cyanoethylated cellulose nanofiber has no glass transition near the room temperature and was difficult to elongate uniaxially. Cyanoethylated dihydroxypropylcellulose nanofiber was viscoelastic at the room temperature with a piezoelectric constant of $d_{14}=3.2\, \text{pm/V}$.

Key words: cellulose, nanofiber, fiber surface modification, cyanoethylation

1. INTRODUCTION

Cellulose is one of the main substances of the plant cell. Cellulose is an extended chain of polysaccharide consisting of several hundred to over ten thousand $\beta$-1,4 connected $D$-glucose units. In plants, there exists a hierarchical structure of cellulose. About ten to twenty cellulose molecular chains pack parallel and form a crystal-like fiber, called cellulose microfibril, which consists of slightly different two polymorphs $I_\alpha$ and $I_\beta$ [1]. The diameter of a cellulose microfibril is ca. 4 nm. We can also find the bundle of about ten to twenty cellulose microfibrils, called cellulose nanofiber (CNF), with a diameter of ca. 16 nm [2]. In the plant cell, CNFs built cross-linked structure fixed by lignins and hemicelluloses.

CNF, also single crystal-like as microfibril, exhibits functional characteristics such as optical birefringence, electrooptic effects, piezoelectricity etc. owing to its crystal structure of low symmetry. If we make simply a dried CNF film, fibers will be randomly arranged in the film plane and these characteristics do not emerge. To obtain them, we must arrange CNF in uniaxial orientation. But on the CNF surface, there are many hydroxyl groups which cause strong interfibrillar hydrogen bonds fixing the position of a CNF to other fibers. Hence interfibrillar hydrogen bonds have to be weakened to realize the uniaxial orientation.

Many researches were examined for the uniaxial orientation of nanofiber or microfibril whiskers from dilute solution using their shape isotropy under the application of external strong force, for example shear force by rotating a vial [3] or magnetic force by a superconducting magnet [4]. Because of the low content of starting solutions and the tiny volume of force fields, fabricated uniaxial films were generally small and it was difficult to evaluate their functional characteristics.

Hirai et al. reported synthesis of cyanoethylated hydroxyethylcellulose molecule whose dried films can be easily elongated uniaxially above the room temperature [5,6]. Uniaxial films were large enough to evaluate their characteristics and showed high piezoelectric constant of $d_{14}=10–20\, \text{pm/V}$. The reason why the uniaxial elongation was possible should be because the cyanoethylated hydroxyethyl groups on the cellulose chain disturbed the ordered distribution of hydroxyl groups and decreased intermolecular hydrogen bonds. Referring to these results, we attempted to modify hydroxyl groups on the CNF surface to enable uniaxial orientation of crystal-like materials. We adapted two groups as modification agent, one, relatively shorter cyanoethyl group and the other, relatively longer cyanoethylated dihydroxypropyl group (Fig.1).

![Chemical structures of cyanoethylcellulose and cyanoethylated $O$-(2,3-dihydroxypropyl)cellulose](attachment:fig1.png)

1. $R$=$C_2H_4CN$ or $H$ for cyanoethylcellulose
2. $R$=$(CH_2-CH(CH_2O))_nC_2H_4CN$ or $H$ for cyanoethylated $O$-(2,3-dihydroxypropyl)cellulose

2. EXPERIMENTAL

2.1 Materials

We prepared CNF water gel from hinoki (chamaecyparis obtusa) wood powder [2]. All CNF fabrication was executed always in water medium to prevent cohesion. First, lignin and hemicellulose were
chemically removed from the wood powder. Then, the reacted material was mechanically disintegrated between two rotating whetstones into separated CNFs.

Glycidol (2,3-epoxy-1-propanol), GC grade of Kanto Chemical, was purified in vacuum distillation just before use. All other chemicals of reagent grade were used without further purification.

2.2 Cyanoethylation of CNF

We applied two methods for cyanoethylation of CNF. One, called “reflux method”, and the other, called “stirring only method”, which is often applied for the cyanoethylation of cellulose molecule [7].

In reflux method, 3.0 g of NaOH granule was little by little added to 30 g of CNF water gel concentrated to 3.3 wt. % in flask. After dissolution of the NaOH to the gel, 30.0 ml of acrylonitrile was added and the mixture was strongly stirred for 1 hour at the room temperature. The reacted liquid was neutralized by acetic acid. White precipitate was transferred to another flask in which 60.0 ml of acrylonitrile was added and refluxed at 78 °C for 1 hour. The cooled reacted material was poured into distilled water to make precipitate. The collected precipitate was transferred to another flask in which 60.0 ml of acrylonitrile was added and refluxed at 78 °C for 1 hour. The cooled reacted material was poured into distilled water precipitated again. This process was repeated further three times.

In stirring only method, 1.5 g of NaOH granule was little by little added to 33 g of CNF water gel concentrated to 3.0 wt. % in flask. After dissolution of the NaOH to the gel, 25.0 ml of acetonitrile and 30.0 ml of acrylonitrile (condition 1), or 50.0 ml of acetonitrile and 60.0 ml of acrylonitrile (condition 2), were added and the mixture was strongly stirred for 20 hours at the room temperature. The reacted liquid was neutralized by acetic acid. Collected precipitate, washed with distilled water, was solvated in acetone. Acetone solvation poured into distilled water precipitated again. This process was repeated further three times.

2.3 Cyanoethylated dihydroxypropylation of CNF

Cyanoethylated dihydroxypropylation of CNF was executed in two steps. The first step is dihydroxypropylation of CNF, and the second is cyanoethylation of reacted material. As to the dihydroxypropylation, Sato et al. [8] reported a homogeneous reaction system and Fukuda et al. [9] reported a heterogeneous reaction system. Here, homogeneous reaction means that uniform substitution occurs along cellulose molecular chains in nonaqueous solvent system, whereas, in heterogeneous reaction, cellulose solution was kept at 0 °C for hours to form, along chains, randomly distributed crystalline regions where reactivity is lower than amorphous or soluble regions. CNF is by nature single crystal-like; therefore we applied dihydroxypropylation reaction conditions referring to Fukuda et al.

At the first step, Disperse medium of CNF gel is replaced to 2-propanol from water using a centrifuge. 1.5 g of CNF dispersed in 175 ml of 2-propanol was put into a flask and strongly stirred at 50 °C. 0.9 g of NaOH aqueous solution was added to the flask, 20 ml to 150 ml of glycidol was dropped at the constant rate of 2.5 µl/s. The mixture was kept stirred for 24 hours after the completion of glycidol drop. The reacted liquid was neutralized by acetic acid. Precipitate was washed with acetone and was solvated in distilled water. Aqueous solution poured into acetone made precipitate again. This process was repeated further three times.

Then at the second step, for 0.42 g of reacted CNF of the first step put in a flask, 10.0 ml of distilled water was added and stirred to be dissolved. Water volume (and the other materials also) was proportionally increased to the reacted CNF weight. For 0.42 g of the reacted nanofiber, 0.1 g of NaOH granule was added to the mixture. After dissolution of the NaOH, 2.5 ml of acetonitrile and 3.0 ml of acrylonitrile for 0.42 g of the reacted CNF were added and the mixture was strongly stirred for 12 hours at the room temperature. The reacted liquid was neutralized by acetic acid. Collected precipitate, washed with distilled water, was solvated in acetone. Acetone solvation poured into distilled water precipitated again. This process was repeated further three times.

2.4 Measurements

FE-SEM micrographs were taken by JSM-6700F, JOEL. Spectrum 100, PerkinElmer was used for FT-IR spectra. XRD patterns were observed by UltraX 18 system, Rigaku with the Cu-Kα radiation. DSC curves were recorded by DSC2920, TA instruments. Film motions by piezoelectricity were detected by SI-F system, Keyence, a laser displacement meter.

3. RESULTS AND DISCUSSION

3.1 Cellulose nanofiber

CNF water gel was dried to be film for FE-SEM imaging (Fig.2) or other measurements. Fig.2 shows that nanofibers were ca. 16 nm in diameter with high uniformity and several hundred nm in length.

3.2 Cyanoethylation of CNF

Dried cyanoethylcellulose films, fabricated from acetone solvation, were yellow by the reflux method and white by the stirring only method. Fig.3 shows the film surface reacted by the reflux method. No fiber structure was observed by the FE-SEM there. It is supposed that also interior hydroxyl groups of the CNF were attacked to be cyanoethylated and the CNF structure was destroyed under the reaction condition of the reflux method. Fig.4 and 5 show respectively the film surfaces reacted by the stirring only method at the condition 1 or 2. In the film at the condition 1 of the stirring only method, fibers of ca. 50nm in diameter were observed. It is supposed that they were bundles of reacted CNF. In the film at the condition 2, fibers with nearly the same diameter as the CNF were confirmed.

Fig.6 shows FT-IR spectra of reacted materials and non-treated CNF. Only for reacted materials, there were absorptions near 2250 cm⁻¹ which means the existence of cyanoethyl group. The absorbance of a material by the reflux method was higher than ones of materials by the stirring only method. This corresponds to high cyanoethyl substitution of hydroxyl groups which were in the inside of CNF. Joining this result with FE-SEM images, the reaction condition of the reflux method was too strong and even hydroxyl groups in the inside of CNFs had been subjected to the cyanoethylation. For products by the stirring only method, especially at the
condition 2, only CNF surfaces were successfully cyanoethlated.

Fig.7 shows XRD patterns normalized by peak values near $2\theta=23^\circ$. The non-treated CNF has a diffraction peak at $2\theta=23^\circ$. The reacted material by the reflux method had a broadened pattern which reaches to the maximum near $2\theta=20^\circ$. This reflects the break of the single crystal-like structure of CNF. The reacted materials by the stirring only method have a diffraction peak near $2\theta=23^\circ$. By this peak, it is supported that the CNF structure has been preserved after the reaction. The products by the stirring only method had another sharp peak at $\theta=10^\circ$ to $12^\circ$, even narrower than the main peak of non-treated CNF. It corresponds with the lattice spacing of 0.8–0.9 nm. The periodic arrangement which caused this diffraction is not yet clear, but it is supposed that the diffraction occurs by a certain structure between cyanoethyl groups on CNF surfaces.

According to these measurements, the reflux method was too strong as reaction condition to answer the purpose to remain the CNF structure. The stirring only method should be proper to modify only the CNF surface and to avoid CNF internal reaction which leads to CNF structure destruction.

DSC curves of reacted materials by stirring only method indicate no glass transition from $-50^\circ$ C to $150^\circ$ C. This means that they remained glass-like state, in other words robust, near the room temperature and that uniaxial orientation of their film, to obtain characteristics such as piezoelectricity, by heating up to the room temperature, was difficult.

3.3 Cyanoethylated dihydroxypropylation of CNF

More glycidol has been used at the first step reaction, more voluminous and softer the reacted material was. Dried cyanoethylated $O$-(2,3-dihydroxypropyl) cellulose films were white and highly viscoelastic. Cyanoethylation of the films was confirmed by FT-IR spectra with absorptions near $2250 \text{ cm}^{-1}$. Caused by their rubber-like state, some films were barely possible to be uniaxially elongated. The piezoelectric constant for a film, for which 20 ml of glycidol was applied at the first step reaction, was $d_{33}=3.2 \text{ pm/V}$. Small value of the constant should be due to buckling during the piezoelectricity measurement.

As group which modified the cellulose nanofiber surface to enable the compatibility between uniaxial elongation and stiffness, cyanoethyl group was too short (cyanoethylated CNF was too stiff) and cyanoethylated dihydroxypropyl group was too long (cyanoethylated $O$-[2,3-dihydroxypropyl] cellulose nanofiber was too
supple). Between them, there should be groups of proper size to control interfibrillar hydrogen bonds, for example, cyanoethylated hydroxyethyl group \([\text{Fig. 1, } R=(\text{C}_2\text{H}_4\text{O})_n\text{C}_2\text{H}_4\text{CN } (n=0,1,2…)]\). Replacement of glycidol by ethylene oxide, a smaller epoxide than glycidol, at the first step of cyanoethylated dihydroxypropylation conduct to this modification, however, ethylene oxide is highly reactive and toxic. Synthesis must be done in closed system, or other reaction processes must be exploited.

4. CONCLUSION

We have successfully cyanoethylated the surface of cellulose nanofiber (CNF) by stirring under acrylonitrile at the room temperature. Preservation of fiber structure and surface cyanoethylation were confirmed by FE-SEM images, XRD patterns and FT-IR spectra. Cyanoethylation of CNF by reflux reacted even in the inside of CNF and broke the nanofiber structure. Cyanoethylated CNF by stirring has no glass transition near the room temperature. Hence, the uniaxial orientation of its film was not achieved. We have also synthesized cyanoethylated \(O-(2,3\text{-dihydroxypropyl})\) cellulose nanofiber by two step reactions, the first, dihydroxypropylation of CNF with glycidol and the second, cyanoethylation of dihydroxypropylcellulose nanofiber by stirring under acrylonitrile. Reacted material was soft enough to elongate uniaxially. The small piezoelectric constant \(d_{14}=3.2\text{ pm/V}\) observed for this material should be caused by the elasticity.

ACKNOWLEDGEMENTS

The authors would like to thank Dr. Shinichi Higai, Murata Manufacturing Co., Ltd., for his helpful discussion and Dr. Hideki Kawamura, Murata Manufacturing Co., Ltd., for the piezoelectric measurement.

REFERENCES


(Received January 24, 2012; Accepted February 26, 2012)