Tribological property of cellulose nanofiber water dispersion using various material pairs

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Abstract
Cellulose nanofibers (CNFs) are synthesized by unraveling cellulose made from wood. CNFs have attracted significant attention among biomass materials owing to their excellent mechanical properties and wide range of applications. This study aims to elucidate the effects of CNFs as a lubricating additive. In order to accomplish this, CNFs were dispersed in water at densities of 0.02–1.0 mass%, and friction tests were performed using a ball-on-plate friction tester with a reciprocating motion configuration. Stainless steel (JIS-SUS304) and polyoxymethylene (POM) were used as sliding plates, while various materials were used for sliding balls. On both the SUS304 and POM plates, friction reductions were observed by adding only a small amount of CNFs (0.02 mass%). Although wear on the SUS304 plate reduced by 0.02 mass%, the water dispersion of CNFs was not distinct; it was observed only at densities of CNFs that were more than 0.2 mass%. On the POM plate, wear was induced by adding 0.02 mass% of CNF water dispersion. Adverse effects may arise with the addition of more than 0.2 mass% CNF. A distinctive feature observed in the water dispersion lubrication of CNFs was that a tribofilm is not formed due to the chemically inert nature of CNFs. It appears highly probable that in the water dispersion lubrication of CNFs, the physical effects of these fibers are much stronger than their chemical effects. These effects include rolling and/or sliding, which occurred in fullerene and carbon nanotubes.

Keywords: Cellulose nanofibers, Water lubrication, Friction coefficient, Wear, Metal substrate, Resin substrate

1. Introduction

The utilization of biomass materials is expected to become independent of petroleum due to various environmental impacts. In particular, cellulose nanofibers (CNFs) have attracted significant attention in recent years. CNFs are synthesized by unraveling cellulose, which is primarily found in wood. CNFs are primarily unraveled by a TEMPO (2,2,6,6-tetramethylpiperidine-1-oxyl radical)-mediated oxidation from cellulose (Isogai et al., 2011)(Nechyporchuk et al., 2016). This method promotes nanofiberization by converting high-density carboxy groups into CNFs. CNFs of 3–4 nm in diameter with a length of several micrometers are obtained using this method. In order to utilize their excellent mechanical properties, CNFs have been studied as fillers of composite materials (Abdul Khalil et al., 2012; Kargarzadeh et al., 2017; Oksman et al., 2016; Siró and Plackett, 2010).

Numerous nanomaterials, such as fullerenes (Spikes, 2015; Valeryevna Gubarevich et al., 2005), graphene oxide (Kinoshita and Nishina, 2015; Kinoshita et al., 2015), nanometals (Choi et al., 2009; Zhang et al., 2010), and carbon nanotubes (Chauveau et al., 2012; Sato et al., 2016) are regarded as notable materials for lubricating additives owing to their excellent mechanical and chemical properties. CNFs show significant potential as a lubricating additive based on two aspects. First, CNFs exhibit high strength (Isogai et al., 2011) and can be expected to maintain their original structure under high contact pressures at friction interfaces; further, these can reduce the friction coefficient by preventing direct
contact between the friction surfaces during boundary lubrication. Second, CNFs contain a large number of polarized functional groups; therefore (Isogai et al., 2011; Rol et al., 2019), these are expected to exhibit high hydrophilicity and adsorption to metal plates. Few tribological studies on CNF composites have been performed (Barari et al., 2016); moreover, no studies on CNFs dispersed in water have been performed.

This study investigated the characteristics of CNFs as a lubricant additive by performing frictional tests using CNF water dispersions with various material pairs. Metal and resin plates were selected to compare the effect of CNF under the different interaction between the sliding plate. JIS-SUS304 stainless steel and polyoxymethylene (POM) plates were slid in the CNF water dispersions by silicon carbide (SiC), silicon nitride (Si₃N₄), SUS304, JIS-SUJ2, and tungsten carbide (WC) balls, which have different hardness and surface roughness, with CNF densities of 0.02–1.0 mass%. The friction coefficients, wear volumes, and wear surfaces were then investigated.

2. Experiments

Distilled water and the CNF water dispersion were used as lubricating liquids. The CNFs (RHEOCRYSTA, DKS Co. Ltd.) used in this study were prepared by TEMPO-mediated oxidation of cellulose and water dispersive. Typical properties of TEMPO-oxidized CNFs include an individual CNF diameter of about 3 nm, and a length of few micrometers, with a composition that is essentially carbohydrate cellulose functionalized by carboxylate. The tensile strength and elastic modulus of the film configuration was reported to be 250 MPa and 6 GPa, respectively (Isogai, Saito, & Fukuzumi, 2011). SUS304 and POM were used as sliding plates. The surface roughness (Ra) was approximately 1.6 µm for the SUS304 plate and 2.2 µm for the POM plate as measured by a confocal laser microscope. The ball materials were SiC, Si₃N₄, SUS304, SUJ2, and WC with the surface roughness (Ra) of approximately 0.07, 0.10, 0.08, 0.02, and 0.04 µm, respectively, and the balls were fabricated as bearing balls. The diameter of the balls was 2 mm.

The densities of the CNF water dispersions used were 0.02, 0.2, 0.6, and 1.0 mass%. Fig. 1 shows photographs of the CNF water dispersions. While the water dispersions at all densities appeared transparent, the CNF water dispersion with a density of 1.0 mass% contained air bubbles arising from the high viscosity of the dispersion. Iwamoto et al. measured the viscosity of CNF water dispersions, and reported complex viscosities that depended on the shear strain of the dispersions (Iwamoto et al., 2014). The viscosity of CNF water dispersions increases with decreasing shear strain. At a shear strain of 1%, the viscosities of the CNF water dispersions are approximately "100 Pa · s" with a density of 1.02%, "50 Pa · s" for 0.29%, and "1 Pa · s" for 0.09%. At a shear strain of 100%, the viscosities are approximately "10 Pa · s" with a density of 1.02%, "4 Pa · s" for 0.29%, and "0.5 Pa · s" for 0.09%. This implies that, in this study, the viscosities of the CNF dispersions were vastly different.

A ball-on-plate friction test with a reciprocating motion configuration was performed. A load was applied vertically
to the ball. The friction condition was a sliding distance of 2.5 mm with a motor rotation speed of 10 Hz (the maximum sliding speed was 0.16 m/s). When the SUS304 plate was used, the load was 1 N. The maximum Hertzian contact pressures were estimated to be approximately 1.7 GPa for SiC, 1.5 GPa for Si$_3$N$_4$, 1.3 GPa for SUS304, 1.3 GPa for SUJ2, and 1.7 GPa for WC. At a load of 1 N, wear was not obvious; thus, a 3 N load was used on the POM plate. The maximum Hertzian contact pressures were estimated to be approximately 0.18 GPa for all balls. Considering the friction forces were stable with a maximum sliding speed of 0.04-0.16 m/s and wear occurred, boundary to mixed lubrications occurred in the frictional experiments. The dynamic friction coefficients were measured by the forces in the oscillating motion detected by a loadcell. The wear volumes of the plate were measured using a confocal laser microscope.

3. Results and discussion

Fig. 2 shows the representative friction coefficients between the SUS304 plate and WC ball using distilled water and 0.02, 0.2, 0.6, and 1.0 mass% CNF water dispersions. The friction coefficient of distilled water was approximately 0.4. Reductions in the friction coefficients (less than 0.3) were observed using the CNF water dispersions. The friction coefficients of the CNF water dispersions were relatively stable, and no run-in period was observed.

![Friction coefficients between SUS304 plate and WC ball using distilled water and 0.02, 0.2, 0.6, and 1.0 mass% CNF water dispersions.](chart-

The friction coefficients and wear volumes of the SUS304 plate that slid against the WC ball with CNF densities of 0 (distilled water), 0.02, 0.2, 0.6, and 1.0 mass% after 36,000 friction cycles are shown in Fig. 3. Average values of 3 tests were plotted, and the error bars denote the maximum and minimum. The friction coefficient decreased even as a small amount of CNFs (a density of 0.02 mass%) were dispersed as shown in Fig. 3(a). The reduction in friction coefficient plateaued at densities higher than 0.2 mass%. The wear volume at the 0.02 mass% CNF water dispersion appeared to increase only slightly compared with that by distilled water as shown in Fig. 3(b). Wear volumes at densities higher than 0.2 mass% were increased by CNF addition.

Fig. 4 shows the friction coefficients and wear volumes of the POM plate that slid against the WC ball as a function of the CNF density. Average values of 2 tests were plotted, and the error bars denote the maximum and minimum. The number of friction cycles was 36,000. When a small amount of CNF (0.02 mass%) was dispersed, the friction coefficient decreased as shown in Fig. 4(a). The friction coefficients of the CNF water dispersions with density of more than 0.2 mass% were almost identical to that of distilled water. Fig. 4(b) shows the wear volumes of the POM plate that slid against the WC ball as a function of the CNF density. The wear volume on the POM surfaces by the CNF water
dispersions increased even at a density of 0.02 mass%; further, the wear volumes with the addition of CNFs were saturated at densities higher than 0.02 mass%. This indicated that for both, the SUS304 and POM plates with the WC ball, even the addition of 0.02 mass% CNFs resulted in friction reductions and wear (especially on the POM plate).

![Friction coefficients](image1)
![Wear volumes](image2)

Fig. 3 (a) Friction coefficients and (b) wear volumes on the SUS304 plate that slid against the WC ball with various CNF densities over 36,000 friction cycles.

![Friction coefficients](image3)
![Wear volumes](image4)

Fig. 4 (a) Friction coefficients and (b) wear volumes on the POM plate that slid against the WC ball with various CNF densities over 36,000 friction cycles.

Friction tests using the SUS304 plate and balls of various materials with a 0.02 mass% CNF water dispersion were performed over 18,000 friction cycles. Fig. 5 (a) shows the friction coefficients of these tests. For distilled water lubrications, the friction coefficients increased in the order of the SiC, WC, SUJ2, SUS304, and Si$_3$N$_4$ balls. Friction reductions were observed for all balls using CNF water dispersion. The friction reduction order of the CNF water dispersion lubrications was approximately the same as that of the distilled water lubrications. The wear volumes after the frictional tests shown in Fig. 5 (a) are presented in Fig. 5 (b). When the Si$_3$N$_4$ ball was used, the wear volumes sliding by both the distilled water and CNF water dispersions, were extremely large compared with those of the other balls. The wear volumes sliding by the CNF water dispersion was less than that by distilled water. The wear volumes using other balls, with the 0.02 mass% CNF dispersion, were about the same as those of distilled water. These results with the SUS304 surface indicate that CNFs have no wear resistance effects except when using the Si$_3$N$_4$ ball, which resulted in a large wear volume.

Using POM plates and balls of various materials, friction tests with a 0.02 mass% CNF water dispersion over 18,000 friction cycles were performed. Fig. 6 (a) shows the friction coefficients of the POM plate. The friction coefficients for
distilled water lubrications increased in the order of the WC, Si₃N₄, SUS304, SiC, and SUJ2 balls. This order was different from that with the SUS304 plate. When CNFs were added, the friction coefficients reduced for all balls. The friction reduction order of the CNF water dispersion lubrications was the same as that of the distilled water lubrications, and the tendency was the same as that of the SUS304 plate. The wear volumes after the frictional tests are indicated in Fig. 7 (b).

Using the SUJ2 ball, the wear volume sliding by distilled water was extremely large, and by adding CNFs, the wear volume was reduced to approximately 15%. Except for the SUJ2 ball, adding CNFs increased the wear volumes. In particular, when using SiC or WC balls, the wear volumes became approximately three times larger with the CNF water dispersions.

Fig. 7 shows optical micrographs of the SUS304 plate with the WC ball, and POM wear surfaces with the SiC ball slid by the 0.02 mass% CNF water dispersion over 36,000 friction cycles. On the contact area, distinct tribofilms were not observed. CNFs are likely to have high strength and exhibit low chemical activity, thus, tribofilms would be difficult to form from CNFs by friction.

In water dispersion lubrications of graphene oxide (GO), GOs can enter between friction interfaces. Tribofilms are formed from GOs that result in friction and wear reductions. In addition, even without tribofilms, the existing GOs present between friction interfaces reduce friction and wear. (Kinoshita and Nishina, 2016). In the water dispersion lubrications
of CNFs, distinct tribofilms were not formed. This implies that only CNFs that existed between friction interfaces affected the tribological properties. The experimental results in this study indicated that even the 0.02 mass% CNF addition was effective, and additions of more than 0.2 mass% might result in adverse effects. This implies that the number of existing CNFs between friction interfaces would be saturated by CNF additions of more than 0.2 mass%. On the SUS304 and POM plates, the friction reduction order of the CNF water dispersion lubrication using balls of various materials was the same as that of distilled water lubrication. If the chemical effects of CNFs were strong, such as adsorption and tribofilm formation, the friction reduction orders of both the distilled water and CNF water dispersions would be disturbed. Moreover, the physical effects appear to be much stronger than the chemical effects for the CNF water dispersion lubrication. The mechanical hardness of CNFs is important for lubrication. Rolling and/or sliding effects between friction interfaces would occur, which are similar to the effects of carbon nanotube and fullerene lubrications (Buldum and Lu, 1999; Falvo et al., 1999). If the mechanical hardness of CNFs was low, they would be broken by friction and would contribute only a small effect. On the POM surface, distinct wear was observed using the CNF water dispersion. Slight wear was observed on the SUS304 plate. This is because CNFs exhibit high mechanical hardness and the mechanical hardness of POM is lower than that of SUS304. The mechanical properties of the CNF film have been reported in literature (Isogai et al., 2011); however, the strength of a single fiber of the CNFs has not been revealed. Elastic modulus and tensile strength of the CNF film achieved 6 GPa and 250 MPa, respectively; these values were higher than the POM plate values of approximately 3 GPa and 70 MPa. In conclusion, for CNF water dispersion lubrications, high mechanical hardness and the chemically inactive nature of CNFs resulted in physical effects (rolling and/or sliding of CNFs) and the formation of the tribofilm was not observed.

Fig. 7  The optical micrographs of the (a) SUS304 and (b) POM plate wear surfaces slid by the 0.02 mass% CNF water dispersion, with 36,000 friction cycles. (c) WC ball slid on SUS304 plate and (d) SiC ball slid on POM plate.
4. Summary

In this study, to clarify the effect of CNFs on tribological properties, friction tests were performed using CNF water dispersions with densities of 0.02–1.0 mass%. Experimental results indicated that in the case of the JIS-SUS304 stainless steel plate, the CNF water dispersion reduced the friction coefficient. However, for the POM plate, there was little reduction effect from the CNF water dispersion on the friction coefficient. Wear on the SUS304 plate was not marked at the 0.02 mass% CNF water dispersion, and increased by adding CNFs at densities beyond 0.2 mass%. Wear on the POM plate increased at even 0.02 mass% CNF water dispersions. Because distinct tribofilms were not observed on both the sliding JIS-SUS304 and POM plates, it was thought that the frictional behavior of the CNF water dispersions was due to only the CNFs existing between the sliding interfaces.

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