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# Tribological Properties of Polyvinyl Alcohol/Uncaria Gambir Extract Composite as Potential Green Protective Film

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#### ABSTRACT

Polyvinyl Alcohol/Uncaria Gambir Extract (PVA/UG) composite provides good UV light protection and antibacterial, tensile, and thermal properties. To continue our previous research, the tribological properties of PVA, PVA/BA, PVA/UG, and PVA/UG with heat treatment (PVA/UGt) were conducted. The ball-on-disk test results show COF reduced by 42% in PVA/UG compared to PVA. It was proved that heating the PVA/UG significantly improves the tribological properties of the PVA composite, resulting lowest COF (0.08) and wear area (390  $\mu$ m<sup>2</sup>). Additionally, incorporating UG also increases the hardness of the PVA composite by up to 73% and. These results corroborate the application of this composite as a potential green protective film.

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#### **1. INTRODUCTION**

The green tribology concept has been studied recently in order to prevent waste and sustain the environment [1]. Polyvinyl Alcohol (PVA) has been widely used as a substitute for petroleum-based non-degradable materials. It is water soluble, flexible, and has low toxicity [2]. It is also

suitable for low environmental impact food packaging and protective film [3]. However, this PVA alone is weak in mechanical properties and does not have ultraviolet (UV) light protection, which is not suitable if applied as a protective film. This weakness can be compensated by adding additives such as nanoparticles [4]. However, the nanoparticle is not green material, hard to prepare, costly, and not environmentally friendly [5]. Various research, including using plants as additive, have been eagerly studied recently. For instance, lubricants, sensors, food packaging, and biomedical equipment [6–9].

Uncaria Gambir extract (UG) and Boric Acid as a filler can improve the properties of the PVA film. UG originated from Southeast Asia and is mainly used as a traditional herbal medicine [10,11]. UG's high amount of catechin exhibits an anti-oxidative activity that could prevent oxidation and corrosion [5]. Meanwhile, boric acid can form strong hydrogen bonds that reduce the hydroxyl group's hydrophilicity of PVA, which leads to low moisture absorption and high tensile strength [12].

Our previous study found that incorporating 1 wt% UG to PVA provides UV light absorption (wavelength of 650 nm) of about 100% and improves PVA thermal resistance [13]. UG also increased tensile strength and toughness by  $\sim$ 67% and  $\sim$ 94%, respectively, compared to pure PVA film. Moreover, it has antibacterial activity [12]. However, to apply this composite for proper protective film, it is necessary to investigate its tribological properties of the film. As far as the author is aware, the tribological study of PVA/UG composite film has not yet been reported.

It is hypothesized that the addition of UG could improve the tribological properties. In our previous work, UG provides the cross-linking capability of UG, which increases the film's mechanical properties [5,13]. According to the literature, material with good mechanical properties tend to have a low coefficient of friction [14]. Additionally, heat treatment could also improve the properties of the film [15]. Thus, we modified the PVA/UG film by heating it in a drying oven at 100 °C.

This work conducted the tribological behavior, including coefficient of friction, hardness, and water contact angle, of PVA, PVA/UG, and PVA/UG with heat treatment (PVA/UGt).

## 2. MATERIALS AND METHOD

## 2.1 Materials

The materials used in this work are similar with to previous work [13]. PVA with 89,000–98,000 g/mol molecular weight and 99% hydrolyzed was purchased from Sigma-Aldrich Pte. Ltd., Singapore. UG, with >95% purity, was supplied by Sumatran Biota Laboratory, Universitas Andalas. Boric acid with >99.5% purity was acquired from Pudak Scientific, Jakarta, Indonesia. Distilled water, toluene, and ethanol were supplied locally. Acetic acid and fuming Hydrochloric acid were purchased from Merck KGaA, Darmstadt, Germany.

### 2.2 Samples Preparation

UG purification: To remove impurities of purchased UG, about 1% UG was incorporated into 100 mL distilled water and stirred by a magnetic stirrer for 30 minutes at high temperatures. The solution was then centrifuged at 5000 rpm for 30 min. The supernate of the solution was acquired by using filter paper (300 mesh) to fully remove the remaining residue or impurites.

PVA film: PVA (10 g) and distilled water (100 mL) were blended. The mixture was heated using a magnetic stirrer (MS-H280-Pro, Scilogex, USA) at 70 °C and 500 rpm for two hours until it became gelatinous. The resultant gel was sonicated at 600 W for five minutes in a sonicator. A treated gel cast on a Petri dish was vacuum dried for 20 hours at 0.6 MPa at 50 °C.

PVA/BA film: PVA (10 g) and BA (0.05 g in distilled water) were added to the water (100 mL). The mixture was heated for two hours at 70 °C and 500 rpm using a magnetic stirrer to achieve gelatinization. A sonicator was used to mix the final gel. The ultrasonicated gel was cast in a Petri plate and dried for 20 hours at 0.6 MPa at 50 °C.

PVA/UG film: The supernate of UG (1 wt%), PVA (10 g), and distilled water (100 mL) was blended using a stirrer at 60 °C and 550 rpm for 2 h until gelatinization. A sonicator was used to treat the resulting gel. The sonicated gel was cast in a Petri plate and dried for 20 hours at 0.6 MPa at 50 °C.

PVA/UGt film: The acquired PVA/UG film was reheated in a vacuum oven at 100 °C for 40 minutes.

The detail, including morphology, thermal and tensile properties, is available in our previous work [13].

## **2.3 FTIR**

FTIR of PVA/UG and PVA/UGt films were characterized using a FTIR (Model: Perkin Elmer; Frontier). The dried samples were formed into a sheet film and scanned at a frequency range of 4000-500 cm<sup>-1</sup> at 4 cm<sup>-1</sup> resolution.

#### 2.4 Tribological Performance Analysis (Hardness, Friction Coefficient, Wear Area)

A ball-on-disk tribometer (POD-FM406-10NT, Fu Li Fong Precision Machine, Kaohsiung, Taiwan) was carried out to measure the tribological performance with a load of 2 N, disk speed of 0.03 m/s, and rotation speed of 764 rpm. The test was carried out according to ASTM G-99. The PVA film, PVA/BA, PVA/UG, and PVA/UGt film were used as the bottom disk test piece, and an upper ball with a diameter of 6.31 mm made of chrome steel (52,100 steel) was used as the upper ball. The wear test was conducted in a setting with an RH of 70% and a temperature of 25 °C. The friction coefficient was continuously recorded and monitored. The average COF value was acquired by averaging the real-time COF value, which slides for 50 m. Figure 1 presents the equipment for conducting tribological tests.



Fig. 1. Ball-on-disk tribometer.

A 3D laser scanning microscope was used to measure the wear volume. Three different locations of the wear scar were taken when measuring the wear scar length of every film. All samples were tested three times to verify the laboratory results. A Vickers machine (Shimadzu, HMV-G, Japan) was operated to determine the hardness of the film after the tribological test. The test for each film was repeated ten times.

### 2.5 Water Contact Angle

The contact angles were obtained in accordance with ASTM D7334 methodology and were measured using the sessile drop method on a representative spot outside of the veneering area using an H<sub>2</sub>O droplet of 10  $\mu$ l. A digital microscope (Keyence VHX-5000, Keyence GmbH, Neu-Isenburg, Germany) with the optical axis horizontal and parallel to the specimen surface was used to measure the angle. The measurement was made 60 seconds after the first contact between the droplet and the surface, at room temperature. The contact angle measurement was conducted one time for each film, and the location of the droplet, for all films, was in the middle of the film.

#### 3. RESULTS AND DISCUSSIONS

#### **3.1 FTIR**

Figure 2 presents the FTIR of PVA, PVA/UG, and PVA/UGt sample. The visible peaks at about 3200, 2900, and 1700 cm<sup>1</sup> are generated by O-H stretching, C-H stretching, and O-H of absorbed water, respectively [16]. PVA, PVA/UG and PVA/UGt show similar patterns, indicating that the treatments did not alter the PVA's functional groups behavior. Nevertheless, heat treatment process affected the wavenumber and peak intensity in the FTIR curves. For instance, the wavenumber of O-H stretching of the blends changed from 3264 cm-<sup>1</sup> (PVA) to 3246 cm<sup>-1</sup> (PVA/UG).



Fig. 2. FTIR of all samples.

The shifting is due to an increase in hydrogen bond density brought on by more free -OH groups in PVA/UG coming in contact with one another, helped along by high temperature during the sonication process. This could change the polarity of molecules, causing the infrared spectrum to shift towards lower wavenumbers. The intensity of hydroxyl functional groups of PVA/UG was decreased due to the presence of less free hydroxyl groups as a result of the higher crosslinking rate.

The PVA film has the strongest band intensity of O-H stretching vibration (T=64%) among all films. The O-H stretching intensity in the films weakened after incorporating UG to the PVA film. The PVA/UG film's T-value for O-H groups is 68%, whereas the T-value for the PVA/UGt film is 82%, confirming the weakest intensity of free O-H groups. The weak intensity indicates low number of free O-H groups, which is correspond to the better crosslinking occurred due to intraand inter-molecular hydrogen bond breaking after the heat treatment [15,17].

## 3.2 Hardness Test

Figure 3 shows the hardness values of all samples. It can be seen that the hardness of PVA is the lowest among all. After adding UG or BA, the hardness is almost three times higher than PVA. Heat-treated PVA/UG (PVA/UGt) increased the hardness even more, making it the highest. This is due to the heat treatment process. The literature stated that in low temperatures, the crosslinking reaction between PVA and UG is not ultimately occurred [15].



Fig. 3. Hardness value of all films.

Thus, in higher temperatures, higher-intensity crosslinking will occur. Increasing the crystal size of PVA will lead to the formation of ordered crystalline structures within the film. Crystalline regions typically have higher rigidity and hardness than amorphous regions, resulting in an overall increase in film hardness [18,19]. Moreover, the literature also stated that PVA films contain residual moisture, which can contribute to material softness. Conducting heat treatment drives off moisture, resulting in a reduction of plasticization effects and an increase in the film's hardness [20]. This result is consistent with FTIR, which shows a lower free hydroxyl group in PVA/UGt sample.

# 3.3 Tribological Properties

The coefficient of friction (COF), average COF, wear area, wear mark, and depth of every composite is displayed in Figure 4. Due to higher friction between the ball and PVA surface, the pure PVA composite has a rough profile. The pits and surface abrasion are shown due to the low hardness of PVA. As shown, the highest and lowest wear length is achieved by PVA and PVA/UG, respectively. The PVA/UG has the lowest wear length, with a 25.2% improvement compared to the PVA.

The PVA/UGt sample displayed the lowest COF (0.08), with a 69% improvement compared to pure PVA (0.26). On the other hand, in Figure 4c(ii), the deepest and shallow wear are acquired by PVA, and PVA/UG, respectively.

This reduction in COF and wear area could be explained by the hardness test results in Figure 2. According to the Archard wear law, the wear volume will be lowered when a material has high hardness [21]. However, it can be seen that PVA/UGt has a rougher surface and higher wear area due to surface abrasion than PVA/UG. This is due to the highest hardness of PVA/UGt, which is very stiff. It also correlates with Figure 4a, in the sliding time of 40 to 50 of PVA/UGt. There is fluctuation in the COF value, which is due to its surface's failure to maintain the load of the ball.

Additionally, the heat treatment is conducted at 100 °C, which at that temperature, cross-linking reactions within the PVA matrix may occur, resulting in a more rigid and brittle material. The increased rigidity can lead to higher contact stresses during wear, accelerating surface damage and wear area formation [17,22].

Our previous work proved that PVA/UG has a lower elastic modulus than PVA [12]. According to Figure 3, the heat treatment process increases the hardness of the film but presumably lowers the elasticity even more, making it brittle [22]. It is also consistent with the FTIR result showing the lowest intensity in the wavelength of 3246 cm<sup>-1</sup> due to the breaking of inter- and intramolecular bonding, making the PVA chain more rigid [12]. J. Joseph et al. investigated the PVA/Graphene/Carbon Nanotubes composites. The sample with low strain but high hardness has a higher wear rate and COF [23].





**Fig. 4.** COF (a) average COF and wear area (b) 3D laser scanning microscope results (c) wear scar length (i) wear depth (ii) of all samples surface after the tribological test.

Another previous work of Likozar. B and Major. Z reported the tribological properties of nitrile rubber/multi-walled nanocomposite. It was reported that the sample with high hardness and low elastic modulus had a high wear rate compared to others [24]. PVA/BA also has good tribological performance compared to pure PVA. However, it can be seen that crack occurs along the wear track. Similar to PVA/UGt, the BA also increase the crosslinking of PVA, resulting in high hardness vet low elasticity [12]. Adding more UG concentration could lead to higher COF due to the increment of the crosslinking reaction, making the film more rigid and brittle, although improves in hardness properties.

## 3.4 Water Contact Angle Analysis

Figure 5 shows the contact angles of the PVA/UG and PVA/UGt composite films. A water contact angle was conducted to confirm the diminishing of the composite free hydroxyl group after the crosslinking process. In our previous work, PVA/BA and PVA/UG had lower moisture absorption than PVA due to UG or BA increasing the hydrogen bonding intensity between the PVA chains, which reduced the hydrophilicity [12]. The contact angle is higher after the heat treatment process (increasing from 140 to 260). A high contact angle indicates that the sample has become less hydrophilic. This is because the high temperature reduced the free hydroxyl groups and increased the crystallinity of PVA, resulting in higher contact angle [25]. This is consistent with hardness value and FTIR. In order to design an entirely hydrophobic film, several methodologies need to be reworked for follow-up research. For instance, UG extracts can be used as surface modifiers for the PVA film by immersing or coating it directly into the film. In this way, it may be possible to introduce hydrophobic compounds onto the PVA's surface.







Fig. 5. Water contact angle of PVA/UG (a) and PVA/UGt (b).

## 4. CONCLUSION

In conclusion, heat treatment of PVA/UG composite film has affected the properties of the films. Compared to the non-heated film (PVA/UG), the PVA/UGt film has higher hardness, hydrophobic, and lower CoF. The heat treatment increases the crosslinking rate by UG, which proved in the weakened intensity in the O-H stretching wavenumber. Moreover, heat treatment can increase the the hydrophobicity level of PVA film. Preparing a PVA film with a higher UG concentration could potentially form a hydrophobic film for future study. However, the PVA/UGt film presented a rougher surface and higher wear rate compared to PVA/UG film due to the higher stiffness. These results indicate that PVA/UGt has good potential as a potential applied as a strong, anti-UV, high thermal resistant and anti-bacteria green protective film.

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