Tribological Performance of Natural Resin Urushi Containing PTFE

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Abstract

The “Urushi lacquer” is a natural resin material and, it has been used since ancient times as a hard coating material of Japanese tableware and Japanese armour. In this paper, friction and wear performance of the urushi lacquer and urushi lacquer with the addition of PTFE has been experimentally investigated. Experiments have been carried out under the dry conditions using a ring-on-plate testing apparatus. It was consequently found that the urushi lacquer containing PTFE has comparable friction properties and superior wear properties compared with the pure PTFE.

1. Introduction

Applications of unlubricated 'dry' bearings have been expanding rapidly in recent years, and there are three main areas in which their use is indicated:

(i) where fluids are ineffective, as at low or high temperatures, or in reactive environments,

(ii) where fluids cannot be tolerated because of the possibility of contamination of the product or the environment,

(iii) where fluids are undesirable because of lack of opportunity for, or the impossibility of, maintenance.

Cost, although always an important consideration, is not usually the decisive reason for choosing a dry bearing. Some of the most successful dry bearing formulations are significantly more expensive than their mass produced metallic counterparts intended for lubricated service. The largest group of self-lubricating formulations consists of materials based on synthetic polymers to which are added various fillers or reinforcements intended to enhance particular properties. Although self-lubricating compositions are widely used, yet under some operating conditions they are considered to be unsuitable. This is especially true when the temperature at the contact zone is high enough to cause decomposition and the release of harmful gasses.

However, there is another important consideration which, especially nowadays, is prominently highlighted and that is “green” materials for tribological applications. This requirement means avoiding synthetic materials, such as polymers, and instead utilising natural products.

The “Urushi lacquer” [1] is a natural resin material available without the need to expend additional energy resources, as is the case with polymers, to acquire it. It has been used since ancient times as a hard coating material of Japanese tableware and Japanese armour.

The main motivation for selecting urushi lacquer is provided by its wide non-tribological use and a relative ease of producing a surface coating together with its green credentials and potential for a dry sliding material. However, it is appropriate to mention that there are other naturally occurring resins such as amber, balm of Gilead, mastic, gum, etc and they might have also potetntial for green tribological applications [2, 3]. The urushi lacquer itself attracted attention of some researchers who assessed its physico-chemical characteristics [4, 5]

In the study presented in this paper, friction and wear performance of the urushi lacquer and urushi lacquer with the addition of PTFE has been experimentally investigated. Experiments have been carried out under the dry conditions using a ring-on-plate testing apparatus.

2. Self-lubricating compositions containing PTFE

Pure PTFE is usually finding utility in high performance mechanical seals due to its unique properties like high chemical resistivity, low coefficient of friction and high temperature stability [6,7]. However, PTFE exhibits poor wear and abrasion resistance, leading to early failure and leakage problems in the seals.

The wear resistance of PTFE can be significantly improved by addition of suitable filler materials [8]. Besides the type, the shape and size of the materials added also influence the tribological properties [9]. In the past, research in this area has been confined to the PTFE filled with conventional filler materials like glass fibres, graphite, carbon fibres, etc. However, with the growing demand for utilizing PTFE in a variety of applications, significant effort is needed towards developing novel composite materials by adding one or more non-conventional filler materials possessing the potential of increasing the wear resistance or, alternatively, using PTFE as an additive improving tribological characteristics of materials with inherently high friction but significant wear resistance. It is established that PTFE exhibits significantly low coefficient of friction when sliding against steels. The low coefficient of friction results from the ability of its extended chain linear molecules, –(CF2–CF2)*n*–, to form low shear strength films upon its surface and mating counter-faces during sliding [10,11]. However, this repetitive formation and destruction of the film occurs at a high rate and results in unacceptable high rates of wear as shown by Steijn [11]. It was proposed by Lancaster [12] that addition of high aspect ratio filler materials (carbon or glass fibres) to PTFE can improve its wear resistance due to preferential load supporting action by these fibres. There have also been some reports on the use of particulate filler materials like MoS_2 and graphite to modify the tribological properties of PTFE [13–15]. Tanaka and Kawakami [16] have studied the effect of incorporation of glass fibres and MoS_2 particulates separately on the friction and wear properties of PTFE. According to them, although the glass fibres are effective in preventing the large-scale fragmentation of the PTFE, they tend to undergo fracture under heavy loading conditions and cause abrasion to the contact surfaces. It was also proposed that the addition of MoS_2 alone does not impart a good wear resistance to PTFE, especially during severe conditions of sliding [14]. This is because the particulates are ineffective in carrying the load and, hence, result in higher wear rate. However, addition of lubricating MoS_2 in the presence of a strengthening (glass fibres) phase has the potential to reduce the abrasion by the latter by maintaining a low friction film. This film would have been disrupted by the strengthening phase if only PTFE were present. Blanchet and Kennedy [17] have argued over the hypothesis by Tanaka and Kawakami [16] that the presence of transfer films on the counter face to be the sole wear reducing mechanism for PTFE and PTFE composites. They proposed that the filler materials embedded in the PTFE matrix reduce the subsurface deformation and interrupt crack propagation. They suggest that the wear mechanism of the PTFE composites is entirely different from that of the bulk PTFE polymer. In the case of the composites, the filler materials obstruct the large-scale fragmentation of the PTFE, resulting in formation of small discontinuous fragments. This reduces the overall wear rate. Pocock and Cadman [18] used differential scanning calorimetry (DSC) to study the chemical reactions occurring between the fillers and the polymer matrix at higher temperatures. Arkles and Schireson [19] have investigated the changes in the crystallinity of the wear debris as compared to the bulk PTFE polymer.

All of the above research findings suggest, that incorporation of two or more filler materials each having a distinct functionality (one providing wear resistance and the other a lower coefficient of friction), can result in a composite with the potential of enhancing tribological performance. The same can be said concerning adding PTFE to the matrix of tribologicaly inferior material (mainly high friction) to produce a composite with augmented tribological characteristic. A classic example of that is to add PTFE to polyetheretherketone (PEEK) to improve performance of this widely used engineering polymer [20].

3. Experimental details

3.1 Urushi lacquer

The urushi lacquer is a cured material of the ki-urushi (raw urushi lacquer) which is the sap of the lacquer tree. The ki-urushi is an emulsion containing the urushiol, which has a similar chemical structure to the phenolic resin, water and the laccase. The ki-urushi can be cured at room temperature by the enzyme activity of the laccase but it is a prolonged process. The curing process can be markedly accelerated at elevated temperature similar to that of a thermosetting resin. A typical composition of the material is: urushiol - 60〜70 wt%; water - 20〜35 wt%; laccase - 0.3〜0.9 wt%. The process of making cured material is schematically shown in Figure 1. Urushi lacquer is characterised by a superior chemical resistance, considerable hardness, and no known harmful effects on a human body. A test for chemical resistance of the urushi lacquer using sodium hypochlorite solution proved its almost total inertness as illustrated by Figure 2.

3.2 Test specimen, apparatus and procedure

Figure 3 shows a photograph of the test specimen and counterface used in this study. The ki-urushi paste and the ki-urushi paste were mixed with PTFE powder (with average dia. of 4 μm). The resulting mixture was then applied to the roughened, with emery paper grade 400, brass block (15 mm x 15 mm x 8 mm) as a thin layer. Afterwards, it was cured in an electric oven at 200^{o} C for 240 minutes. Finally, cured urushi lacquer layer was polished with the help of a fine polishing paste. The counterface was made of a stainless steel with OD = 12 mm and ID = 4 mm. This resulted in the nominal contact area of 100 mm^2. Figure 4 illustrates, in a schematic way, preparation of test specimens used. Test conditions used are summarised in Table 1.

Figure 5 shows, in a schematic way, test apparatus used. The main feature of the apparatus is the ring-on-plate configuration of the contact area. Rotation of the counterface, fixed to a shaft driven by a DC motor, is controlled by an electronic controller. Test specimen is attached to a spindle supported by an aerostatic bearing. The load on the contact is applied through the pneumatic cylinder and can be finely controlled. Load cell attached to the spindle, which is normally stationary, measures the friction torque under set rotational speed of the shaft and the load applied on the contact. Figure 6 shows a photograph of the test apparatus with its main components labelled.

A typical test began by fixing cleaned and degreased test specimen into the spindle’s chuck. Next the rotation of the shaft to which the counterface was attached was initiated. Two rotational speeds, corresponding to 0.005 m/s and 0.025 m/s sliding speed at the centre line of the nominal contact area, were used. Once the initial unloaded contact between the specimen and its counterface was made, the load of 50 N (corresponding to 0.5 MPa nominal contact pressure) was applied via the pneumatic cylinder. Under the above conditions the test was run for the sliding distance of 125 m without any external lubrication. Using load cell, friction torque was continually measured and recorded. Its values were then converted into the variations of the friction coefficient. Wear of the test specimen was assessed by taking a profile of the cross-section through the contact path with the help of a laser scanning confocal microscope. This is illustrated in Figure 7. The intensity of wear was measured as the depth of the groove created on the specimen’s surface due to the loaded contact with the counterface.

4. Results and discussion

Figure 8 shows variations of friction coefficient at the sliding speed of 0.005 m/s for test specimens with different contents of PTFE varying from 0% (pure urushi lacquer) to 100% (pure PTFE). It can be noticed that pure urushi lacquer exhibits rather high friction coefficient, almost 0.6 at the end of the test. However, increased amount of PTFE additive results in considerable decrease of the friction coefficient so from the 40% PTFE addition to urushi lacquer friction coefficient is low indeed, around 0.1, and stays at this level even though there are further increases in the PTFE contents. This is equal to the friction coefficient recorded for pure PTFE test specimen.

Test results for the sliding speed of 0.025 m/s are shown in Figure 9. The overall pattern of friction coefficient changes with the amount of PTFE additive is quite similar to that observed for the sliding speed of 0.005 m/s. As before, for small contents of PTFE in the urushi lacquer (0 to 10% by weight) the friction coefficient is rather high. However, with the increase in the PTFE contents it rapidly decreases and reaches the level around 0.1 at the 20% PTFE in the urushi lacquer. Another interesting observation is that at the increased sliding speed (0.025 m/s) the friction is usually high at the beginning of the test and gradually decreases towards the end of the test. This is especially pronounced at 10% PTFE contents suggesting that thermal effects at the contact interface reduce the hardness of the urushi lacquer and thus facilitate lubricating effect of the PTFE. This could be envisaged as some sort of squeeze mechanism, pushing PTFE particles out from the urushi lacquer matrix.

In order to estimate wear performance of the composite, cross-section profiles of the wear track created on the surface of the test specimen were taken by a laser scanning confocal microscope (Keyence corp. ,VK-X150) and a wide-area 3D measurement System(Keyence corp. ,VR-3050). The results are shown in Figure 10. It can be easily observed that the addition of PTFE to the urushi lacquer does not affect, in any appreciable extent, the wear resistance of the composite. At both test sliding speeds and two levels of PTFE contents (0% and 30% by weight) urushi lacquer composite prove to have superior wear resistance compared to that of pure PTFE. This is also true when friction and wear performance of urushi lacquer composite is compared with the performance of other well-known self-lubricating substances.

The morphologies of pure urushi lacquer and its composite containing 30% PTFE by weight obtained by a Mitutoyo optical microscope are shown in Figures 11-14. The images were taken at the x10 magnification and recorded with the camera COMOS setting of 8.8 mm by 13.2 mm. Figure 11 shows pure urushi lacquer before the test. It can be seen that the surface is covered by markings resulting from a final polishing of its surface. Figure 12 shows appearance of the contact track surface. The only difference is that the clearly visible polishing markings are now less pronounced due to wear. Figure 13 illustrates surface morphology of the composite of urushi plus 30% PTFE by weight before testing. Again, polishing markings are clearly visible but PTFE particles are less pronounced which indicates that they are thoroughly mixed with urushi paste and do not form lumpy aggregates. Finally, Figure 14 shows the wear track surface of the composite of urushi with 30% PTFE additive. Comparing to the surface morphology image shown in Figure 13, the only difference is the less pronounced visibility of the polishing markings. Furthermore, there are no signs of PTFE being smeared over the contact track surface which can be explained by recalling that the composite was made from a urushi paste and 4 micron PTFE particles – a very homogeneous mixture.

5. Conclusions

The results of experimental research into the tribological performance of urushi lacquer and its composites containing PTFE additives allow the formulation of the following conclusions.

(i) Friction of pure urushi lacquer is high and can be substantially reduced by the addition of PTFE. At the 30% contents by weight of PTFE the friction of the composite is comparable to that of pure PTFE when in contact with stainless steel counterface.

(ii) Wear resistance of the urushi lacquer is not affected by the addition of PTFE. The wear of pure urushi lacquer and that containing 30% by weight of PTFE is unchanged and minimal as measured by the depth of the wear track formed on the surface of test specimens.

(iii) It is permissible to observe that urushi lacquer – a substance naturally occurring and with green credentials is a new self-lubricating composite with the potential for many practical applications.

6. References

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Figure Legends

Figure 1. The process of making cured material – urushi lacquer
(a) Sumac tree with grooves to collect sap;
(b) Raw urushi sap;
(c) Cured urushi;
(d) Phenolic structure;
(e) Urushiol main structure.

Figure 2. A test for chemical resistance using sodium hypochlorite solution.
(a) Phenolic resin before immersion;
(b) Phenolic resin after immersion;
(c) Cured urushi lacquer before immersion;
(d) Cured urushi lacquer after immersion.

Figure 3. The test specimen and counterface used in the study.
(a) Test specimen;
(b) counterface;
(c) geometry of the contact area.

Figure 4. Schematic illustration of test specimens' preparation.
(a) Urushi lacquer
(b) Urushi lacquer + PTFE
(c) Pure PTFE block

Figure 5. Schematic of the test apparatus.

Figure 6. Photograph of the test apparatus showing its main components.

Figure 7. Measurement of the wear track depth formed on test specimen (PTFE 100 wt%, V=0.025m/s).
(a) Top view of the test specimen
(b) Surface profile of the test specimen (Cross section A-A')

Figure 8. Variations of friction coefficient with the sliding distance at the sliding speed of 0.005 m/s for test specimens with different contents of PTFE varying from 0% (pure urushi lacquer) to 100% (pure PTFE).

Figure 9. Variations of friction coefficient with the sliding distance at the sliding speed of 0.025 m/s for test specimens with different contents of PTFE varying from 0% (pure urushi lacquer) to 100% (pure PTFE).

Figure 10. Average depth of the wear track formed on various test specimens.
(a) V=0.005m/s

(b) V=0.025m/s

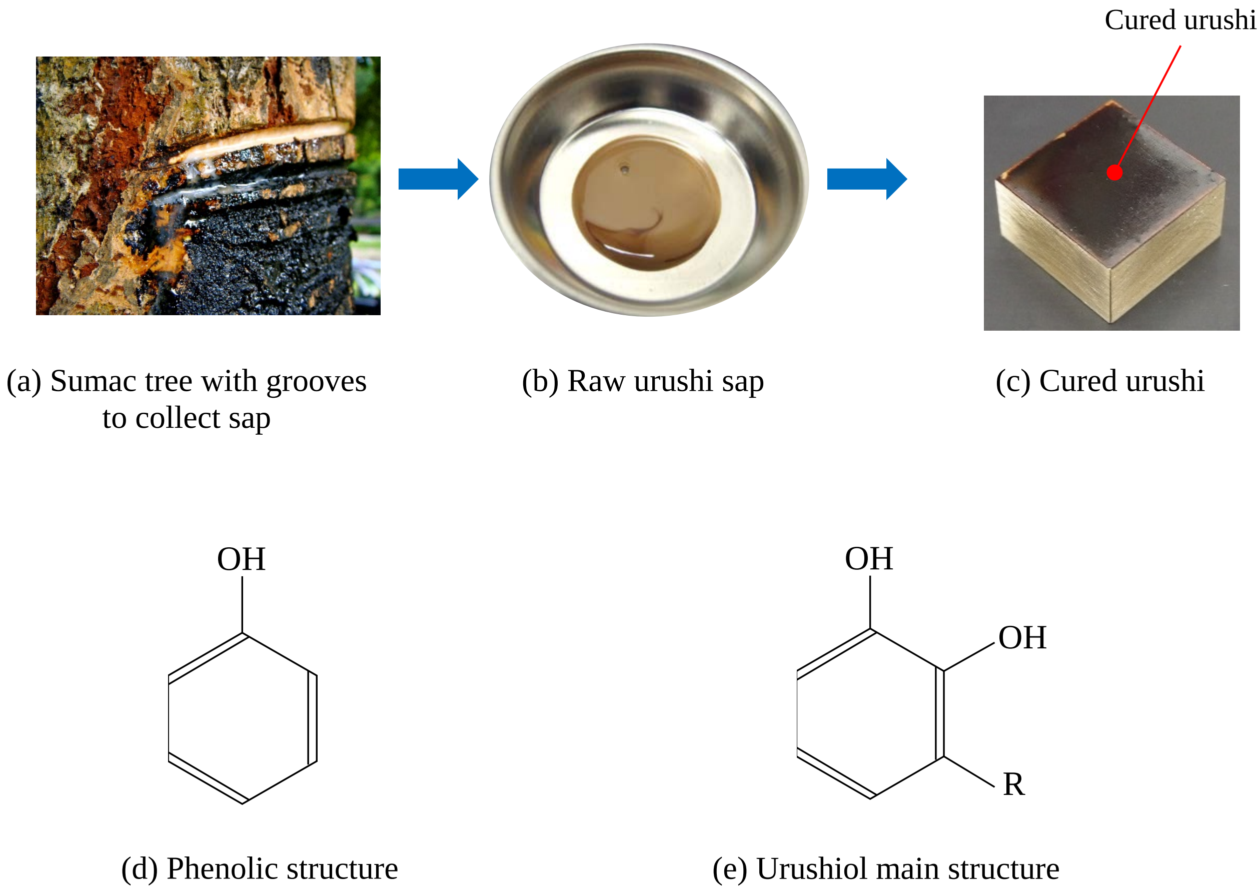
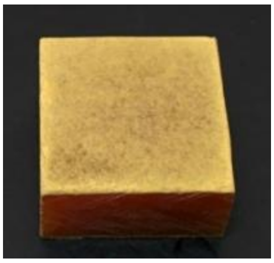


Figure 1 The process of making cured material – urushi lacquer

(a) Phenolic resin
before immersion

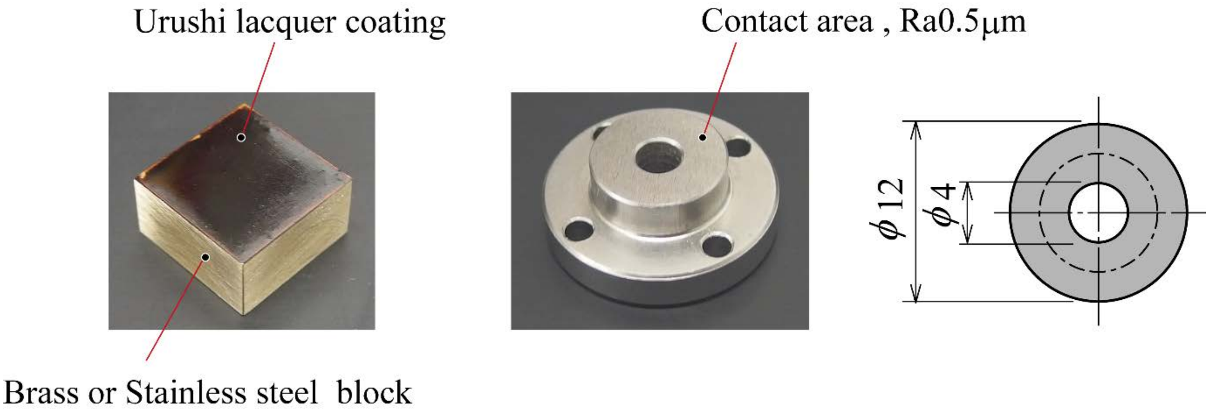


(b) Phenolic resin
after immersion

(c) Cured urushi lacquer
before immersion

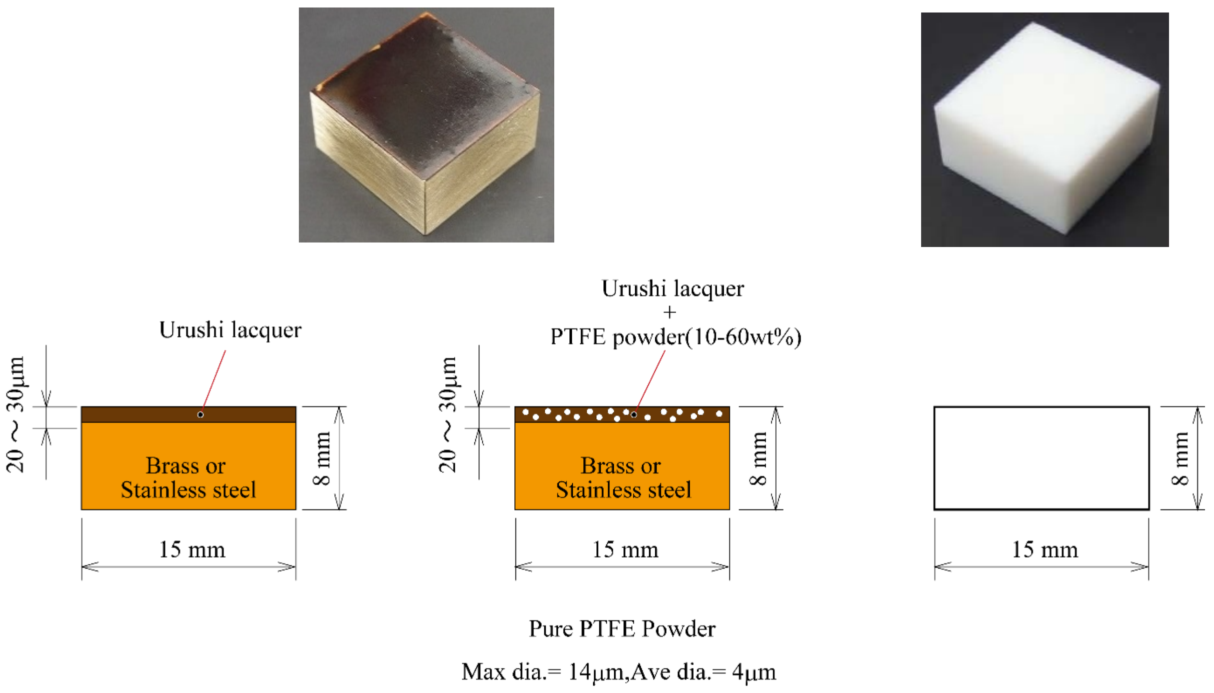
(d) Cured urushi lacquer
after immersion
（No changes in appearance）

Figure 2 A test for chemical resistance using sodium hypochlorite solution.



(a) Test specimen (b) Counterface (c) Geometry of the contact area

Figure 3 The test specimen and counterface used in the study.



(a) Pure urushi lacquer (b) Urushi lacquer +PTFE (c) Pure PTFE block

Figure 4 Schematic illustration of test specimens' preparation.

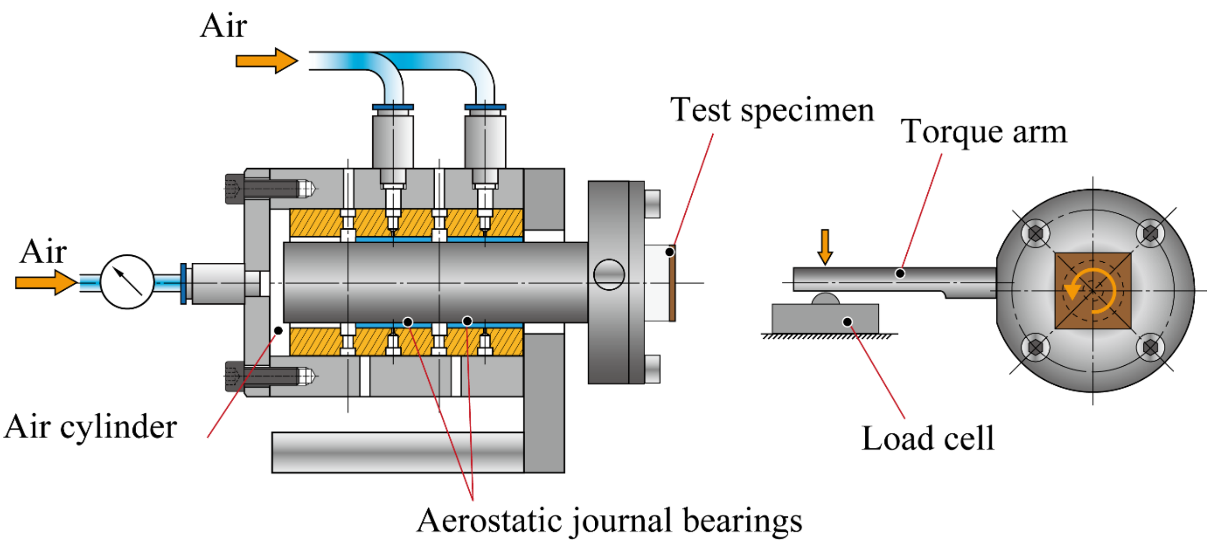


Figure 5 Schematic of the test apparatus

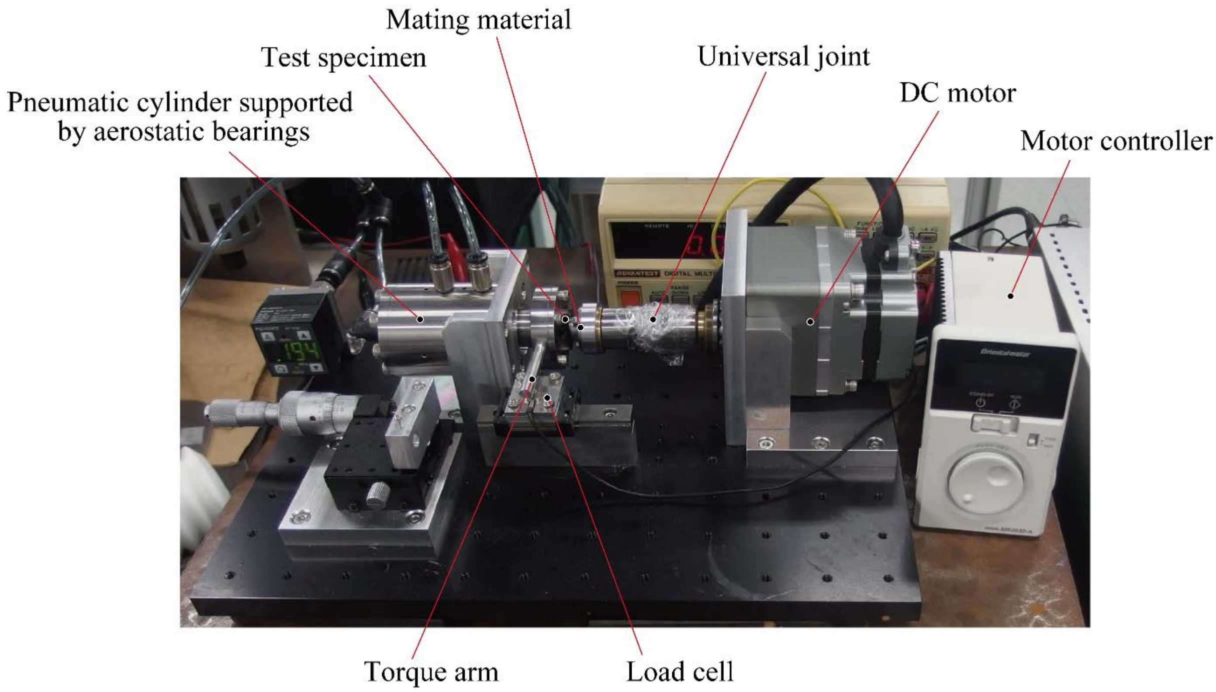
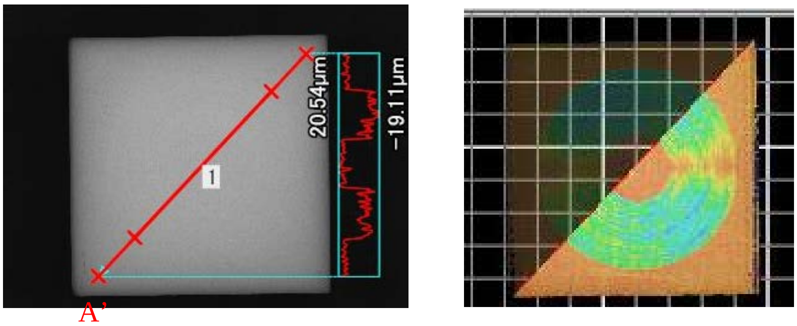
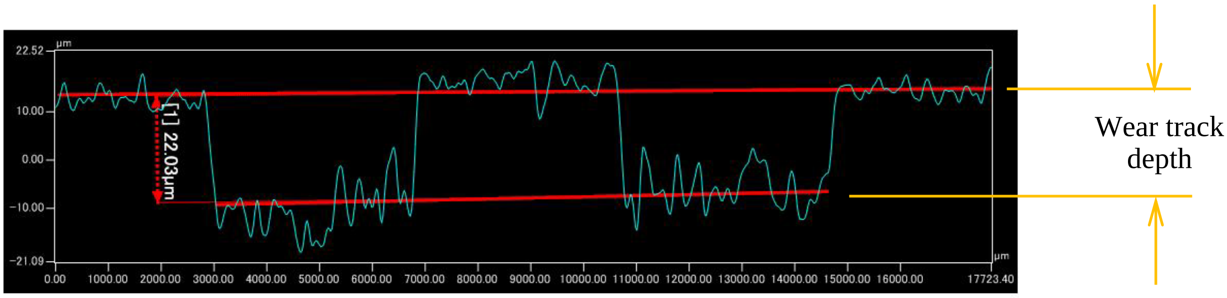


Figure 6   Photograph of the test apparatus showing its main components



(a) Top view of the test specimen



(b) Surface profile of the test specimen (Cross section A-A’)

Figure 7 Measurement of the wear track depth formed on test specimen (PTFE 100 wt%, *V*=0.025m/s).

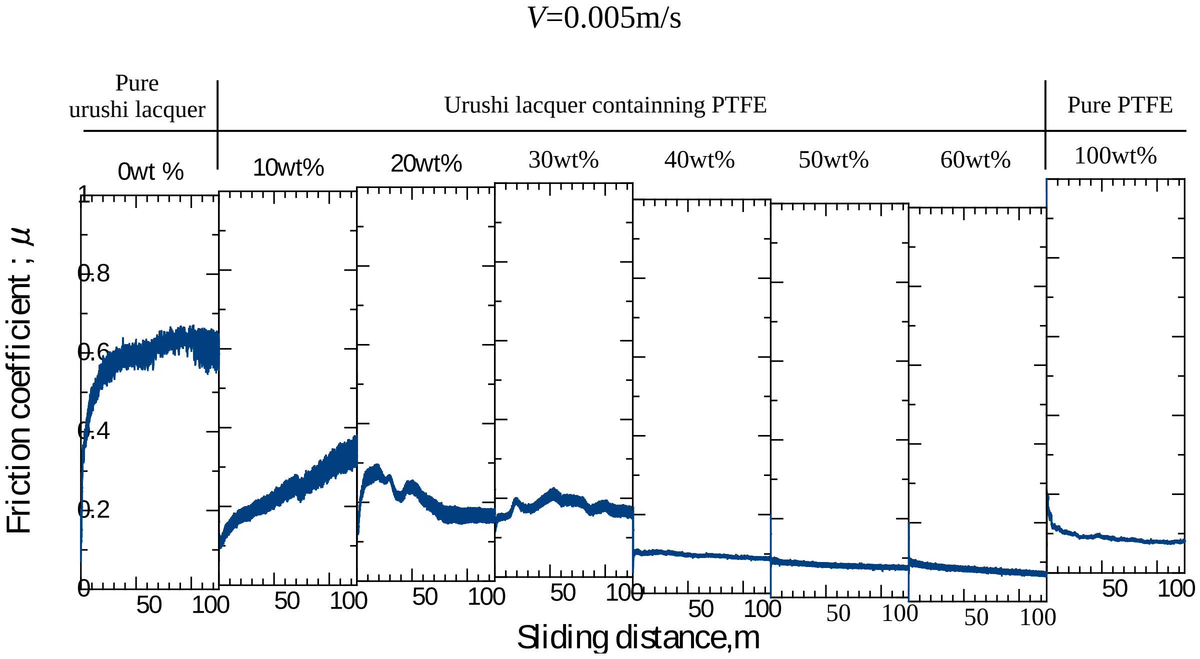


Figure 8 Variations of friction coefficient with the sliding distance at the sliding speed of 0.005 m/s for test specimens with different contents of PTFE varying from 0% (pure urushi lacquer) to 100% (pure PTFE)

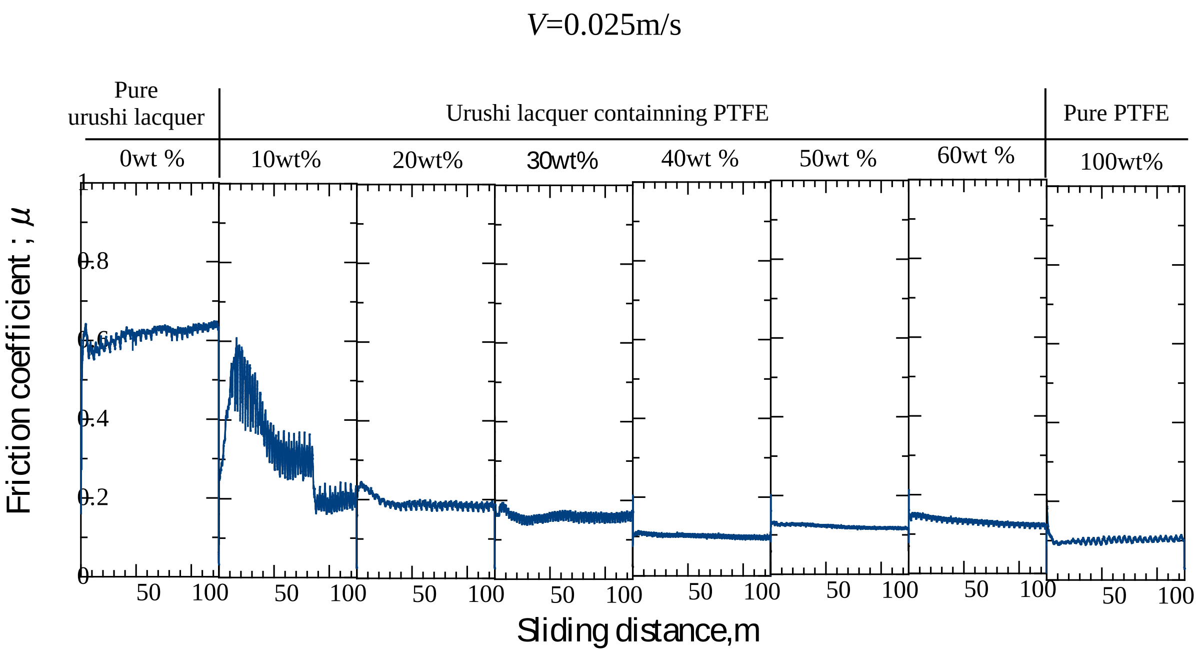


Figure 9 Variations of friction coefficient with the sliding distance at the sliding speed of 0.025 m/s for test specimens with different contents of PTFE varying from 0% (pure urushi lacquer) to 100% (pure PTFE).

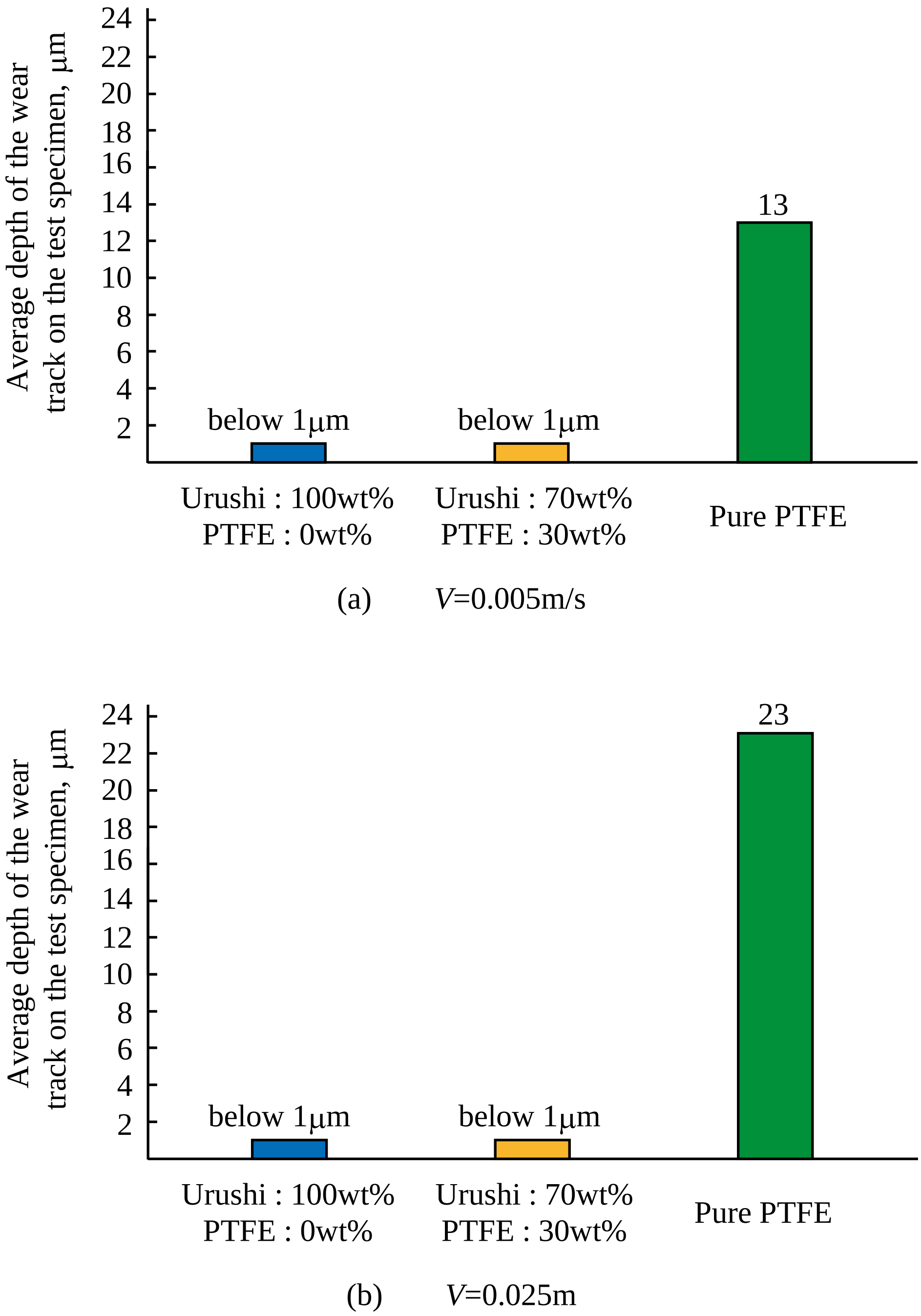


Figure 10. Average depth of the wear track formed on various test specimens.

Load : *W* [N]	50	
Nominal contact area : *A* [mm^2]	100	
Nominal contact pressure : $p = W/A$ [MPa]	0.5	
Sliding speed (at the centre line) [m/s]	0.005	0.025
Total sliding distance [m]	125	

Table 1. Test conditions applied during experiments.