

Nano/Micro-friction properties of Chemical Vapor Deposited (CVD) Self-assembled monolayers on Si-wafer

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Abstract – Nano/micro-scale studies on friction properties were conducted on Si (100) and three self-assembled monolayers (SAMs) (PFOTC, DMDM, DPDM) coated on Si-wafer by chemical vapor deposition technique. Experiments were conducted at ambient temperature ($24\pm 1^\circ\text{C}$) and humidity ($45\pm 5\%$). Nano-friction was evaluated using Atomic Force Microscopy (AFM) in the range of 0-40nN normal loads. In both Si-wafer and SAMs, friction increased linearly as a function of applied normal load. Results showed that friction was affected by the inherent adhesion in Si-wafer, and in the case of SAMs the physical/chemical structures had a major influence. Coefficient of friction of these test samples was also evaluated at the micro-scale using a micro-tribotester. It was observed that SAMs had superior frictional property due to their low interfacial energies. In order to study of the effect of contact area on friction coefficient at the micro-scale, friction was measured for Si-wafer and DPDM against Soda Lime balls (Duke Scientific Corporation) of different radii (0.25 mm, 0.5 mm and 1 mm) at different applied normal loads (1500, 3000 and 4800 μN). Results showed that Si-wafer had higher friction coefficient than DPDM. Furthermore, unlike that in the case of DPDM, friction was severely influenced by wear in the case of Si-wafer. SEM evidences showed that solid-solid adhesion to be the wear mechanism in Si-wafer.

Keywords - nano, micro, friction, tribology, AFM, SEM

1. Introduction

Self-assembled monolayers, popularly known as ‘SAMs’ are molecular assemblies that form spontaneously by adsorption to substrates via high affinity chemisorption [1]. Their conventional applications are in the areas of bio/chemical and optical sensors, and for use as drug delivery vehicles [1]. In 1996, Linford and Chidsey [2] demonstrated for the first time that robust monolayers can be prepared and could be bonded to silicon substrates. Since then, these molecular assemblies have found their niche as solid lubricants in MEMS tribology [3]. In MEMS devices, the surface area to volume ratio is large due to the scaling law [3]. Moreover, due to lateral and vertical gaps (clearances) between components being around $1\mu\text{m}$ [3], conventional liquid lubricants cannot be used, as they cause liquid-mediated adhesion leading to high static friction [4]. Further,

during sliding, frictional effects not only due to external load but also due to the intrinsic liquid-mediated adhesive force needs to be overcome. Under such conditions, SAMs provide an ideal solution for lubrication [3,4] owing to their properties such as thermodynamic stability, formation of close packed structures, hydrophobicity and strong bonding (chemisorption) to the substrates [3,4].

For SAMs to be ideal candidates in tribology - to mitigate friction and wear, (i) the head group should be a polar group, for it provides strong adherence to the substrate through a chemical bond and (ii) the terminal group (tail group) of the organic molecular chain should be a non-polar group [3]. An in depth overview on various end and head groups, and classes of SAMs can be found in Ulmann’s report [1]. Roya Maboudhian et al. [3] and Komvopolous [5] provide insightful reviews on the

tribological challenges in MEMs with the main focus on the evaluation of SAMs as lubricants. From their reports it is seen that the trichlorosilane class of SAMs exhibit the best performance, but are difficult to produce due to their sensitivity to water content and humidity during their preparation [1]. SAMs can be produced by various methods such as dipping, microcontact printing, sol gel, spin coating and by chemical vapor deposition [1,3-6].

In the present work, we have evaluated the nano/micro-frictional properties of three SAMs namely, Perfluoro-octyltrichlorosilane ($C_8F_{13}H_4SiCl_3$, PFOTC), DimethylDimethoxysilane ($C_4H_{12}O_2Si$, DMDM) and DiphenylDimethoxysilane ($C_{12}H_{14}O_2Si$, DPDM) coated on Si-wafer by the chemical vapor deposition (CVD) method. In this article, the underlying mechanisms that influence the friction in these SAMs at nano/micro-scales have been reported. Further, the effect of contact area on the micro-friction property of the DPDM, in comparison with that of the un-coated Si-wafer is also reported.

2. Experimental

2.1 SAMs Preparation

Three different SAMs namely, Perfluoro-octyltrichlorosilane ($C_8F_{13}H_4SiCl_3$, PFOTC), DimethylDimethoxysilane ($C_4H_{12}O_2Si$, DMDM) and DiphenylDimethoxysilane ($C_{12}H_{14}O_2Si$, DPDM) were coated on Si-wafer ((100), produced by LG Siltron) by the chemical vapor deposition (CVD) method. Prior to the coating of Si-wafers by SAMs in the CVD reactor, the Si-wafers were cleaned in Piranha solution ($H_2SO_4: H_2O_2$ in the ratio 7:3) for about 30 minutes at a temperature of about 85 °C. Subsequently, they were ultrasonically cleaned with isopropyl alcohol before being placed in the CVD reactor. The detailed procedure regarding the coating is given elsewhere [7]. Table 1 shows the

temperature and time duration at which the SAMs were deposited on Si-wafer in the CVD reactor. The choice of the temperature mainly depends upon the boiling point of the precursor molecules [Table 1]. Figure 1 shows the schematic of the structure of the SAMs used in the present study.

Table 1. Details of preparation conditions of SAMs.

NAME	Boiling Point (° C)	Temperature (° C)	Time (Hours)
PFOTC	192	100	2
DMDM	82	50	3
DPDM	176	100	3

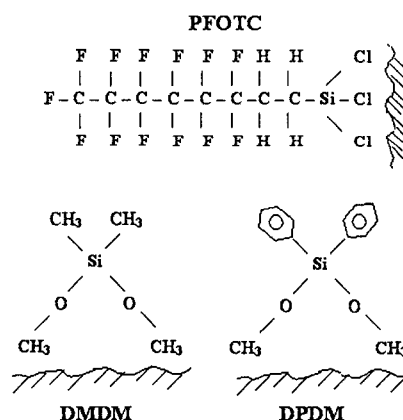


Fig.1 Schematic of structures of SAMs

2.2 Test apparatus

2.2.1 Friction measurements at nano-scale

Nano-scale friction tests were conducted using a commercial Atomic Force Microscope (AFM) (Multimode SPM, Nanoscope IIIa, Digital Instruments). A view of the AFM used in the present study is shown in Figure 2. The friction force was measured in LFM (Lateral Force Microscope) mode. Friction measurements were made at applied normal loads in the

range of 0-40 nN. Measurements were conducted at the scanning speed of 2 $\mu\text{m/s}$ for the scan size of $1\mu\text{m} \times 1\mu\text{m}$ using a contact mode type Si_3N_4 tip (NPS 20) that had a nominal spring constant 0.58 N/m. Each test was repeated for 15 times and the average values were plotted.

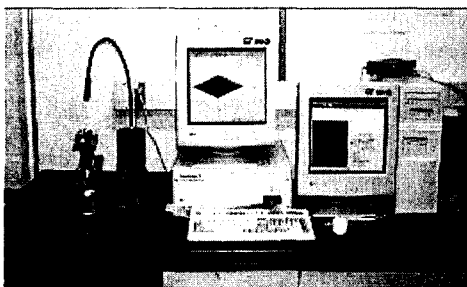


Fig. 2 A view of AFM used for the measurement of nano-friction.

2.2.2 Friction measurements at micro-scale

Micro-scale friction tests were performed with a ball-on-flat type micro-tribotester (shown in Figure 3) under reciprocating motion. Two different sets of experiments were conducted: (i) friction was measured for Si-wafer and for the SAMs against a 2 mm diameter Si_3N_4 ball (applied normal load: $4000\mu\text{N}$, sliding speed: 3 mm/sec, scan length: 3 mm). (ii) To study of the effect of contact area at the micro-scale, friction was measured for Si-wafer and DPDM against Soda Lime balls (Duke Scientific Corporation) of different radii (0.25 mm, 0.5 mm and 1 mm). Tests were also conducted at three different applied normal loads (1500, 3000 and $4800\mu\text{N}$) for duration of about 30 minutes (sliding speed: 1 mm/sec, scan length: 3 mm). Tests were repeated more than three times and the average values were plotted. All experiments mentioned above, at nano- and micro-scales were conducted at ambient temperature ($24\pm 1\text{ }^\circ\text{C}$) and humidity ($45\pm 5\%$).

3. Results and Discussion

Figure 4 shows the topography of the SAMs taken in AFM in a scan area of $1\mu\text{m} \times 1\mu\text{m}$, at the data scale of 100nm. It is interesting to note that all the SAMs exhibited uniform coating. Further, in the present case, particles (agglomerates) are absent, which in the dipping method is a regular feature that forms because of polymerization during

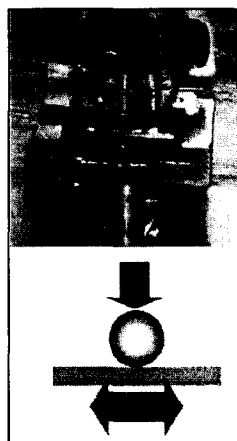


Fig. 3 A close-up view of the ball-on-flat type micro-tribotester.

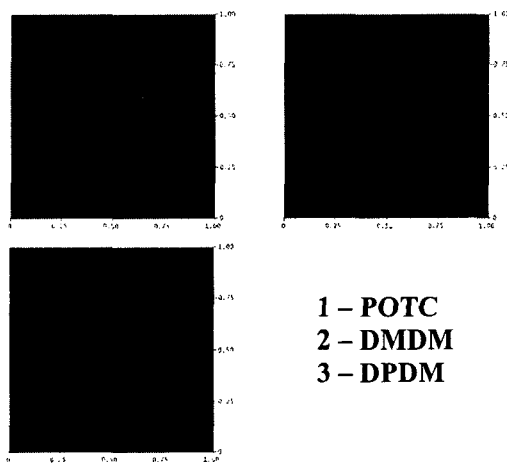


Fig. 4 Topography of SAMs taken using AFM (Data Scale: 100nm).

coating. The absence of particle formation is an important difference between the two methods namely the dipping method and the CVD method [6,7]. Table 2 shows the properties of test specimens used.

3.1 Friction at nano-scale using AFM

Figure 5 shows the variation of friction at nano-scale for Si-wafer and the SAMs. From the figure it is worth noting that the friction force exists even at the zero applied normal load. This is mainly attributed to the

Table 2. Properties of test specimens
(E: Young's Modulus, PR: Poisson's Ratio, R: Roughness, WCA: Water Contact Angle, IE: Interfacial Energy)

MATERIAL	E (GPa)	PR	R (nm)	WCA (Deg)	IE (mN/m)
Si-Wafer	165	0.28	0.15	22	72
Soda Lime	68	0.16	-	-	-
PFOTC	-	-	0.20	106	-
DMDM	-	-	0.17	82	-
DPDM	-	-	0.18	88	-

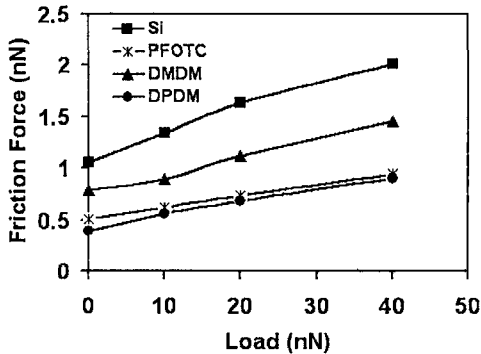


Fig. 5 Friction force measured using AFM as a function of applied normal load.

influence of the intrinsic adhesive force on the friction force [8]. This adhesive force arises due to the contribution of various attractive forces such as capillary, electrostatic, van der Waal and chemical

bonding under different circumstances [3]. In Si-wafer, owing to its hydrophilic nature [Table2,3,9] it is considered that the capillary force due to the formation of meniscus-bridge (condensation of water from the environment) between the tip and the sample, contributes to a major extent. Van der Waal forces also contribute [10], but their magnitude is less when compared to that of the capillary force [3]. In contrast to Si-wafer, SAMs are hydrophobic in nature (Table 2) and hence, capillary force gets suppressed to a large extent. Friction in nano-scale is in a regime where the contribution from intrinsic adhesion can outweigh those from the asperity deformation and ploughing [3,11]. In the present case, the applied normal load has been limited to 40nN, in an effort not to deform or wear the SAMs, but rather to probe the frictional properties of only the outermost portions of the SAMs. Studies [12] have shown that substantial deformation of monolayers occurs at loads greater than the loads used in the present case. Further, as seen in Figure 5, the approximately linear response of friction force versus applied load indicates that there has been no significant deformation or wear of the monolayers. Under the condition that the friction in the present case has not been influenced by the deformation, the intrinsic adhesion contributes strongly to the friction force [3,11], thus rendering the SAMs to have lower friction force than the Si-wafer.

Another strong reason for the SAMs exhibiting lower friction force than the Si-wafer is their smaller real area of contact. From Figure 5 it is observed that for both Si-wafer and the SAMs, the friction force increases linearly with the applied normal load. These trends could be explained by considering the fundamental law of friction given by Bowden and Tabor [13]. According to this law, the friction force is directly dependent on the real area of contact, for a single asperity contact. Equation 1 gives the expression for the friction force.

$$F_f = \tau A_r \quad (1)$$

Where, τ is the shear strength, an interfacial property and A_r , the real area of contact.

The behavior of the friction force in Si-wafer and SAMs is very much consistent with this law of friction, as in both these materials the friction force increases with the increase in the real area of contact. Assuming the contact at nano-scale to be a pseudo-single asperity contact, the real area of contact can be estimated from the JKR equation (Equation 2) [14] for Si-wafer, as it exhibits high interfacial energy (lower water contact angle) [Table 2]. To estimate the real area of contact for SAMs, the Hertzian equation (only the first term in the equation 2) can be used because of their low interfacial energies (higher water contact angles), which could be more than one order less in comparison to that of Si-wafer [15].

$$A_r = \pi \left[\frac{R}{K} (F_n + 6\pi\gamma R + [12\pi\gamma R F_n + (6\pi\gamma R)^2]^{1/2}) \right]^{2/3} \quad (2)$$

Where, R is the size of the tip, K the effective elastic modulus, F_n the applied normal load and γ , the interfacial energy of the material.

For SAMs, the values of Young's modulus and Poisson's ratio are unavailable and hence, we estimate $A_r(K)^{2/3}$ for both the Si-wafer and the SAMs. This would provide a first order comparison between the contact area of Si-wafer and SAMs. Figure 6 shows $A_r(K)^{2/3}$ estimated for these two different kinds of materials for the applied normal load of 40nN. It is seen from the figure that Si-wafer exhibits higher contact area than the SAMs, which explains for its higher friction force when compared to that of the SAMs (Figure 5).

From Figure 5 it is also seen that both PFOTC and DPDM show lower friction force when compared to DMDM. DPDM shows low friction owing to the nature of its benzene ring (Figure 1). Rings are expected to be stiff (probably because of their

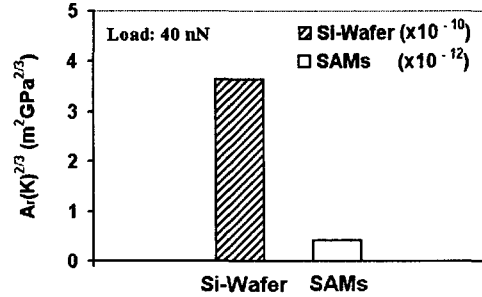


Fig. 6 Estimated $A_r(K)^{2/3}$ for Si-wafer and SAMs at nano-scale (Normal Load: 40nN)

saturated bonds (double bonds)); therefore, their frictional properties are expected to be superior to that of linear molecular structures [16]. Overney et al. [17] too have observed similar relation between the friction and stiffness in their work on phase-separated monolayers. Superior friction properties of phenyl terminated SAMs due to the influence of rings has also been observed earlier by Bhushan et al. [18]. Further, the low friction values exhibited by PFOTC could be attributed to its structure of long carbon chain (Figure 1). It is well known that long carbon chain molecular assemblies exhibit lower friction force when compared to assemblies with short carbon chain [4]. Furthermore, what is interesting here is that, although PFOTC has long chain structure than DMDM and DPDM, its friction value is not the least. This could be attributed to the presence of fluorine atom in its chemical structure. Fluorine atoms have larger Van der Waals radii [13,19]. Consequently, they interact more strongly with the neighboring chains, giving rise to long-range multi-molecular interactions [13,19]. To overcome the energetic barrier due to the long-range multi-molecular interactions, more energy gets imparted to the film during sliding and results in higher frictional property. This explains the reason why the friction in PFOTC is not the least, although it has the long carbon chain structure [13,19].

3.2 Friction at micro-scale using micro-tribotester

3.2.1 Comparison between the friction coefficients of SAMs

Figure 7 shows the coefficient of friction values of Si-wafer and SAMs. From the figure it could be observed that all SAMs

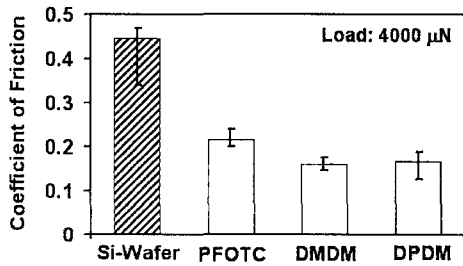


Fig. 7 Friction Coefficient measured at micro-scale (Normal load: 4000μN).

show values of coefficient of friction lower than that of the Si-wafer. This is mainly attributed to their smaller contact areas (Figure 8) in comparison to that of the Si-wafer, which in turn is due to their low interfacial energies [15]. Figure 8 shows $A_r(K)^{2/3}$ estimated for Si-wafer and SAMs at micro-scale. These estimations have been done on similar lines as explained in Section 3.1.

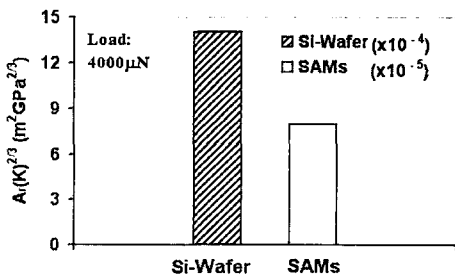


Fig. 8 Estimated $A_r(K)^{2/3}$ for Si-wafer and SAMs at micro-scale (Load: 4000μN)

From Figure 7, it is also seen that there is no significant difference between the friction coefficient values for DMDM and DPDM. As said earlier in Section 3.1, the difference in the frictional behavior between these two

SAMs was basically due to the difference in their terminal groups. This difference was markedly recorded at the nano-scale, as the probe (AFM tip), the applied load and the contact between the probe and the sample were all at a finer scale. In the present case, at micro-level, unlike at the nano-scale, all the three above-mentioned parameters namely, the probe size (ball), the applied normal load and the contact area between them are all at a coarser level. Coupled with this, under micro-loads, the bi-directional sliding for long duration (30 minutes) would induce deformations unseen at the nano-scale. All these factors together make the influence of the finer aspects of SAMs structures (DMDM, DPDM) on their frictional properties undetectable at micro-scale. In comparison to that of DMDM and DPDM, PFOTC shows high values of coefficient of friction; even though it has long carbon chain (Figure 7) and that the long chain structures usually reduce the values even at micro-scale [4]. The reason that could possibly explain for the high frictional value of PFOTC is the presence of the fluorine atom in its chemical structure. As mentioned earlier in Section 3.1, fluorine terminated SAMs exhibit higher frictional properties than the hydrogen terminated ones [13,19] due to the larger Van der Waals radii of the fluorine atom. At micro-scale, the larger contact area than that at the nano-scale could lead to this effect getting more pronounced, which would finally lead to higher friction values in the case of PFOTC.

3.2.2 Effect of contact area on the coefficient of friction at micro-scale

Figures 9 and 10 show the variation in the coefficient of friction as a function of applied normal load, for various ball sizes in the case of Si-wafer and DPDM respectively. It is seen from the figures that the friction coefficient increases with the ball size in both the specimens and also that DPDM shows low values in comparison with that of Si-wafer, under all the test conditions. Another important observation was that the

Si-wafer exhibited significant wear, which was clearly visible even to the naked eye. Such a severe wear that could even be recognized by the naked eye was absent in DPDM. Although, deformations at this scale cannot be ruled out in DPDM,

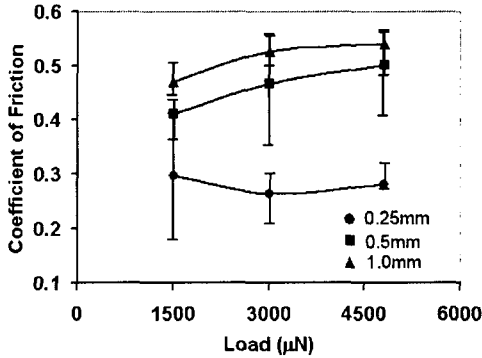


Fig. 9 Friction Coefficient measured in Si-wafer at micro-scale.

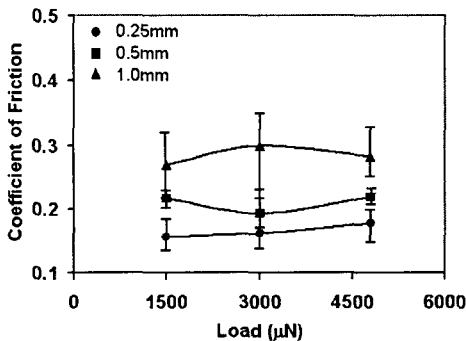


Fig. 10 Friction Coefficient measured in DPDM at micro-scale.

wear in the case of Si-wafer was comparatively severe. Figures 11a shows the wear track seen on Si-wafer tested against glass balls of radius 1 mm at 3000μN. Wear debris are seen on these tracks. Figure 11b is a micrograph that shows debris smeared at the center of the wear track. These evidences indicate that wear occurred in Si-wafer by solid-solid adhesion, which could be attributed to its high interfacial energy that supports such a mechanism and furthermore, the friction was influenced by its wear. In the past,

experiments conducted by Gardos [20] have shown that Si-wafer exhibits high adhesive friction followed by shear-induced micro cracking in the wake of the sliding. Figure 12 shows $A_r(K)^{2/3}$ estimated for Si-wafer and DPDM (estimated on similar lines as

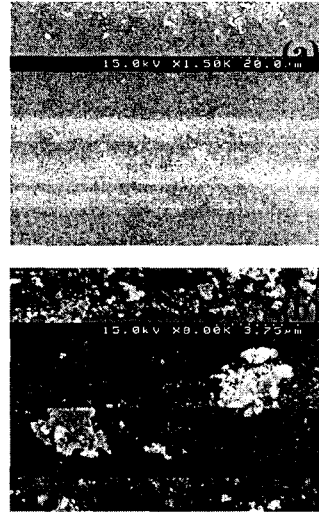


Fig. 11 (a) SEM micrographs of wear track on Si-wafer (1mm ball radius, 3000μN) (b) Wear debris at the center of the wear track

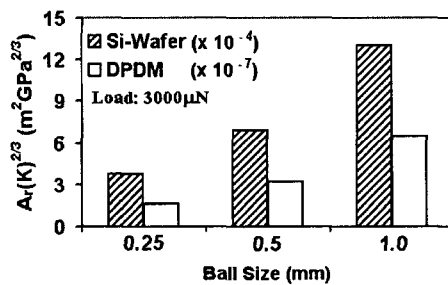


Fig. 12 Estimated $A_r(K)^{2/3}$ for Si-wafer and DPDM at micro-scale (Load: 3000μN)

explained previously) for different ball sizes at 3000μN loads. The estimation of $A_r(K)^{2/3}$ for Si-wafer was done using the JKR model as it includes the contribution of adhesion, whereas for DPDM, the Hertzian model was

used. It is seen from this figure that Si-wafer exhibits higher contact area than DPDM at all ball sizes owing to its high interfacial energy. Further, the increase in the contact area with the increase in the ball size directly assists the adhesive mechanism is Si-wafer and increases the friction force, thereby increasing its coefficient of friction. In the case of DPDM although the increase in the contact area with the increase in ball size increases the coefficient of friction, its lower interfacial energy [15] affects lower contact area in comparison to that of Si-wafer leading to lower values of coefficient of friction than that of the Si-wafer.

4. Conclusions

Nano/micro-frictional properties of three SAMs coated on Si-wafer by the chemical vapor deposition (CVD) method were evaluated. The following are the conclusions drawn from the present work:

(1) At nano-scale, SAMs exhibit superior frictional property than Si-wafer owing to their smaller contact area effected by their lower interfacial energies.

(2) In SAMs, friction at nano-scale is influenced by the structure of their assembly and their end terminal group. Long carbon chain morphology (PFOTC) and phenyl-terminated monolayers (DPDM) exhibit lower friction.

(3) Similar to that at nano-scale, SAMs exhibit superior frictional property than Si-wafer even at the micro-scale owing to their smaller contact area effected by their lower interfacial energies.

(4) Unlike at the nano-scale, the finer influence of the end terminal group on the frictional property in DMDM and DPDM is not detectable at the micro-scale. PFOTC exhibits higher frictional value because of its larger Van der Waal radius.

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