Self-lubricating SU-8 Nanocomposites for Microelectromechanical Systems Applications

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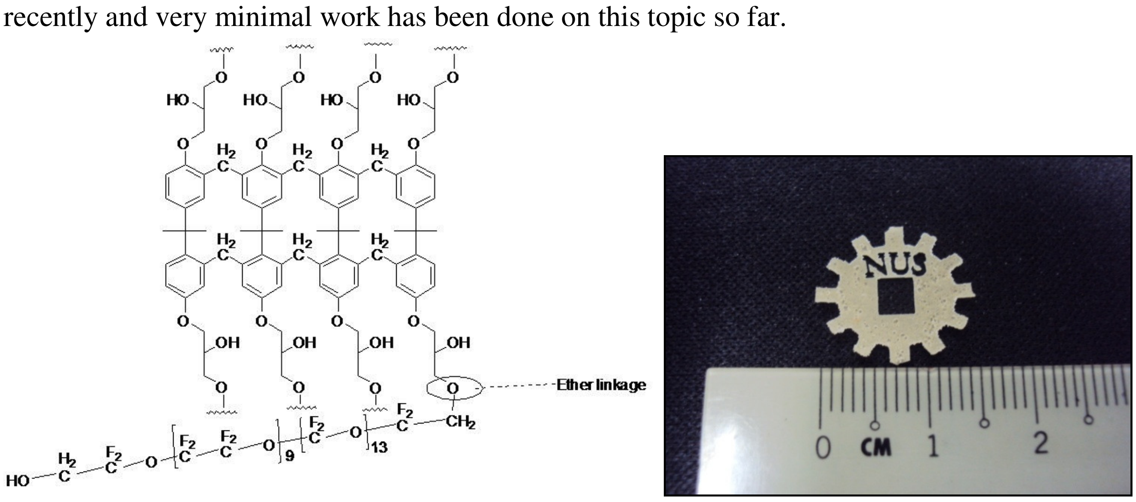
Abstract:

SU-8 is an industrially useful photoresist polymer for micro-fabrication because of its unique UV-sensitive curing property. It is also used as a structural material for micro-machines such as micro-electro mechanical systems (MEMS). However, it has poor tribological and mechanical properties which make SU-8 inferior to Si, the mainstay MEMS material today. In this paper, we report the fabrication of SU-8 nanocomposites which are self-lubricating and have better mechanical properties. The liquid lubricant i.e. perfluoropolyether (PFPE) and nanoparticles such as SiO_2, CNTs and graphite were added into SU-8 for this purpose. These self-lubricating SU-8+PFPE and SU-8+PFPE+nanoparticle composites have shown a reduction in the initial coefficient of friction by ~6-9 times and increased wear life by more than four orders of magnitude. The mechanical properties such as the elastic modulus and the hardness have increased by ~1.4 times. These SU-8 nanocomposites can be used as a self-lubricating structural material for MEMS applications requiring no external lubrication. As well, these nanocomposites can find applications in many tribological components of traditional machines.

Introduction

MEMS is an emerging field of interest in almost every industry including automotive, bio-engineering/biomedical, telecommunications, electronics, space, military and gaming industry etc[1]. There are many challenges to the effective operation of these devices primarily because of their small length scale. As the size of the MEMS devices is in micrometer (or sub-millimeter) range, the surface-to-volume ratio is very high and hence surface forces such as van der Waals, capillary, electrostatic, and chemical forces play important roles when compared to the gravity and inertial forces on the device performance[2]. Hence, in these devices, the interfacial forces are comparable or higher than the forces causing the device motion. The major challenge is from the tribological issues i.e. high friction, high adhesive force and low wear durability [2,3,4]. Hence, if these tribological issues are not addressed properly, they limit the performance, durability and reliability of the MEMS devices [2]. Though, Si has been the mainstay structural material for fabricating MEMS devices, recently SU-8 has been replacing Si for certain applications. Si has the advantage of compatibility with MEMS micro-fabrication processes, however it has many inherent drawbacks such as brittleness, high friction and adhesion force coupled with hydrophilic nature, non-biocompatibility etc. SU-8 is a negative thick-film photoresist patented by IBM in 1989[5]. SU-8 consists of three basic components: (a) an EPON™ SU-8 epoxy resin; (b) a solvent such as gamma-butyrolactone (GBL) and (c) a photoacid generator such as triaryl sulfonium salts. Each SU-8 molecule consists of an average of 8 epoxy groups (and hence the name SU-8). The molecular structure of the SU-8 with 8 epoxy group is shown in Figure 1 (a). SU-8, which is compatible with many different MEMS fabrication processes, is relatively soft and biocompatible and hence it is replacing Si for several applications such as some specific MEMS devices, Bio-MEMS, membrane applications, micro-fluidics etc [6]. The main limitation of SU-8 has been identified as low elastic modulus, low hardness and poor tribological properties. Because of the small length scales of MEMS devices, the macro scale oil/grease-based lubrication methods are not applicable and hence researchers have developed some nano-meter to sub-micrometer thick films (mostly solid lubricants) which reduce friction, adhesion force and wear. These thin films include self-assembled monolayers (SAMs), polymer coatings, vapor deposited organic layers, fluorine-based organic layers, solid coatings etc, which have been developed and tested on Si surface [7,8,9,10,11,12,13,14,15,16,17,18,19]. The need for improving the tribology of SU-8 has been realized only recently and very minimal work has been done on this topic so far.



(a) (b)

***Figure 1**: **(a)** A depiction of the cross-linking in SU-8+PFPE composite through the formation of ether bonds. **(b)** Digital Image of a 200 micron thick gear made of SU-8+PFPE composite using UV lithographic process.*

Jiguet et al [20,21] have studied the effect of the addition of silica nanoparticles (diameter: 13 nm and concentration: 5 wt%) and the effect of the thermal treatment on the friction and wear properties of SU-8. The sliding tests were conducted against steel and POM (polyoxymethylene) balls. The SU-8 nanocomposites reduced wear rates and friction coefficients only marginally when compared to the un-reinforced SU-8. This study has also shown that the heat treatment has considerably reduced the wear rate of reinforced and un-reinforced SU-8.

Singh et al. [22] have developed a two-step surface modification method which has improved the tribological properties of SU-8 film surfaces by several folds. The two-step surface modification consists of first treating SU-8 film surface with oxygen plasma followed by the application of a nanolubricant such as perfluoropolyether (PFPE). By the application of the two-step surface modification method to thin (thickness: 500 nm) and thick SU-8 (thickness: 50 µm) films on Si surface, the initial coefficient of friction has been reduced by ~4-7 times, the steady-state coefficient of friction has been reduced by ~2.5-3.5 times and the wear durability has been increased by >1000 times. The two-step surface modification method has slightly reduced the elastic modulus and hardness of pristine SU-8 thick films as observed in the nanoindentation tests.

Singh et al.[23]have also developed a chemical surface modification method for SU-8 with improved tribological properties. The two-step chemical modification method consists of first chemically treating an SU-8 film using ethanolamine-sodium phosphate buffer, followed by the coating of PFPE nanolubricant. By this method, the steady-state coefficient of friction has been reduced by ~4-5 times and the wear durability has been increased by >1000 times. The tribological tests were conducted under the loading conditions of a normal load of 150 g and a rotational speed of 200 rpm. The authors have attributed the significant reduction in the friction coefficients to the lubrication effect of PFPE nanolubricant, whereas the exceptional increase in their wear life was attributed to the bonding between the –OH functional groups of ethanolamine treated SU-8 films and the –OH functional groups of PFPE.

Voigt et al.[24] have demonstrated the miscibility of epoxy resin surface-modified SiO_2 nanoparticles (average particle diameter: 20 nm) into epoxy photo material to create a photo-patternable material with improved lithographic, optical and mechanical properties. The addition of the epoxy resin surface-modified SiO_2 nanoparticles to epoxy resin has increased the Young's modulus; the Young's modulus increased with the content of the SiO_2 particles (E = 8.7 GPa with the highest wt% of SiO_2).

Chiamori et al.[25] have investigated the mechanical properties of diamondoids and SWCNTs (single-walled carbon nanotubes) (average diameter: 0.8 nm and concentration: 1 wt% and 5 wt%) added SU-8 composite materials. Uniaxial tensile tests were conducted and the SU-8 has shown an elastic modulus of 1.6 GPa whereas the diamondoid and SWCNTs added SU-8 have shown elastic modulii of 1.9 GPa and 1.3 GPa, respectively.

Mionic et al.[26] have fabricated SU-8+MWCNTs (multi-walled carbon nanotubes) (concentration: 5 wt%) composites and measured their mechanical properties using nanoindentation. They have also studied the influence of SU-8 solvent on the structural homogeneity and mechanical properties of the composites. They have observed that the solvent type and the functionalization of MWCNTs affect the Young's modulus of the composites. In their study, the highest increase of the Young's modulus by 104% was observed when acetone was used as the solvent.

Okhlopkova et al. [27] have developed PTFE composites impregnated with liquid lubricants and natural absorbents to improve the tribological properties of those materials. They also reduced the molding pressure of the polymer materials to increase the porosity of the polymer and these porosities help to absorb the lubricants inside for tribological improvement. The new materials displayed a long-lasting self-lubrication effect and increased the load bearing capacity.

Esa Puukilainen et al. [28] have developed lubricant-treated ultra high molecular weight polyethylene (UHMWPE) composites by compression molding. Two solid lubricants (MoS_2 and carbon black) and one liquid lubricant (PFPE) were added to UHMWPE to improve the tribological properties. The authors have observed slight reduction in the coefficient of friction with increasing amount of PFPE, however, both tensile strength and abrasion properties deteriorated.

Guo et al. [29] have studied the incorporation of microcapsules containing lubricant oil into epoxy which led to the materials with ultra-low friction and improved wear performance. They observed that the microcapsules were damaged by the asperities of the counterface during sliding wear tests and as a result of that the oil was released to the contact area. The lubrication effect of the released oil and the entrapment of the wear particles in the cavities left by the ruptured capsules led to the improved tribological performance of the epoxy composites.

From the above literature survey, it is clear that there are very minimal works found on improving the tribological properties of SU-8. In the current work, we have developed SU-8 based hybrid nanocomposites by adding PFPE lubricant and nano-fillers such as SiO_2, CNTs and graphite. These hybrid nanocomposites have reduced the coefficient of friction of SU-8, improved the wear life by several orders with some noticeable enhancement in the elastic modulus and hardness.

Experimental Procedures:

Materials and Sample Preparation:

Si wafers were cut into ~2 cm x 2 cm pieces and were thoroughly cleaned with soap-water, distilled water and isopropyl alcohol (IPA, 99.9% purity obtained from Sigma -Aldrich), respectively, and finally dried with N_2 gas. The cleaned Si wafers were then subjected to heating at 150 °C for about 3-4 min to remove any adsorbed moisture content and then subsequently treated with oxygen plasma for about 15-20 min using plasma cleaner PDC-32G (Harrick plasma, NY, USA). The purpose of oxygen plasma treatment was to remove the contaminants and to generate hydroxyl groups on the surface which enhance the adhesion between the substrate and the coating [21]. The cleaned Si wafers were then subjected to SU-8 (grade 2050 supplied by Microchem Ltd USA) spin-coating immediately on SCS P6700 spin coater

(Speciality Coating Systems, Indiana, USA). SU-8 was spin-coated onto Si at an initial speed of 500 rpm for duration of 5 seconds, followed by 3000 rpm for a duration of 30 seconds which results in SU-8 films with a thickness of ~150 microns. The spin-coated SU-8 films were then subjected to pre-baking at a temperature of 65 ^oC for 4 minutes followed by at 95 ^oC for 9 minutes. The pre-baked SU-8 films were then exposed to UV (ultra-violet) rays (wavelength: 365 nm and power: 210 mJ/cm^2) for a duration of 30-60 seconds using Black-Ray B-100SP UV lamp (UVP, LLC, upland, CA, USA). A post exposure bake was carried out at a temperature of 65 ^oC for 1 minute followed by at 95 ^oC for 7 min, after UV exposure. The samples were then stored in the desiccators before any further characterization. The conditions of the spin-coating, pre-baking, UV curing, post-baking were approximately same for both pristine SU-8 films and SU-8 nanocomposite films.

For the preparation of the SU-8+PFPE nanocomposites, 5 wt% of PFPE was added to SU-8 2050 and then the composite material was thoroughly mixed using ultra-sonication for about 12 hr before spin-coating. For the preparation of SU-8+PFPE+NP (NP stands for nanoparticle, SiO_2 with 100% purity, CNT (MW) with 98% purity, graphite with 99.9% purity), 5wt% of PFPE and 5 wt% of NP was added to SU-8 (grade 2050) along with few drops of SU-8 thinner and the whole mixture was thoroughly mixed using ultra-sonication for about 12 hr before spin-coating.

Contact Angle Measurements:

The pristine SU-8 and SU-8 nanocomposites were characterized for their static water contact angles (WCAs) using VCA Optima Contact Angle System (AST Products Inc, USA). A water droplet of 0.5 µl was used for contact angle measurements. At least five replicate measurements, for three different samples, were carried out and an average value is reported in the paper. The variation in water contact angles at various locations of a sample was within ±3^o. The measurement error was within ±1^o. The water contact angles were also measured inside the wear tracks after tribological tests.

X-ray Photoelectron Spectroscopy (XPS) Characterization:

XPS characterization of pristine SU-8 and SU-8+PFPE composite was done using VG ESCA Lab-220i XL XPS. Mg Ka X-ray was employed for analysis of one spot on each sample with photoelectron take-off angle of 90^o. The analysis area was 4 mm x 4 mm, whereas the maximum analysis depth lies in the range of ~4-8 nm. Charge compensation was performed by means of low-energy electron flooding and further correction was made based on adventitious C1s at 285.0 eV using the manufacturer's standard software. The voltage of the X-ray beam was 15 KV. The pass energies for survey scan and high resolution scans were 150 eV and 20 eV, respectively.

XPS characterization was also done inside the wear track after tribological tests for SU-8+PFPE samples using the Thermo Fisher Scientific Thetaprobe XPS. Monochromatic Al Ka X-ray was employed for the analysis of one spot on each sample with photoelectron take-off angle of 50^o (with respect to surface plane normal). The analysis area was 100 µm x 100 µm. The maximum analysis depth lay in the range of ~4-8 nm. A specially designed electron flood gun with a few eV Ar+ ion was used for the charge compensation. Electron beam and ion beam were focused and steered towards the analysis position. The voltage of the X-ray beam is 15 KV. The pass energies for survey scan and high resolution scans were 200 eV and 40 eV, respectively.

Tribological Testing:

Friction and wear tests were carried out using UMT-2 (Universal Micro Tribometer, CETR, USA) in ball-on-disk setup where the coefficient of friction was measured with respect to the number of sliding cycles. Si_3N_4 balls of 4 mm diameter with a surface roughness of 5 nm were used as the counterface. The tests were conducted at different normal loads (up to 300 g) and at different rotational speeds (up to 2000 rpm). All experiments were performed in air at room temperature (23 ^oC) and at a relative humidity of approximately 60%. From the sliding tests, an initial coefficient of friction (μ_i) was noted as an average of the first twenty sliding cycles. The steady-state coefficient of friction (μ_s) was measured as the average of all coefficients of friction from the point where the steady-state behavior (after the observation period of initial coefficient of friction) was observed until the end of the test or until the failure point, whichever was earlier. The wear life for the tested conditions was taken as the number of sliding cycles after which the coefficient of friction exceeded 0.3 or a visible wear track was observed on the substrate with abnormally fluctuating friction values, whichever occurred earlier. Similar definition for wear life determination has been used in the literature [30-32] and present authors' works [16, 22]. As will be shown in results and discussion section, the lubricating property of the nanocomposites formed depends upon the ability of the composite to form a thin lubricating film *in situ*. A reduction in the thickness of the film (due to the lack of lubricant supply) or displacement of the lubricant molecules away from the interface leads to high friction and wear particle generation. Hence, for the present case the wear-failure criteria involving the coefficient of friction have been found to be sufficient. For each nanocomposite, at least 3 tests were repeated and average data are reported. An optical microscope was used to image the worn surfaces after the sliding tests to assess the damage to the film surfaces and the ball, respectively.

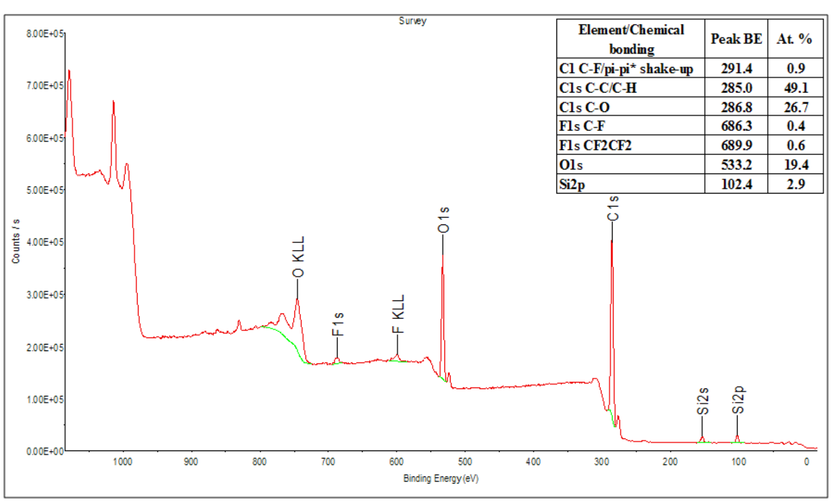
Nanoindentation Testing:

The elastic modulus and the hardness of the pristine SU-8 and SU-8 nanocomposite films were measured using MTS Nano Indenter XP with a continuous stiffness measurement (CSM) technique. A triangular pyramid Berkovich diamond indenter was employed for nanoindentation tests. The depth of indentation was set to 3,000 nm. The CSM technique has the load and the displacement resolutions as 50 nN and <0.01 nm, respectively. A total of 10 indents were conducted on each sample and the tests were repeated on 3 different samples and an average value is reported.

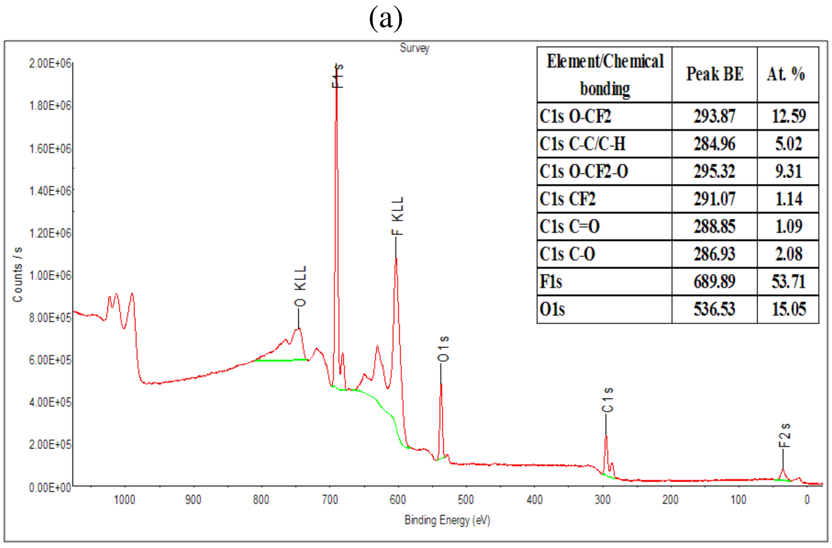
Results and Discussion:

The SU-8 nanocomposite films formed under the conditions provided in the experimental section have shown a thickness of ~150 µm. Both the pristine and the SU-8 nanocomposite films have shown the same thickness values. We have fabricated a millimeter-scale gear (with letters: "NUS" on top of it) using the SU-8+PFPE composite following UV-lithography process to demonstrate that the addition of PFPE does not deteriorate the photo-patternable property of SU-8. A digital picture of the fabricated gear is shown in Figure 1(b). This proves that the addition of PFPE does not affect or deteriorate the photo-patternable property of SU-8.

Table 1 shows the water contact angles on pristine SU-8 and SU-8 nanocomposite surfaces in freshly prepared condition and after tribological tests (inside worn regions). Pristine SU-8 has shown a water contact angle of 84^o whereas the nanoparticles added SU-8 has shown water contact angle values in the range of 79^o to 89^o (SU-8+graphite: 79^o; SU-8+SiO_2: 85^o and SU-8+CNTs: 89^o). The PFPE added SU-8 has shown a water contact angle of 98^o. The hybrid SU-8 nanocomposites have shown water contact angles in the range of 91^o to 106^o (SU-8+PFPE+CNTs: 91^o; SU-8+PFPE+graphite: 91^o and SU-8+PFPE+SiO_2:106^o). Broadly, the addition of PFPE alone and the addition of PFPE and nanoparticles have increased the water contact angle of SU-8. The highest water contact angle (106^o) was observed when both PFPE and SiO_2 particles were added which was about 22^o higher than that of pristine SU-8. The fluorine-based groups of PFPE must have led to the observed hydrophobic property of the nanocomposites.



(a)



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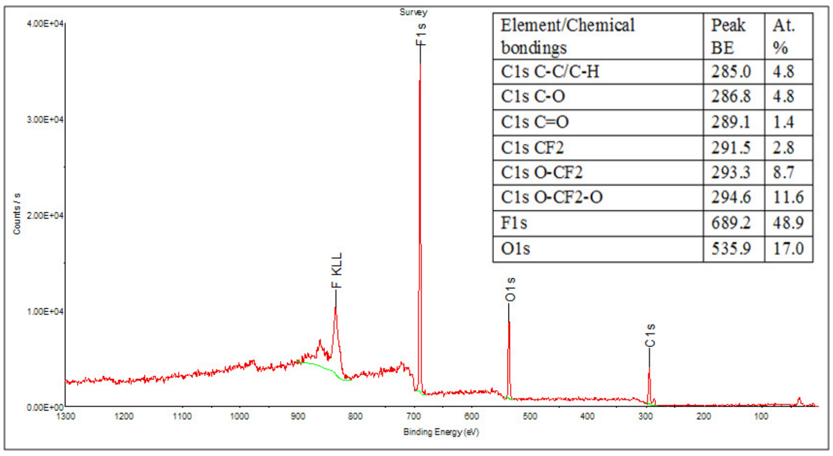


(c)

Figure 2: *XPS Wide-scan survey spectrum results for **(a)** pristine SU-8, **(b)** SU-8+PFPE composite and **(c)** inside the wear track (after sliding for 1 million cycles at a normal load of 300g and a rotational speed of 2000 rpm) of SU-8+PFPE composite.*

XPS characterization was carried out on pristine SU-8 and SU-8+PFPE nanocomposites and Figures 2(a) and 2(b) shows the wide-scan spectra, respectively. The insets in Figures 2(a) and 2(b) show the major peaks observed with the corresponding bond assignments and atomic percents, respectively. The SU-8+PFPE wide-scan spectrum shows a high intensity F1s peak which confirms the presence of PFPE in the composite and especially on the top surface of the composite coating. The SU-8+PFPE shows O-CF2, O-CF2-O and CF2 groups which were not present on the pristine SU-8 and mainly arise from the presence of PFPE.

Table 1: *Water contact angle measurements for all SU-8 based nanocomposites with and without PFPE over fresh (pristine surface of composites before experiment) and worn surfaces (wear track or the spot where the sliding test conducted). The data reported here for bare SU-8 and SU-8+NP composites without PFPE were recorded after 10^4 cycles and for SU-8 and SU-8+NP composites with PFPE were recorded after 10^6 cycles respectively.*

Sample Description	Water Contact Angle Measurements in Degrees	
	On Fresh Surface	On Worn Surface (wear track)
Bare SU-8	84	54
SU-8+CNTs	89	60
SU-8+SiO_2	85	54
SU-8+graphite	79	50
SU-8+PFPE	98	94
SU-8+PFPE+CNT	91	120
SU-8+PFPE+SiO_2	106	105
SU-8+PFPE+graphite	91	97

A good cross-linking is expected in SU-8+PFPE composite because of etherification reaction between hydroxyl groups of PFPE and epoxy groups of SU-8[33,34]. The possible etherification reaction is depicted in Figure 1(a). At present, this reaction cannot be verified using XPS because PFPE molecules themselves have ether linkages and hence the ether linkage formed due to chemical bonding between PFPE and SU-8 cannot be shown exclusively. Possibly, the presence of OH functional groups in the PFPE polymer will interact with the carbocations (C^+) in the SU-8 polymer (epoxide ring), which breaks the existing bond and forms new linkage which is called ether bond.

Table 2(a) shows the initial coefficient of friction (μ_i), steady-state coefficient of friction (μ_s) and wear-lives of pristine SU-8 and SU-8 nanocomposites tested at two normal loads and rotational speeds, respectively. The tribological properties obtained at a normal load of 300 g and a rotational speed of 2000 rpm will be mainly discussed in this section and the data at other testing conditions can be referred from Table 2(a). It is to be noted that the SU-8+PFPE sample at 30 g load and 200 rpm rotational speed performed equally well as all other samples with PFPE lubricant and the test was stopped at 100,000 in this case because of the long test duration at lower rpm. Figures 3(a) and 3(b) shows the coefficient of friction versus the number of sliding cycles graph for all the samples tested in this study. The tribological properties summarized in Table 2(a) have been obtained from these graphs. Figure 4 shows the optical micrographs of the ball surface after sliding tests, the tested balls after cleaning with acetone and the optical images of worn surfaces after appropriate number of sliding cycles. The pristine SU-8 film has shown high frictional properties (μ_i: 0.52) and low wear-life (n~0) when tested at a normal load of 300 g and a rotational speed of 2000 rpm. The optical images of SU-8 after 10,000 cycles shows severe damage to the surface with accumulation of wear debris along the wear track which have also transferred to the ball (Figures 4 (a) and 4 (g), respectively).

Table 2(a): *Initial coefficient of friction (μ_i), Steady-state coefficient of friction (μ_s) and wear life (number of sliding cycles) of SU-8 and SU-8 nanocomposites obtained from sliding tests against 4 mm diameter Si_3N_4 ball at different normal loads and sliding rotational speeds.* ***Table 2(b):*** *Elastic modulus (GPa) and hardness (GPa) of SU-8 and SU-8 nanocomposites obtained through nanoindentation tests using MTS Nano Indenter XP with a Continuous Stiffness Measurement (CSM) technique.*

(a)

Test Condition and Nanocomposite Description		Initial coefficient of friction, COF (μ_i)	Steady- state coefficient of friction, COF (μ_s)	Wear Life (Number of Cycles)
30g, 200 rpm, Spin Coated on Si	Bare SU-8	0.82	-	0
	SU-8+SiO2	0.77	-	0
	SU-8+CNTs	0.39	-	0
	SU-8+graphite	0.35	-	0
	SU-8+PFPE	0.03	0.09	>100,000 (*Experiment stopped due to long test duration*)
300g, 2000 rpm, Spin Coated on Si	Bare SU-8	0.52	-	0
	SU-8+PFPE	0.07	0.09	>1,000,000
	SU-8+PFPE+SiO2	0.04	0.11	>1,000,000
	SU-8+PFPE+CNTs	0.11	0.17	>1,000,000
	SU-8+PFPE+graphite	0.09	0.14	>1,000,000

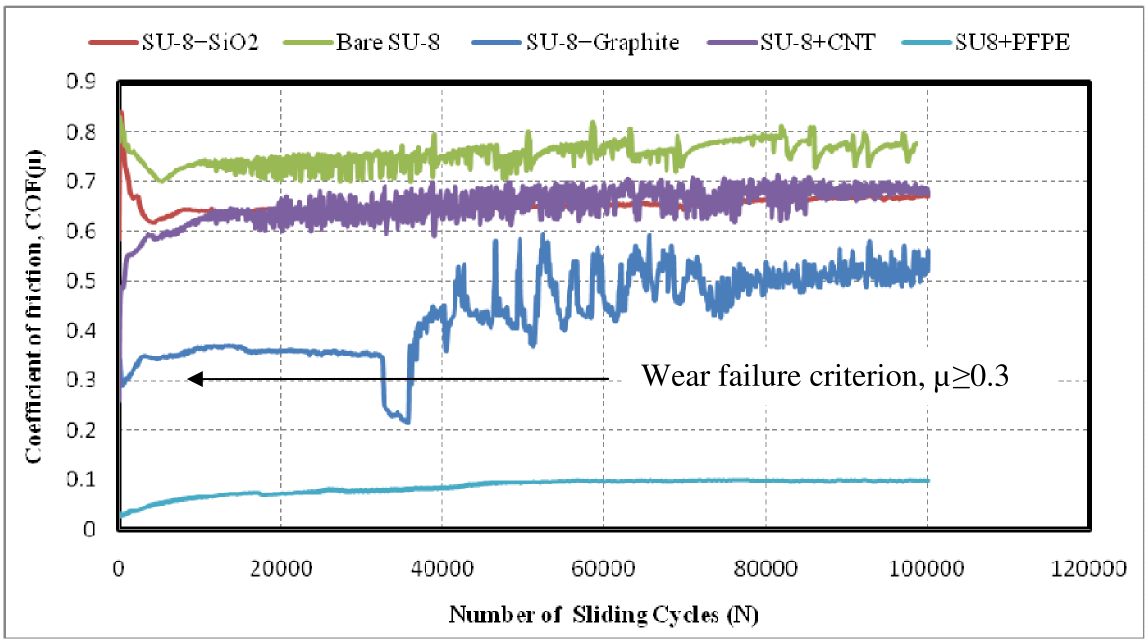
[Note: Steady-state values are not mentioned for specimens that did not contained PFPE as these specimens failed right in the first sliding cycle according to the wear-failure criteria followed in this study]

(b)

Nanocomposite Description	Elastic Modulus (GPa)	Hardness (GPa)
SU-8	3.8	0.27
SU-8+NP (SiO_2, CNTs)	3.9	0.17
SU-8+PFPE	4.0	0.32
SU-8+PFPE+SiO2	4.5	0.40
SU-8+PFPE+CNTs	4.0	0.28
SU-8+PFPE+graphite	5.0	0.16

A slight wear of the ball was also observed after sliding for 10,000 cycles (Figure 4 (m)). The high coefficient of friction and low wear-life of SU-8 clearly indicate the necessity for the improvement in the tribological properties of SU-8. SU-8 molecules have poor lubricious nature due to cross-linked structure, and also low elastic modulus of SU-8 (E: ~3.8 GPa) (Table 2(b)) usually shows high contact area when pressed by the Si_3N_4 ball under the applied load and hence shows high friction. The high coefficient of friction and brittle nature of SU-8 (SU-8 being thermoset exhibits brittle property in fully cross-linked state) lead to the generation of wear particles within the first cycle of sliding and probably the sliding process will change from two-body to three-body sliding which eventually exaggerates the wear process. Hence, severe wear was observed after sliding for 10,000 cycles (Figures 4 (a), 4 (g) and 4 (m)).

Under the loading conditions of the normal load of 300 g and the rotational speed of 2000 rpm, SU-8+PFPE has shown very low coefficients of friction (μ_i: 0.07 and μ_s: 0.09) and high wear-life (n>1,000,000). This is a dramatic improvement when compared with the pristine SU-8. Table 2(b) shows the elastic modulus and the hardness data of SU-8 and SU-8 nanocomposites. Pristine SU-8 film shows an elastic modulus of ~3.8 GPa and a hardness of ~0.27 GPa and the addition of PFPE does not have any significant effect on the mechanical properties of SU-8 (for SU-8+PFPE, E: 4.0 GPa and H: 0.32 GPa) except a slight increase. The composites of SU-8+PFPE shows significant improvement in tribological properties (the μ_i has been reduced by ~8 times (a) and the wear life has been improved by >10^4 times) with a marginal improvement in the mechanical properties when compared to pristine SU-8. After sliding for 1 million cycles at a normal load of 300 g and a rotational speed of 2000 rpm, SU-8+PFPE sample has shown a distinct wear mark with the generation of some transfer material onto the counterface ball with no wear to the ball surface (Figures 4 (c), 4 (i) and 4 (o)). Incorporation of nano-fillers has not improved the tribological performance much; they only slightly reduced the coefficient of friction of SU-8 and marginally improved the wear durability. The SU-8+NP samples have shown μ_i in the range of 0.35 to 0.77 and the wear-lives of zero to a few cycles when tested at a normal load of 30 g and a rotational speed of 200 rpm. It is seen that the presence of graphite has better effects on the coefficient of friction and wear life when compared to other nano-fillers i.e CNTs and SiO_2.



(b)

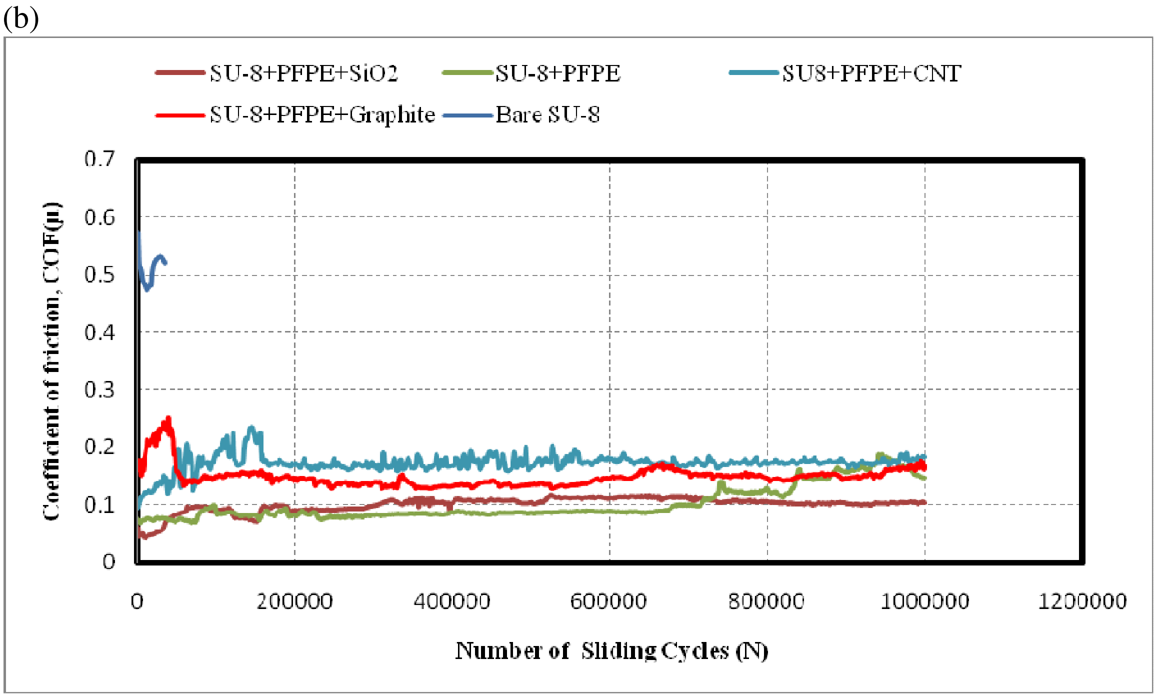


Figure 3 (a): *Coefficient of friction versus number of cycles data for SU-8, SU-8+PFPE, SU-8+SiO_2, SU-8+CNTs and SU-8+graphite nanocomposites obtained from the ball-on-disk sliding tests against 4 mm diameter Si_3N_4 ball at a normal load of 30 g and a sliding rotation of 200 rpm.* ***(b):*** *Coefficient of friction versus number of cycles data for SU-8, SU-8+PFPE, SU-8+PFPE+SiO_2, SU-8+PFPE+CNT and SU-8+PFPE+graphite obtained from the ball-on-disk sliding tests against 4 mm diameter Si_3N_4 ball at a normal load of 300 g and a sliding rotation of 2000 rpm. The tests were stopped at 1 million cycles because of the long test duration as the samples had not failed.*

After sliding for 10,000 cycles, SU-8+NP samples have shown severe wear to the sample surface as well as the ball surface (Figures 4 (b), 4 (h) and 4 (n)). SU-8+NP samples have shown E of 3.9 GPa and H of 0.17 GPa, respectively. Therefore, the composites of SU-8 with only the nanoparticles improved the tribological properties only marginally and have shown the elastic modulii same as that of pristine SU-8 and also have slightly reduced the hardness. SU-8+PFPE+SiO_2 has shown μ_i of 0.04, μ_s of 0.11 and wear life of >1,000,000 cycles. The elastic modulus and hardness were measured as 4.5 GPa and 0.4 GPa respectively. These properties are significantly improved when compared to those of pristine SU-8. When compared to SU-8+PFPE, SU-8+PFPE+SiO_2 has shown similar tribological performance and improved mechanical properties. SU-8+PFPE+CNTs has shown μ_i of 0.11, μ_s of 0.17 and wear life of >1,000,000 cycles, together with E of 4.0 GPa and H of 0.28 GPa. SU-8+PFPE+graphite has shown μ_i of 0.09, μ_s of 0.14 and wear-life of >1,000,000 cycles with E of 5.0 GPa and H of 0.16 GPa. Among the three hybrid

SU-8 nanocomposites, all three have shown similar improvements in their tribological performance and SU-8+PFPE+graphite has shown highest elastic modulus wheheras SU-8+PFPE+SiO_2 has shown highest hardness.

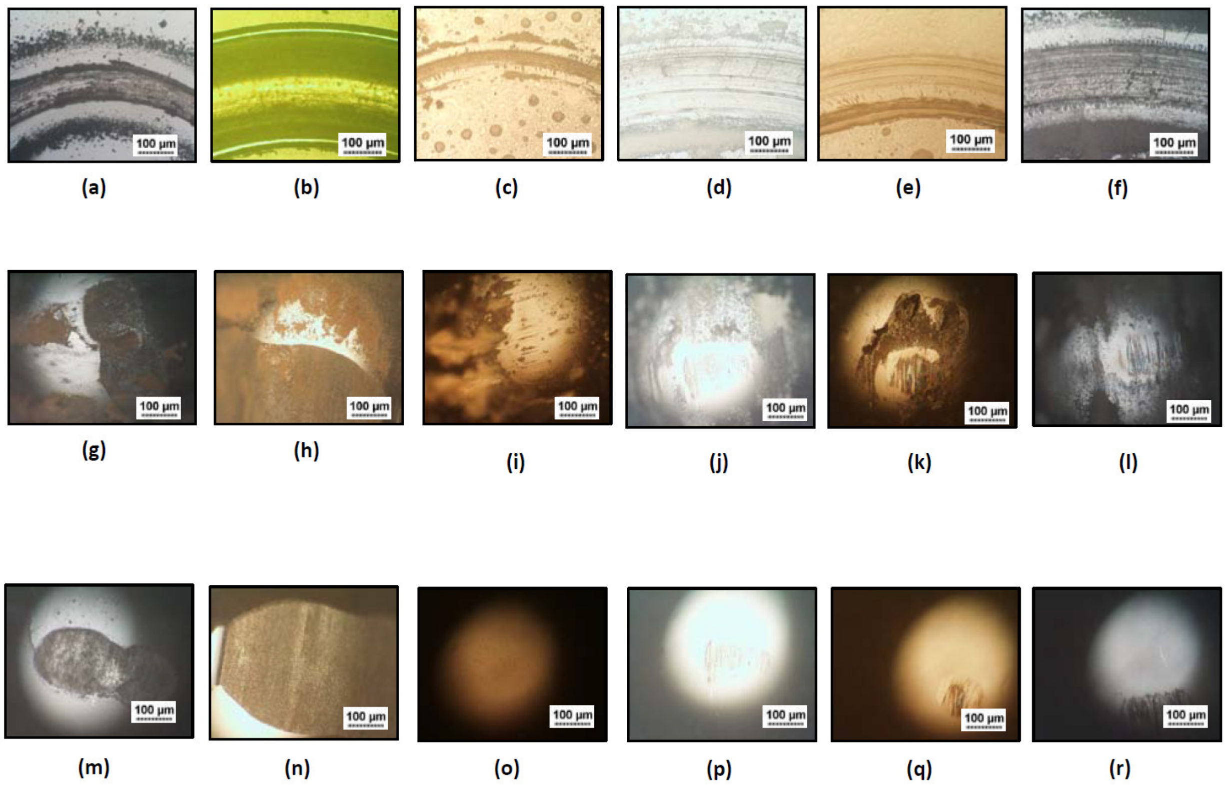


Figure 4: *Optical micrographs of worn surfaces: (a) Bare SU-8 (at 10,000 cycles), (b) SU-8+Nanoparticles(SiO2,CNT) (at 10,000 cycles), (c) SU-8+PFPE (at 1 million cycles), (d) SU-8+PFPE+CNTs (at 1 million cycles), (e) SU-8+PFPE+SiO_2 (at 1 million cycles), (f) SU-8+PFPE+graphite (at 1 million cycles). Images (g), (h), (i), (j), (k),(l) and (m), (n), (o), (p), (q), (r) are Optical micrographs of the counter face balls surface after sliding tests and micrographs of the tested counterface balls after cleaning with acetone corresponding to the worn surfaces shown in (a), (b), (c), (d), (e) and (f) respectively. The length of the scale bar is 100 μm in all images.*

In these three SU-8 hybrid nanocomposites, there was a distinct wear track with the generation of transfer material on the counterface ball, but no wear to the ball surface (Figures 4 (d-f), 4 (j-l) and 4 (p-r)). Overall, these hybrid nanocomposites have shown improved tribological performance and mechanical properties, both at the same time. In terms of the mechanical properties, the selection of right composite entirely depends on the application i.e. high hardness/modulus requirements.

As there was a distinct visible wear track and a small amount of the transferred material on the counterface ball surface after 1 million cycles of sliding in the case of all SU-8 nanocomposites, we have measured the WCAs inside the wear tracks of all tested materials and XPS characterization inside the wear track of SU-8+PFPE to qualitatively ascertain the extent of wear. Table 1 shows the WCAs of all tested materials measured inside the wear tracks after appropriate number of sliding cycles (after 100,000 cycles for SU-8 and SU-8+NP samples and after 1 million cycles for the remaining samples). In the case of the pristine SU-8, the WCA inside the worn region is about 30^o less than that observed on the untested region. This can be attributed to the removal of large amount of SU-8 inside the wear track. In the case of SU-8+NP samples, there was a reduction of about 29^o-31^o of WCA inside the wear tracks when compared to those on the untested regions which also indicates the loss of material inside the wear track. Whereas in the case of all SU-8 nanocomposites, there was either no change or an increase in the WCAs inside the worn regions when compared to the corresponding WCAs on untested regions which clearly indicate that there is very minimal loss of material inside the worn regions. The increase in the WCAs in the worn regions in the case of SU-8+PFPE+graphite and SU-8+PFPE+CNTs can be attributed to the sliding induced morphological changes inside the worn region though the exact mechanism is not clear now. The wide scan spectrum inside the worn region of SU-8+PFPE sample after sliding for 1 million cycles at a normal load of 300 g and a rotational speed of 2000 rpm is shown in Figure 2 (c) (the inset shows the major peaks observed with their bond assignments). There is a distinct F1s peak in the spectrum which clearly shows the presence of PFPE inside the worn region in spite of sliding for 1 million cycles at the severe loading conditions used. This result infers that the SU-8 hybrid composite samples still have improved lubricious property beyond 1 million cycles.

We postulate that the improved tribological properties of SU-8 hybrid nanocomposites are due to the good cross-linking in the nanocomposites through ether bonds between SU-8 and PFPE, presence of the lubricant throughout the composite matrix which results in the supply of the lubricant on demand (*in-situ* supply) and thus maintaining a thin PFPE film and improved bulk mechanical properties. We also postulate that the PFPE molecules, the SU-8 molecules and/or the nanoparticles might form some kind of cohesive 3D networks which shows anti-wear properties and delay the initiation of the wear process, unlike the case of pristine SU-8 where the wear particles generate quite early in the sliding process. Further to this, there is a plenty of the PFPE nanolubricant which is available in the sliding region which

reduces friction and eventually minimizes wear particle generation. Even when the wear starts, the lubricant in the inside region will then be exposed to the sliding contact and reduces further wear process. Hence, the SU-8 hybrid nanocomposites have improved the tribological properties to a large extent. From the current work, it is not very clear whether or not the addition of nanoparticles have any contribution in enhancing the wear durability of SU-8+PFPE because SU-8+PFPE and SU-8+PFPE+NP samples have shown the same wear-lives at the tested tribological conditions. Further work is necessary to elucidate this effect.

In the current work, the improved tribological behavior of SU-8 nanocomposites was also ascertained at very low loads of 10g and 5g and at high speed of 3000 rpm (data are not included).

Conclusion:

In summary, we have developed self-lubricating SU-8 hybrid nanocomposites using *in situ* nanolubricant (PFPE) and nanoparticles (SiO_2, CNTs or graphite as filler materials). The developed SU-8 nanocomposite is hydrophobic (with a maximum water contact angle of 106°C for SU-8+PFPE+SiO_2), highly lubricious and have exceptional wear durability without any detrimental effect on its photo-sensitive curing property. When compared with pristine SU-8, the SU-8+PFPE and SU-8+PFPE+nanoparticle nanocomposites have reduced the initial coefficient of friction by ~6-9 times, increased the wear life by $>10^4$ times and increased the elastic modulus and the hardness by ~1.4 times. The presence of PFPE film at the interface due to *in situ* lubricant supply is the main reason for superior tribological performance whereas the nanoparticles help in the mechanical property enhancement. These SU-8 nanocomposites can be used as self-lubricating structural materials for MEMS requiring no external lubrication. Apart from this, the SU-8 nanocomposite can also find application as a lubricious and wear resistant coating for several tribological components made from different materials. Examples are journal bearings, raceways of a ball bearing, gears, medical equipments and tools, bio-devices, precision positioning stages, electronics components such as those inside cameras and printers, plastic bearings etc.

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