Tribology of Self- lubricating SU-8 composites for MEMS applications

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1. Abstract

SU-8 is an epoxy based negative photoresist and its unique UV-sensitive curing property makes it a useful polymer for micro-fabrication. It has also been used as a structural material for certain micro-electro mechanical systems (MEMS) applications. However, its poor tribological and mechanical properties make it inferior to its counterpart Si, the mainstay MEMS material today. This paper addresses the fabrication of self–lubricating SU-8 composites with improved tribological and mechanical properties. A liquid lubricant (perfluoropolyether or 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 reductions in the initial and steady-state coefficient of friction by *~6-9* and *~3-6* times, respectively, and increased wear life by more than five orders *($>10^5$)* of magnitude. The mechanical properties such as the elastic modulus and the hardness have increased by *~1.4* times. It is postulated that adding PFPE lubricant to SU-8 promoted chemical reaction between the SU-8 and PFPE molecules to form ether bond between them and helped in the boundary lubrication, enhancing the wear durability of SU-8 by more than five orders of magnitude. These self-lubricating SU-8 composites can be used as structural materials for MEMS applications requiring no external lubrication, and also these composites can find applications in many tribological components of traditional machines.

2. Introduction

Tribology (i.e. adhesion, friction and wear) is becoming an important factor while designing any micro-electro mechanical systems (MEMS). MEMS are micro sized devices, which are designed to perform variety of operations in various industries including automotive, bio-engineering, bio-medical and military etc. The surface forces are becoming highly detrimental to operation of these devices, as the surface area-to-volume ratio becomes large. These forces, for small devices, are capable of stopping the operation of machine against its inertial forces [1]. Though, Si has been conventional MEMS structural for the past few decades, this legacy may be about to change with SU-8 as the mainstay structural material for certain applications. SU-8 is a negative thick-film photoresist patented by IBM in 1989[2]. 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). Because, SU-8 has certain advantages over Si, such as bio-compatibility, compatible with micro-fabrication process by its unique UV sensitive property and less hydrophobic [3]. Despite of above mentioned advantages, it has two major drawbacks. Those drawbacks are its poor tribologoical and mechanical properties. Very few works can be found on improving the tribology of SU-8. One of them by Jiguet et al [4] have studied the effect of silica particles reinforcement with SU-8 and heat treatment of SU-8. The improvements in tribology from reinforcement are very marginal, but the heat treatment improved tribology considerably. Few other studies by singh et al [5, 6], one is two-step surface modification process, which uses the oxygen-plasma treatment of SU-8 surface, followed by coating of lubricant such as perfluoropolyether (PFPE). The tribology of SU-8 improved significantly by this method. Another one is chemical-modification of SU-8 surface by treating chemically with ethanolamine-sodium phosphate buffer, followed by the coating of PFPE lubricant. The wear life is increased considerably, which attributed to end groups bonding between PFPE and ethanolamine.

In order to solve the design and manufacturing related problem in modifying the surface, we have developed bulk SU-8 composites by blending the liquid lubricants such as PFPE lubricant and nano-fillers such as SiO_2, CNTs and graphite. These SU-8 composites have yielded better tribological properties by reducing the coefficient of friction and increasing wear-life very significantly.

3. Material and Experimental Procedure

The detailed procedure for the preparation of pristine SU-8 and SU-8 composite films was reported in our previous publication [7]. The main difference in the fabrication procedure between the pristine SU-8 and SU-8 composite film is addition of liquid lubricant (i.e.PFPE) and a nano particle (i.e. SiO_2, CNTs or graphite) to SU-8.

Water contact angle measurements (WCAs) were carried out for pristine SU-8 and SU-8 composites using volume of 0.5µl water. The WCA measurements were also performed in inside the wear track also.

X-ray photoelectron spectroscopy (XPS) characterization were performed for pristine SU-8 and SU-8+PFPE composite at fresh surface and inside the wear track as well. Two separate XPS instruments were used for fresh and inside the wear track.

Tribological tests (friction and wear tests) were performed using UMT-2 (universal Micro Tribometer, CETR, USA) in a ball-on-disk setup. The typical number of sliding cycles Vs coefficient of friction (COF) plot is outcome of the sliding tests, where COF were derived to any corresponding sliding cycles. 4 mm diameter Si_3N_4 balls with a surface roughness of 5 nm were used as the counterface. 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.

Nanoindentation characterization was done for pristine SU-8 and SU-8 composites using MTS Nano Identator XP with CSM (continuous stiffness measurement) methodology.

4. Results and Discussion

The water contact angle (WCA) values for pristine SU-8, SU-8+NP combinations and SU-8+PFPE, SU-8+PFPE+NP combinations are shown in Figure.1. WCA measurement were performed on freshly spin-coated surfaces and worn surfaces (after tribological tests) also shown in Figure.1.

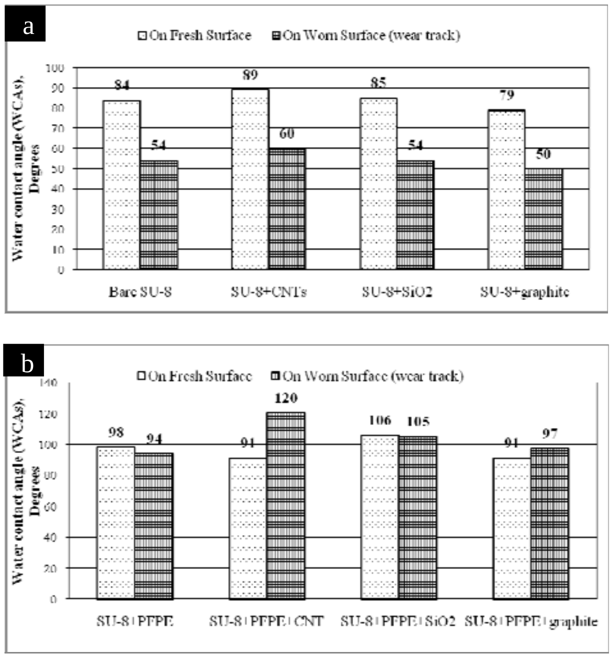


Figure 1: *WCA values for pristine SU-8 and SU-8 based composites over fresh (pristine surface of composites before experiment) and worn surfaces (wear track).* **(a)** *: Non-PFPE combinations at 10^4 cycles (composites did not contain PFPE).* **(b)***: PFPE combinations at 10^6 cycles.*

Pristine SU-8 and SU-8+NP combinations without PFPE are showing contact angle values ~80° in fresh surface condition and ~55° in worn surface condition. The PFPE combinations are showing WCA value of >90° in fresh surface condition and increased significantly up to 120° in worn surface condition. There is 100% increase in WCA values from non-PFPE combinations to PFPE combinations in worn surface condition. The PFPE might be responsible for this enhanced hydrophobic behavior.

Table 1*: 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.*

Composite Description	Initial coefficient of friction, COF (μ_i)	Steady- state coefficient of friction, COF (μ_s)	Wear Life (Number of Cycles)
Normal load :30g, Sliding Speed: 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
Normal load :300g, Sliding Speed: 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: Experiment stopped due to long test duration for all PFPE contained films. No μ_s were reported for all non-PFPE samples as they fail very early.]

Table.1 shows the summary of the tribological results. Tests were conducted at different normal loads and sliding speeds. Pristine SU-8 and all non-PFPE composites were tested at 30g normal load and 200 rpm sliding speed. The pristine SU-8 exhibited very high μ_i ~0.82 and low wear life of n~0. SU-8+SiO2, SU-8+CNTs and SU-8+Graphite showed μ_i of 0.77, 0.38 and 0.35 respectively and low wear life of n~0.

All the PFPE contained composites were tested at 300g normal load and 2000 rpm sliding speed and exhibited much superior tribological properties than non-PFPE composites. These self-lubricating SU-8+PFPE and SU-8+PFPE+nanoparticle composites have reduced the initial and steady-state coefficient of friction by *~6-9* and *~3-6* times, respectively, and increased wear life by more than five orders *(>10^5)* of magnitude.

The significant improvement in tribological properties of SU-8 can be attributed to the possible ether bond formation between the SU-8 and PFPE molecules [8, 9]. The possible etherification reaction is depicted in Figure 2. It is postulated that the -OH terminal groups in the PFPE polymer and the carbocations (C^+) in the SU-8 polymer (epoxide ring) undergoes the reaction, which breaks the existing bond and forms new linkage which is called ether bond.

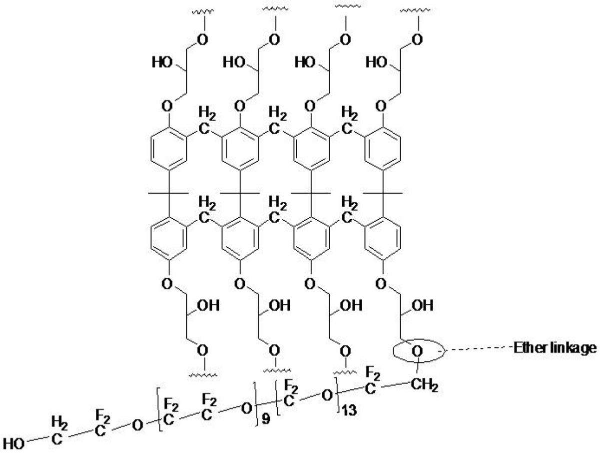
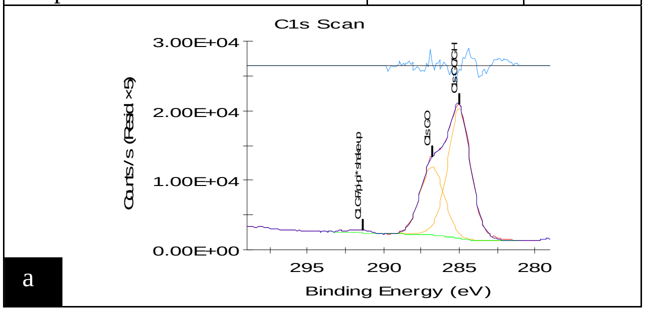
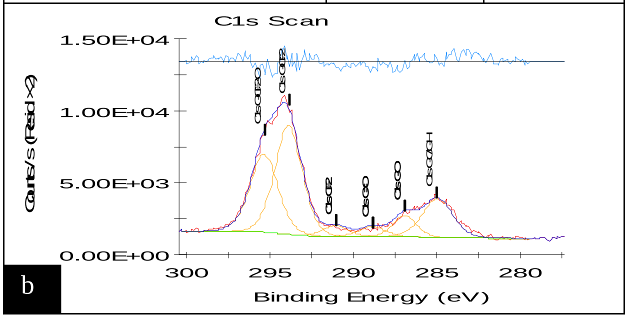


Figure 2: *A depiction of the formation of ether bonds between SU-8 and PFPE in SU-8+PFPE composite.*

Element/Chemical bonding	Peak BE	At. %
C1 C-F/pi-pi* shake-up	291.4	0.9
C1s C-C/C-H	285.0	49.1
C1s C-O	286.8	26.7
F1s C-F	686.3	0.4
F1s CF2CF2	689.9	0.6
O1s	533.2	19.4
Si2p	102.4	2.9



Element/Chemical bonding	Peak BE	At. %
C1s O-CF2	293.87	12.59
C1s C-C/C-H	284.96	5.02
C1s O-CF2-O	295.32	9.31
C1s CF2	291.07	1.14
C1s C=O	288.85	1.09
C1s C-O	286.93	3.08
F1s	689.89	52.71
O1s	536.53	15.05



Element/Chemical bonding	Peak BE	At. %
C1s C-C/C-H	285.0	4.8
C1s C-O	286.8	4.8
C1s C=O	289.1	1.4
C1s CF2	291.5	2.8
C1s O-CF2	293.3	8.7
C1s O-CF2-O	294.6	11.6
F1s	689.2	48.9
O1s	535.9	17.0

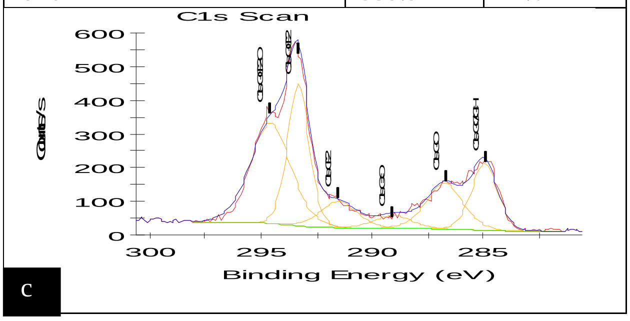


Figure 3: *XPS analysis At% table (top) and Cls scan (bottom). (a) Pristine SU-8 (fresh surface). (b) SU-8+PFPE (fresh surface). (c) SU-8+PFPE (worn surface).*

Figure 3a, b and c show the XPS results of pristine SU-8, SU-8+PFPE in fresh surface and SU-8+PFPE in worn surface conditions respectively. Since the pristine SU-8 is an organic polymer, C-C/C-H are the major chemical groups, followed by C-O. The At% table of SU-8+PFPE in Figure 3(b) shows new groups of O-CF_2, O-CF_2-O and CF_2, which confirm the presence of PFPE, none of these chemical groups are present in pristine SU-8 (At% table of Figure 3(a)). (C-C/C-H)/C-O ratio was reduced from 1.8 for pristine SU-8 to 1.6 for SU-8+PFPE, which indicates the possibility of chemical interaction between the SU-8 and PFPE molecules. The worn surface results also show the same trend of exhibiting the PFPE functions groups and increase in C-O groups. However, the chemical reaction cannot be confirmed for sure, as the C-O bond appears in PFPE as well.

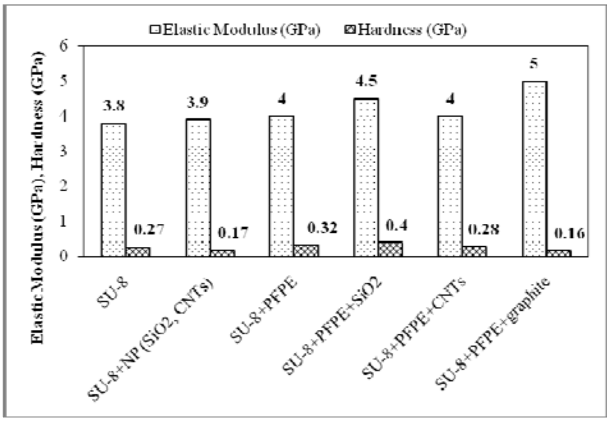


Figure 4: *Elastic Modulus (E) and Hardness (H) values of pristine SU-8 and SU-8 composites from nano-indentation characterization.*

The Pristine SU-8 (Figure 4) has shown E and H values of ~3.8 and ~0.27 GPa respectively, while SU-8+PFPE has shown E and H of ~4 and ~0.32 GPa respectively. The improvement in mechanical properties of SU-8 by PFPE addition could be attributed to the chemical bonding between SU-8 and PFPE, which results in increased cross-linking. SU-8+PFPE+SiO_2 has shown H of ~0.4 GPa, which is 40% in H. SU-8+PFPE+Graphite has shown E of ~ 5 GPa, which is 22% increase in E. However, the selection of right composite entirely depends on the application i.e. high hardness/modulus requirements.

5. Conclusions

1. The developed self-lubricating SU-8 composites with PFPE are much more hydrophobic than SU-8 and SU-8+NP composites in fresh and worn surface conditions.
2. The self-lubricating SU-8 composites reduced initial coefficient of friction of SU-8 by ~6-9 times and increased wear life by $>10^5$ times.
3. The elastic modulus (E) and hardness (H) were also increased by ~1.4 times.
4. The chemical bonding between SU-8 and PFPE molecules were partially verified by XPS characterization indirectly.

Acknowledgements

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