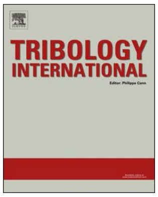
Tribology International 102 (2016) 44–51

Contents lists available at ScienceDirect

Tribology International

journal homepage: www.elsevier.com/locate/triboint



A study on frictional behavior of PMMA against FDTS coated silicon as a function of load, velocity and temperature

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ARTICLE INFO

Article history:
Received 5 December 2015
Received in revised form
14 April 2016
Accepted 16 April 2016
Available online 3 May 2016

Keywords:
Friction coefficient
FDTS coating
PMMA
Wear

ABSTRACT

Rapid developments of soft polymeric materials have inspired for a better understanding of their tribological characteristics. The tribological behavior of polymethylmethacrylate (PMMA) against 1H,1H,2H,2H-perfluorodecyltrichlorosilane [$CF_3(CF_2)_7(CH_2)_2SiCl_3$] (FDTS) coated silicon (Si) substrate (F-Si) as a function of the applied-temperature, load and sliding velocity was studied and reported in this paper. It was observed that friction coefficient vs. applied-temperature curves follow the viscoelastic behavior of PMMA, which indicates that molecular relaxation of PMMA is the dominating factor of its tribological properties at temperature below its glass transition temperature (T_g). Furthermore, consistent shifts of friction coefficient vs. temperature curves toward low temperatures with increase in load in addition to sliding velocity further signified, the importance of friction induced-temperature on the tribological properties of PMMA.

1. Introduction

The increasing importance of polymeric materials has attracted attention of the research communities, mainly due to their accessible extraordinary range of properties, such as light weight, easy disposability, low cost, good toughness, ductility, transparency and biocompatibility. Its applications and uses in advance engineering include: artificial hip joint, actuator, micro–nano fluidic device, gear, etc. [1–4]. In most of these applications, tribological properties are an important criteria in the evaluation of its performance. Therefore, a deeper understanding of the tribological behavior of polymers at various operating conditions is essential for the further improvement of their performance.

Traditionally, Da Vinci, Amonton and Coulomb have all proposed a friction model, which describes that friction force is proportional to load, and independent of contact area and velocity [5]. Although this friction model is very much applicable to most materials, many studies have found that for soft polymeric materials, such as polymethylmethacrylate (PMMA), polyethylene terephthalate (PET), polystyrene (PS), polyisobutylene (PIB) materials, deviate from this model. It was however, found that friction is actually a function of contact area and surface adhesion [6–8]. Meanwhile, Hammerschmidt and Gladfelter have reported that PMMA, PET and PS show special kind of frictional behavior because of the structural relaxation of their molecular chains, which is governed by energy dissipation, therefore the frictional response of the polymers is correlated with the its glass to rubber transition and secondary relaxation mechanisms [6]. On the other hand, several studies have also revealed the effects of velocity and load on the frictional properties of PMMA, polyaryletherketone and gelatin, which indicate that the friction peak is in fact a function of the secondary relaxation of polymer chain [9–12]. Tribological behavior of materials as a function of load has been reported by Enachescu et al., which shows direct correlation between friction and contact area [13]. In addition to all of the above studies, the exception of Coulomb's law ($F = \mu \cdot W$, where F, μ and W are the friction force, friction coefficient and load, respectively) was also encountered by various researchers [14–16]. Last but not least, tribological properties of various materials have also been found as a function of environment conditions, such as relative humidity, pH and temperature [6,17–21].

The heat due to friction is generated at contact zones and this causes an increase in temperature of the contact surfaces. As the friction of the polymeric materials is also a function of temperature even at temperature below its glass transition temperature (T_g), therefore it is highly likely that the friction induced-temperature

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http://dx.doi.org/10.1016/j.triboint.2016.04.018

could further alter the friction behavior of the polymers. That being said, a systematic study is still lacking on the combined effects of operating temperature, sliding velocity, load and friction induced-temperature on polymeric materials. This work aims to correlate friction coefficient of PMMA and Si substrate with experimental temperature, friction induced-temperature, sliding velocity and load. To avoid any form of confusion or whatsoever, the input temperature within the tribometer that is set during tribological tests is designated as the applied-temperature and the temperature generated as a result of friction is termed induced-temperature.

PMMA is one of the most commonly used thermoplastic in the microelectronics, lab-on-chip, optical applications, etc. [8,22,23]. Additionally, PMMA was used in our previous work for the fabrication of microfluidic device via hot-embossing and injection molding [24–26], where the structures are prone to friction and adhesion between the PMMA and the Si substrate. Hence, in this study PMMA was chosen as the polymeric material for the better understanding of its tribological properties. The Si substrates were coated with thermally stable 1H,1H,2H,2H-perfluorodecyltrichlorosilane [$CF_3(CF_2)_7(CH_2)_2SiCl_3$] (FDTS) to reduce the effect of adhesion on friction, because PMMA has the tendency to stick to Si surface even at temperatures much lower than its glass transition temperature (T_g) [27]. In addition, Si substrates having a favorable surface finish have been commonly used to make micromolds for replication of micro/nanostructures. However, the lifespan of Si micromolds is typically short because of their high adhesion and friction with workpiece materials. An FDTS coating on a Si mold (F-Si) helps decease friction and adhesion, thus improving the replication quality on PMMA workpieces via hot-embossing, which in this instance, is the ultimate objective of our work [25,28–30].

2. Experimental

Si substrates were cleaned thoroughly in deionized (DI) water, and subsequently deep in piranha solution and isooctane solvent. After cleaning, the Si substrates were immediately immerged into a solution comprising of isooctane solution (Sigma-Aldrich) solvent and 0.1 mM FDTS (Meryer Chemical) for a duration of 60 min to prepare the Si substrates for FDTS self-assembled monolayer (SAM) coating. Subsequently, The F-Si substrates were sequentially rinsed in isooctane, followed by DI water for several times.

The F-Si substrates were then heated in ambient condition from 100 °C to 300 °C with a step increment of 100 °C, and 300–500 °C with a step increment of 50 °C to evaluate the thermal stability of the FDTS coating. The thermal stability of heat treated FDTS coating was evaluated by calculating the surface energy from the average contact angles of water and ethylene glycol at five randomly selected locations on the coating.

The friction coefficients of the F-Si substrate were measured by a ball-on-disk micro-tribometer (CSM). A PMMA ball of 6 mm in diameter, slides on each sample for 600 s at loads of 1, 2 and 3 N and sliding speed of 2, 4 and 6 cm/s. The sliding tests were carried out at various applied-temperatures starting from 22 °C to 110 °C with a step increment of about 10 °C along a track of radius 1 mm. Each sample was tested for five times at one particular temperature and the average values were considered. The wear scars on the PMMA balls were examined via scanning electron microscopy (SEM, JSM-5600LV).

The PMMA balls used for the tribological test were prepared by injection molding, which has been described in the previous paper [26]. A summary of the properties of Si and PMMA are listed in Table 1, which were either experimentally measured or collected from suppliers and literatures [31–34].

Table 1
Properties of PMMA and Si.

Property	Material	
	PMMA	Si
Poisson ratio	0.37	0.27
Young Modulus (GPa)	2.4	175
Density (kg/m^3)	1185	2330
Thermal conductivity (W/m k)	0.2	149
Specific heat (J/kg K)	1466	730

3. Results and discussion

The SEM micrograph in Fig. 1a shows the surface morphology of the PMMA ball prior to tribology test, and the SEM micrographs in Fig. 1b–g show the worn surfaces of the PMMA balls after tribology tests at various conditions. Nonetheless, no worn scar was observed on Si substrates under the selected test conditions; since the Si substrate is much harder than the PMMA counter ball. The wear scar diameters of the PMMA balls as a function of the applied-temperature and load are presented in Fig. 2, which shows that the wear scar diameters remain almost unchanged for temperature up to 80 °C with a standard deviation of ± 10 μm for all load conditions. On the other hand, the wear scar diameter increase with increase in load. Not to mention, a drastic increase in wear scar diameter was observed at temperature beyond 80 °C because of the softening of the PMMA balls at elevated temperatures.

Fig. 3 shows the contact angles and surface energies of the as-prepared and heat treated F-Si substrates, where the contact angles fluctuate within a range of ± 1°. The surface energies are calculated from the average values of the contact angles of the respective F-Si substrates using Young equation presented below [2,3]:

$$\gamma_{sv} = \gamma_{sl} + \gamma_{lv} \cos\theta + \pi_e \tag{1}$$

where γ is the surface energy and the subscripts "*sv*", "*lv*" and "*sl*" represent the solid–vapor, liquid–vapor and solid–liquid interfaces, respectively. θ is the measured contact angle, while π_e is an equilibrium pressure of the adsorbed vapor on the solid. In this case, the equilibrium pressure of the adsorbed vapor on the solid π_e is the assumed to be zero.

The relationship between two components of surface energies, namely, dispersive and polar components, are related by the following equations:

$$\gamma_{sv} = \gamma_{sv}^d + \gamma_{sv}^p \tag{2}$$

$$\gamma_{lv} = \gamma_{lv}^d + \gamma_{lv}^p \tag{3}$$

$$\gamma_{sl} = \gamma_{sl}^d + \gamma_{sl}^p \tag{4}$$

$$\gamma_{sl}^d = \gamma_{sv}^d + \gamma_{lv}^d - 2\left(\gamma_{sv}^d \times \gamma_{lv}^d\right)^{1/2} \tag{5}$$

$$\gamma_{sl}^p = \gamma_{sv}^p + \gamma_{lv}^p - 2\left(\gamma_{sv}^p \times \gamma_{lv}^p\right)^{1/2} \tag{6}$$

where the superscripts "*d*" and "*p*" represent the dispersive and polar components, respectively. Eqs. (1)–(6) are combined to obtain Eq. (7), which establishes co-relation among the dispersive and polar components of surface energies with contact angles.

$$(1+\cos\theta)\left(\gamma_{lv}^d + \gamma_{lv}^p\right) = 2\left(\gamma_{sv}^d \times \gamma_{lv}^d\right)^{1/2} + 2\left(\gamma_{sv}^p \times \gamma_{lv}^p\right)^{1/2} \tag{7}$$