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Ice friction of ultra-high molecular weight polyethylene: The effects of fluorine additives and plasma (PECVD) treatment

Christos Stamboulides, Peter Englezos, Savvas G. Hatzikiriakos *

Department of Chemical and Biological Engineering, The University of British Columbia, Vancouver, BC, Canada V6T 1Z3

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ABSTRACT

Various new polymer additives were blended into ultra-high molecular weight polyethylene (UHMWPE) in order to examine their effects on ice friction. A certain type of a new liquid perfluoropolyalkylether was proven to improve the surface and sliding characteristics of UHMWPE on ice. It was shown for the first time that an optimum amount of additive (about 2.5 wt%) reduces the ice friction coefficient significantly at temperatures greater than $-7\,^{\circ}$C. Moreover, plasma chemical vapour deposition of UHMWPE under a fluorinated gas was also utilized to examine its effect on its surface and sliding characteristics. This treatment increased the static water contact angle, from 85° to 138° and decreased the friction coefficient to about 25% at the highest sliding velocity of 1.96 m/s.

1. Introduction

It is common in polymer science to aim to optimize surface properties, such as morphology, surface energetics, hydrophilicity and/or hydrophobicity depending on the application, while maintaining the desirable and characteristic properties of the bulk such as mechanical properties in specific applications [1–4]. Proven methods for altering polymer surface characteristics is by blending these polymers with small amounts of various additives [5–7] and plasma treatment [8–10]. The specific polymer of interest in the present work is ultra-high molecular weight polyethylene (UHMWPE) which is extensively used as ski base. The main objective is to find ways of increasing its hydrophobic character, which would possibly decrease its coefficient of friction with ice. It is widely accepted that hydrophobicity is related to ice friction [11]. For example, Shimbo [12] has shown that the coefficient of friction of a ski sliding base decreased with a hydrophobic fictionalization on its surface.

Puukilainen and co-workers [7] have prepared composites of UHMWPE with solid and liquid lubricants and found that the solid additives had little effect on the hydrophobicity of UHMWPE. A similar mixing approach was performed by Ebbens and Badyal [5] who prepared polypropylene films by melt blowing. They found that the surface energy of the polymer was lowered by mixing a small amount of fluorine-containing material into the polymer melt. Interestingly, they also found that migration of the fluorochemical additive towards the surface occurred. Puukilainen and Pakkanen [6] and Puukilainen and co-workers, [7] altered the hydrophobicity of high-density polyethylenes (HDPE) and polypropylenes (PP) by melt blending with perfluoropolyethers.

As referred above, another method to render polymeric surfaces hydrophobic is by utilizing non-thermal plasma treatment and more specifically the plasma enhanced chemical vapour deposition (PECVD) [13–16]. A *plasma* is an ionized gas and PECVD is the process used to deposit thin films from a vapour to a solid state on a substrate [1,13,17,18]. Proper selection of gases from which the plasma is generated can result in deposition of organic or inorganic films. Chemical surface modification results when the species generated in the gas react at a surface to form stable products with physical and/or chemical properties that are different from those of the bulk. In many instances, etching and modification occur simultaneously. The nature of the interaction of the plasma constituents with the polymeric surfaces is determined by the configuration and processing parameters that can be adjusted to modify (chemically and/or physically) the various polymer surfaces. PECVD occurs when precursors to the deposited film are generated by fragmentation of the gas in the plasma and transported to a surface where they react to form a solid layer [1,13,17,18]. Plasma treatment in the presence of O_2 and CF_4 is a method that has been used to render polyethylene based polymers hydrophobic and superhydrophobic [13,14,17,19].

The application of plasma treatment on polymeric surfaces provides superhydrophobicity in short treatment times. Fresnais

* Corresponding author.
E-mail addresses: savvas.hatzi@ubc.ca, hatzikir@interchange.ubc.ca (S.G. Hatzikiriakos).

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and co-workers [13] demonstrated that the synthesis of superhydrophobic polymer surface is possible by the simple plasma surface modification, either in one- or two-step process. The resulted static contact angles reported were up to about 160°. Milella and co-workers [10] deposited nanostructured films from modulated C_2F_4 plasmas. Although the time-scale for this process was very long, superhydrophobic slippery films were obtained on different commercial polymeric substrates.

The rationale behind the utilization of the aforementioned techniques was first to create a structure in the micro- or nano-level on the surface and second to deposit a fluorine-film that will increase its hydrophobicity [8,13,14,19]. It is well known that wettability, or liquid (water in this case) high repellency (superhydrophobicity), of a given surface is a combination of its surface structure in the micro- and nano-level and its chemical nature, a phenomenon known as lotus effect [3,9,18,20,21]. Therefore, in order to render the UHMWPE surface superhydrophobic (i.e., exhibiting water contact angles greater than 150°) two factors must come in play: the micro- and nano-pattern of the surface (dual roughness) as well as it naturally exhibiting hydrophobicity.

The objective of this work is to identify ways that would increase the hydrophobicity of ultra-high molecular weight polyethylene (UHMWPE), aiming at decreasing its coefficient of friction (COF) with ice, while retaining its excellent mechanical properties. In this work, liquid fluorinated additives as well as plasma enhanced chemical vapour deposition in a fluorinated gas are utilized in order to improve the hydrophobicity of UHMWPE and decrease its coefficient of friction (COF) over ice.

2. Experimental details

2.1. Experimental equipment

2.1.1. Friction measurements

A standard conventional rotational rheometer (Physica MCR 501) was used and converted into a tribometer by designing a new fixture, essentially modified rotational parallel-plate geometry. The parallel plates are enclosed in an environmental chamber that can produce temperatures as low as −150 °C through the use of an evaporator and liquid nitrogen. The rotating top plate in the parallel plate setup is substituted by a ring slider sample attached to a sample holder, and the stationary bottom plate is the ice dish (Fig. 1a). To account for non-perfect parallelism between the two surfaces the ice dish holder is mounted via a miniature ball coupling and a compression spring to the rigid lower shaft (Fig. 1b). More details can be found elsewhere [22,23]. All results reported here were obtained with a fixed normal force of $F_N = 3$ N. The instrument recorded the torque, T, which can be used to calculate the tangential force, F_T ($F_T = T/\bar{r}$), which was converted into the coefficient of friction μ using the following equation:

$$\mu = \frac{F_T}{F_N} \tag{1}$$

where $\bar{r} = \frac{1}{2}(r_o + r_i)$ is the average radius of the slider ring and F_N is the applied normal force. Since the operation controls the normal force, F_N and measures the tangential force, F_T, the calculation of the COF through Eq. (1) becomes independent of the actual area of contact. To limit the variability of experimental results each ice surface was used for only two runs, before it was polished again using the commercial drill press as described by Stamboulides [22]. At each temperature setting, runs with different linear speeds were randomized to average out changes in the slider sample's surface over time. In the end, 10 runs were carried out for each sliding velocity setting; each data point represents the average of 10 measurements, the error bars in the graphs represent the corresponding 95% confidence interval.

2.1.2. Plasma enhanced chemical vapour deposition (PECVD)

Gas plasma treatment processes are used for chemical modification of polymer surfaces [13,14,17,19]. Stated simply, a plasma is an ionized gas that conducts electricity and plasma techniques are among the most widely studied subjects in modern science [1,3,9]. In this work the one-step synthesis was used to treat UHMWPE substrates; this treatment consists of a simple fluorination through CF_4 plasma treatment where under the electrical discharge of CF_4 gas is dissociated by electronic impact and CF_x radicals and mostly CF_2 act as functionalization agents [13,24]. During plasma treatment the surface is being etched, while the amorphous phase of the bulk of the polymer is being removed [9,10,18,19]. The Trion PECVD, with O_2 and CF_4 gases, was used in this study to create super-hydrophobic films on the UHMWPE surfaces.

2.1.3. Contact angle measurements

Contact angle, θ, measurements were conducted by using the sessile drop technique and they were performed at room temperature (25 °C). The static contact angle of water, θ, with all substrates with distilled and de-ionized water was measured using images obtained with a high resolution camera—Nikon D80, Digital SLR Camera. The camera was attached to a Sigma AF–MF zoom lens (105 mm, F2.8 EX DG Macro) and a Kenko extension tube set for better image magnification and resolution. The FTA32 software from First 10 Angstroms was used to analyze the images and calculate the static water contact angles of the various surfaces under study. The volume of the water droplet was maintained constant for all the substrates, 1 μL, in order to prevent possible changes in the droplet due to gravity effects.

2.1.4. X-ray photoelectron spectroscopy (XPS)

X-ray photoelectron spectroscopy (XPS) is a surface elemental analysis technique with a sampling volume that extends from the

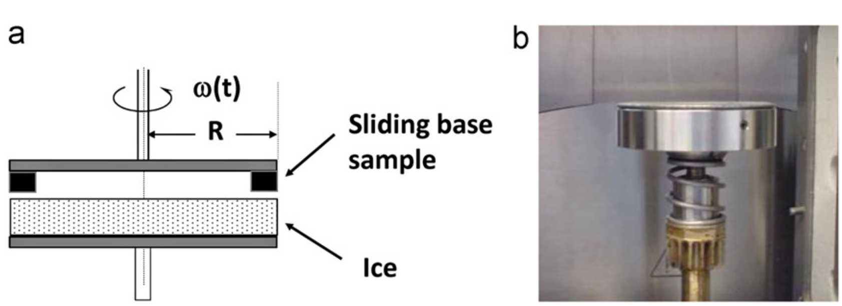

Fig. 1. (a) Schematic of the parallel plate geometry used for the friction measurements, (b) a picture of the dish holder that instantaneously keeps parallel the two surfaces under sliding (lower plate).