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Micro- to nanoscale surface morphology and friction response of tribological polyimide surfaces

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ABSTRACT

Sintered polyimide surfaces that were worn under macroscale conditions at different temperatures, were further characterised by contact-mode atomic force microscopy for getting insight in the tribophysical and -chemical processes at the micro- to nanoscale. Depending on the temperature, either mechanical interaction ($23\,^\circ C < T < 100\,^\circ C$), hydrolysis ($120\,^\circ C < T < 140\,^\circ C$), or imidisation ($180\,^\circ C < T < 260\,^\circ C$) results in different microscale surface characteristics. At low temperatures, surface brittleness and inter-grain fracture has been observed with an almost homogeneous friction pattern. At intermediate temperatures, the formation of a protecting local film leads to smoother surfaces with local lubricating properties. At high temperatures, different topographical and frictional patterns are observed depending on local imidisation or degradation. From AFM scans at the sub-micronscale, local debris depositions are observed and correspond to surface locations with locally reduced friction. From AFM scans at the nanoscale, polymer chain orientation is observed with formation of zig–zag or stretched molecular conformation: the latter is not induced by purely mechanical surface interactions or hydrolysis, but mainly results from tribochemically induced imidisation at high sliding temperatures. The present investigation describes the influences of local tribological interactions onto the macroscale wear behaviour of a polymer, and therefore aims at contributing to a better understanding of scaling between macro- to nanolevel tribological response.

1. Introduction

Gaining better insight in the sliding performance of polymers is primordial for improving their friction and wear performance and for designing new high-performance polymers with, e.g., in-build lubricating properties that become active under certain sliding conditions. While polymers have self-lubricating ability, it is often only effective in a certain interval of sliding parameters such as normal loads, sliding velocities and/or thermal regimes, as represented in so-called *pv*-sliding maps. In this respect, polyimides have been frequently studied [1–4], as they offer a unique combination of mechanical strength, thermal resistance and self-lubrication under specific sliding conditions, but show transitions in performance. The friction and wear mechanisms of polymers are generally determined by the molecular architecture (depending on synthesis) and micro-structure (depending on processing). They can be attributed to a combination of tribochemical and tribophysical modifications in the sliding interface varying the surface properties, and the interaction of wear debris particles acting as third bodies or forming a transfer film on the counterface [5].

Tribological studies of polymers are complex and require an interdisciplinary approach, combining mechanical, physical and chemical studies of the interfacial interactions. The complexity of interactions arises from multiple phenomena occurring simultaneously at various structural levels, and mutually influencing each other. Therefore, understanding the macroscopic mechanical behaviour requires thorough characterisation at the micro- to nanoscale of all components involved in the tribological processes, i.e. the transfer film, wear debris and polymer surfaces. While in situ monitoring of the sliding interface would provide the most useful information, it often cannot be applied because of the limited access and high specificity in space and time. Although on-line spectroscopy was successfully applied [6,7], post-mortem evaluation methods are more often used. Commonly, morphological and compositional characterisation of the *transfer film* provides best insight in the wear mechanisms and frictional stability. Smooth, lumpy or flake-like transfer films can be distinguished by means of optical or scanning electron microscopy (SEM), changing polymer/counterface contacts into local polymer/polymer contact

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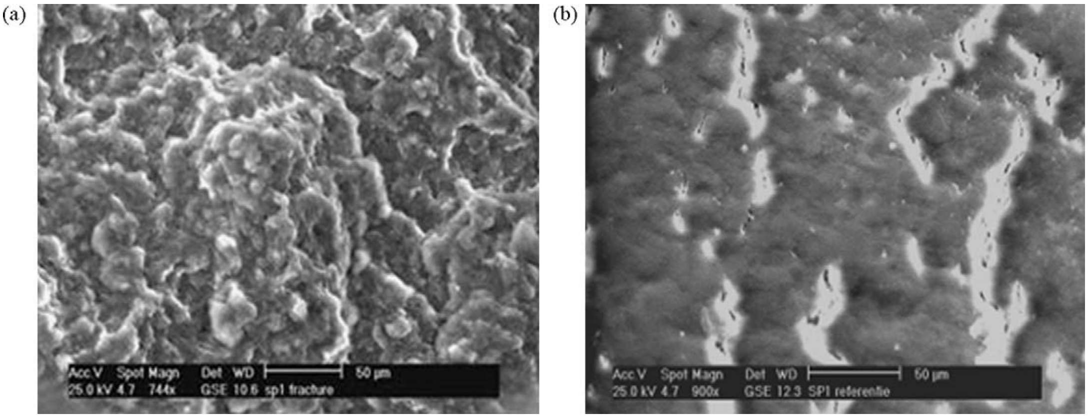

Fig. 1. Scanning electron microscopy of unworn sintered polyimide samples, (a) fractured cross-section and (b) sliding surface.

[8]. The chemical composition of transfer films is often studied by means of energy dispersive X-ray detection (EDX) [9], Auger electron spectroscopy (AES) [10] or X-ray photoelectron spectroscopy (XPS) [11,12], revealing the formation of metal/polymer complexes that provide good adherence to the counterface. Further characterisation of *wear debris* provides information on the interfacial reactions and residence time of the particles. Due to the joint action of repeated loading and frictional heating, the wear debris undergoes physical and chemical reactions since its generation. As a result, the debris properties are not identical to those of the bulk material and contain information on the wear history. The tribochemical reactions can be monitored by thermal analysis (thermogravimetric analysis, TGA; differential scanning calorimetry, DSC) in order to reveal thermal degradation or crystallisation reactions of the amorphous polymer phases under sliding [13,14]. The debris shape is often analyzed with quantitative image processing techniques [15] or fractal analysis [16]. Gao et al. [17] investigated radical reactions in wear debris by means of electron spin resonance (ESR). In recent years, more attention has been paid to chemical analysis of the worn *polymer surfaces*. Besides monitoring surface damage by image processing [18], the technical viability of more quantitative methods to investigate structural changes in a thin surface layer activated by wear should have (i) a sensitivity adequate to distinguish the surface structure from the bulk, (ii) a detection depth equivalent to the surface layer thickness to study the structure of interest, and (iii) a signal-to-noise ratio high enough to avoid possible interference originating from foreign matter adhering to the wear surface. Many authors apply EDX for evaluation of worn polymer surfaces [19,20]. Using XPS, Li et al. [21] demonstrated that chain scission and oxidation is prevalent on the worn surface, while branching and cross-linking was observed in the subsurface. Using Raman spectroscopy, Stuart [22] investigated solvent-induced and thermally induced surface plasticisation for tribological polymers. Briscoe et al. [23] studied the relation between high speed sliding of PEEK and C–O–C stretching. Samyn et al. [24] gained quantitative and qualitative information about the chemical nature (structural units or additives), conformational order (trans-gauche molecular isomerism), state of order (amorphous, crystalline) and orientation (alignment of polymer chain and side groups) of worn polyethylene terephthalate surfaces. Hanchi and Eiss [25,26] investigated the development of crystallinity on PEEK surfaces by means of wide-angle X-ray diffraction (WAXD). Bexell et al. [27] evaluated tribologically induced chemical changes of organic coatings by means of secondary ion mass spectroscopy (ToF-SIMS), concluding that mechanical failure of the coating dominates while tribochemical changes of the coatings were not detected in the wear track. Static SIMS is suitable for analysis of molecular conformation and orientation [28], but the response and interpretation of the latter technique strongly depends on the detection depth. New potential to get additional insight in the tribochemical or -physical reactions on polymer surfaces under sliding is offered by combining surface analysis techniques. An interesting overview of surface micrography and analysis tools is given in Ref. [29].

The purpose of the present paper is to investigate the suitability of contact-mode atomic force microscopy (AFM) for exploring the underlaying mechanisms of macroscopic sliding processes, by examination of worn polyimide surfaces. Mechanical solicitations of a polymer often induce microstructural changes, such as shear banding after yielding [30], or alignment after nano-rubbing [31], which were successfully monitored with AFM. The present evaluation aims at visualizing how the polyimide structure is locally affected by sliding processes, and it is complementary to our previous investigations where chemical surface modifications were mapped by spectroscopy and thermal analysis [32]. The AFM scanning is able to provide more details than scanning mechanical microscopy, as applied to worn PET surfaces by Branco and Campos [33]. This characterisation step is a very important key in scaling polymer tribology at macro-, micro- and nanolevel. The study of micro- and nanotribological polymer features primarily focused on polymeric films [34,35]. Han et al. [36] applied AFM characterisation to determine local variations in tribological response of various phases in polymer composites. Recently, Liu et al. [37] investigated the relations between friction and molecular orientations in drawn and undrawn PTFE. While friction-induced molecular orientation is evident for thermoplastics, it happens more difficult in rigid molecular structures and importantly

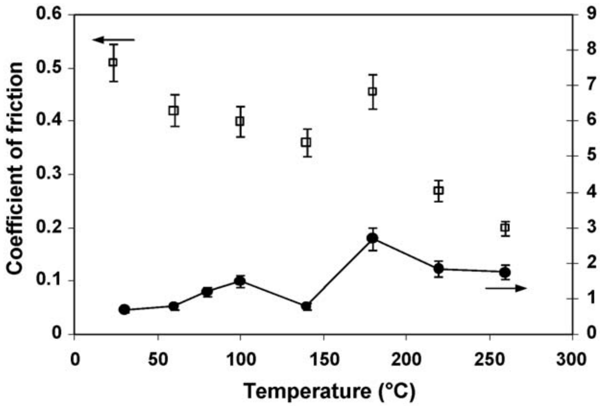

Fig. 2. Coefficients of friction (□) and wear rates (●) during macroscale sliding of sintered polyimides as a function of the counterface bulk temperature, under 50 N normal loads and 0.3 m/s sliding velocity (values after 15,000 m sliding distance).