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Third body effects in the wear of polyamide: Micro-mechanisms and wear particles analysis

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ABSTRACT

The wear micro-mechanisms at a frictional interface between a polyamide 4,6 (PA 46) substrate and a spherical sapphire counterface have been investigated using in situ contact observation. Experiments were carried out under reciprocating sliding conditions with varying values of the overlap ratio, Δ, defined as the ratio of the displacement amplitude to the contact diameter. Using this procedure, it was found possible to vary the extent of wear particles accumulation within coherent third body agglomerates. For low overlap ratios ($\Delta < 0.2$), particles detached from the PA 46 substrate were extensively agglomerated within distinct third body corrugations. In this regime, the rate limiting process regarding the wear degradation was found to be the extrusion of fibril-like wear particles from the extremities of sheared third body agglomerates. On the other hand, no substantial debris accumulation was found to occur when the overlap ratio was greater than 0.2. Additional infrared thermal contact imaging showed that these wear mechanisms were induced under essentially isothermal conditions. From differential scanning calorimetry (DSC) and size exclusion chromatography (SEC) analysis, micro-structural changes within wear particles were found to be associated with a strong reduction in the molecular weight of the PA 46 molecules by virtue of stress-induced chain scission mechanisms.

1. Introduction

Polymers in their bulk and film forms are widely used as self-lubricating materials in many tribological applications where their wear resistance is of primary importance. In order to derive relevant wear models, much attention has been paid to the analysis of tribological damage micro-mechanisms in relation to surface mechanical properties (for a review, see for example Refs. [1–3]). Most of these analyses concentrate on the primary processes involved in the detachment of particles from the polymer surface. Within this context, scratching experiments have especially emerged over the past years, as a useful route to mimic and characterize the deformation and failure modes which occur as a consequence of specific interactions between asperities touching each other in discrete areas of contact between polymeric substrates and rough rigid counterfaces [4]. Such approaches provided insights into the elementary particles detachment mechanisms involved in the so-called abrasive wear situations [4,5]. However, particles detachment processes are only one of the facets of the overall wear degradation. Investigations of interface tribology [6] have widely demonstrated that debris are usually trapped within the contact for varying periods of time during which they are subjected to a variety of mechanical and tribo-chemical processes and ultimately form what is often termed the 'third body'. This third body plays an essential role in the way differences in the velocities between rubbing surfaces (the so-called 'first bodies') can be accommodated [7]. In the case of polymer surfaces, it often acts as a solid lubricant which reduces the stresses transmitted to the first bodies and ultimately decreases the wear rate. In a set of experiments where the level of third body accumulation within the contact was varied by changing the contact zone kinematics, Briscoe et al. [8,9] have shown that the wear rate of poly(methylmethacrylate) is primarily governed by the flow of distinct third body agglomerates under the action of shearing stresses. In such situations, the mechanical and rheological properties of third body compacts emerge as important parameters regarding the wear resistance of polymer systems. However, these properties are likely to be very different from that of the original substrate, as third body agglomerates are subjected to a variety of friction-induced mechano-chemical and/or mechano-physical changes. These processes have been especially investigated within the context of transfer film formation, which is a generic wear mechanism of

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many semi-crystalline polymers [10,11]. Complex tribo-chemical effects are known to occur during the formation of polymer transfer films to metal counterfaces, which are related to the molecular structure of the polymer, mating metal, friction and environmental conditions as well as to the presence of fillers.

The nature of the molecular mechanisms involved in transfer film and wear debris formation remains largely unsolved, as well as their relationships with the molecular and micro-structural characteristics of the virgin substrate. Using X-ray photoelectron spectroscopy (XPS) and Fourier transform Raman (FT-Raman) spectroscopy, Li et al. [12] have found evidence of the occurrence of both chain scission and oxidation during the sliding friction of poly(etheretherketone) (PEEK) against steel counterfaces. Similar conclusions were drawn from wear studies using polyamides materials, which are the subject of the present investigation. Using Fourier transform infrared microspectroscopy (FTIRM), Weick et al. [13] evidenced dissociation of the N–C bonds in the backbone of nylon 6,6 rubbed against sapphire. Size exclusion chromatography (SEC) analysis of the wear debris produced from PA 66/PA 66 contacts under mixed rolling/sliding conditions also showed a twofold reduction in the molecular weight as compared to the virgin polyamide substrate [14]. In a recent study, Cong et al. [15] concluded from infrared and X-ray spectroscopy that the strength of hydrogen bonds decreased in PA 46 transfer films and wear debris. It was also found by these authors that the amount of amorphous phase was increased in the transfer film and wear debris as compared to the virgin semi-crystalline substrate. For nylon 10,10 Wang et al. [16] showed that some hydrolysis of amide groups may occur in presence of water. The resulting decrease in hydrogen bonds between nylon 10,10 molecules was pointed out as an important factor that led to a high wear rate of nylon in water. The dependence of transfer film and wear debris formation on the molecular and micro-structural characteristics of polyamide substrates remains unclear. Samyn et al. [17,18] have observed that the nature of the catalyst used to polymerise polyamides can affect the softening of the material and the subsequent formation of a coherent transfer film during friction. The differences in softening mechanisms were correlated to structural changes evidenced by thermal analysis and Raman spectroscopy. In the case of oriented PA 6 fibres, Cayer-Barrioz et al. [19,20] also showed that the abrasive wear resistance was correlated to the level of molecular orientation within the amorphous phase, the later being varied when the molecular weight of the polyamide polymer was changed.

Changes in the crystallinity or in the molecular weight of wear particles can have a significant effect on third body rheology, which in turn can affect the ultimate wear properties of polymer systems. However, it is not clear whether these changes in the molecular and micro-structural characteristics of the wear debris only result from friction-induced increases in the contact temperature or if they can also occur under the purely mechanical action of the shearing stresses. In many of the above-mentioned studies, tribological conditions indeed resulted in a substantial heating – and even melting – of the polymer surfaces.

Within the framework of this study, third body formation and flow within a PA 46/sapphire contact were investigated under essentially isothermal contact conditions. By changing the relative displacement amplitude under reciprocating sliding conditions, it was found possible to vary the extent of wear particles accumulation and compaction within third body agglomerates. The associated wear micro-mechanisms were investigated from in situ contact observation through the transparent counterface. Infrared contact imaging also allowed evaluating the temperature rise at the worn contact interface. In addition, some of the features of wear processes, such as the extrusion of fibril-like debris from third body corrugations, were qualitatively accounted for from SEC and differential scanning calorimetry (DSC) analysis of the microstructure and molecular weight distribution of the wear particles.

2. Materials and experimental details

2.1. Polyamide material

The selected PA 46 was a commercial Stanyl TW200 grade provided by DSM (Geelen, Netherlands). This polymer was processed from dried pellets in the form of injection moulded bars 4 mm in thickness and 10 mm in width. The bars were cut into parallelepiped specimens (10 mm × 10 mm × 4 mm) for the wear tests. They were subsequently cleaned with ethanol and hexane and rinsed with distilled water. Prior to wear testing, the samples were dried 12 h under vacuum at 80 °C and stored in a dessicator. The sliding direction was set perpendicular to the injection flow direction.

2.2. Wear experiments

Wear experiments were carried out using a home-made reciprocating tribometer fully described in Refs. [21,22]. The flat PA 46 specimens were rubbed at imposed displacement amplitude against a smooth ($R_a < 5$ nm) plano-convex sapphire lens (Melles Griot, France) with a radius of curvature of 7.7 mm. Unless otherwise specified, all the experiments were carried out at a constant applied normal load of 200 N. The corresponding initial mean contact pressure was close to 110 MPa and yielded a contact radius of about 750 μm. The wear experiments were repeated at various imposed relative displacements between 0.3 and 2 mm, while the sliding velocity was kept constant and equal to 2 mm s^{-1}. The number of sliding cycles was varied between 2.5×10^3 and 10^5 cycles. Optical microscopy observations did not reveal any substantial wear damage of the sapphire lens. During the experiments, the relative displacement and the tangential force were continuously monitored. Polyamide materials being very sensitive to water plasticization, special care was taken in order to ensure controlled environmental conditions during the tests. For that purpose, an environmental cell was designed which allowed performing the wear tests under a dry air flow. Prior to injection within the cell, compressed air was dried out within columns filled with silica gel. This procedure provided a relative humidity less than 10% around the specimens during the course of the wear tests.

An optical zoom equipped with a CCD camera also allowed in situ video recording of images of the contact area through the sapphire lens. Alternatively, in situ infrared thermal contact imaging was performed using a CEDIP JADE MWIR InSb camera with 320 × 256 pixels (pixel size of 30 μm × 30 μm) and a 3–5.1 μm wavelength band detection. The thermal sensitivity of the system is 20 mK. It was calibrated prior to the experiments using a black body. While the polymer underwent cyclic sliding, the IR camera was coupled with a "lock-in" device and the system processor accumulated dated infrared images at the frame frequency (100 Hz). Mathematical signal processing (FFT, filters) allowed to compute the amplitude and the phase of the infrared distribution at the frequency of the modulated contact loading. The contact temperature was calculated from the IR signal assuming that the sapphire counterface was transparent to infrared and that the emissivity of the PA 46 surface was close to 1.

2.3. Differential scanning calorimetry

The melting and crystallization behaviour of the PA 46 wear particles was investigated using differential scanning calorimetry (DSC 2920, TA instruments). All experiments were carried out under dry nitrogen flow using aluminium pans. Two successive melting/crystallization cycles were applied to the material. The