ORIENTATION AND DEGRADATION OF POLYMER SLIDING SURFACES EVALUATED BY RAMAN SPECTROSCOPY

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ABSTRACT
Present study investigates changes in the conformation of functional groups at the polymer sliding surface by post-mortem Raman spectroscopy, thermomechanical analysis and SEM/EDX. Two case studies on sintered polyimide (SP) and thermoplastic polyethylene-terephthalate (PET) are presented, indicating the influences of sliding temperature, counterface type and internal lubricants (PET/PTFE) on some characteristic absorption bands in the Raman spectrum of the sliding surfaces.

INTRODUCTION
Polymer tribology is characterized by the formation of a transfer layer through softening and orientation of the sliding surface. Higher temperatures generally increase the polymer chain moveability, allowing for different transfer mechanisms and transitions in friction and wear behaviour. Tribochemical reactions were previously discussed by, e.g., Jintang [1] and are most widely examined by XPS, however only useful for identification of atomic concentrations of transferred elements.

EXPERIMENTAL
Tribological experiments on SP are performed on a PLINT TE 77 reciprocating test-rig with polymer cylinders (diam. 6 mm, length 15 mm) in line-contact with a fixed steel plate under 50 N, 0.3 m/s, 80°C to 260°C. Large-scale PET blocks (150 x 150 x 20 mm³) in pure and PTFE-filled conditions are slid against 42 CrMo4 steel and X2CrNi18.2 stainless steel under 590 kN (25 MPa) on a home-made tribotester [2].

Raman spectra are measured on a Brucker FT equipment Equinox 55S (Bruker Optik, Ettlingen, Germany) with a Raman module FRA 106 fitted to a nitrogen cooled (77 K) germanium high sensitivity detector D418-T. The applied wavelength was the 1.064 µm line from a Diode Laser Pumped Nd:YAG laser. The spectra are recorded at a resolution of 3 cm⁻¹ using a non-focused laser beam with a power of 70 mW. A quantitative interpretation is made using the baseline theory for correction of the individual spectra. Normalised relative intensities are used to compensate for any change in experimental conditions such as excitation intensity and sample positioning.

FRICTION AND WEAR DATA
As shown in Fig. 1, the coefficient of friction for SP shows a transition at 180°C above which friction decreases sharply under 50 N and 200 N normal load. This temperature corresponds with an endothermic reaction related to dehydration as revealed by thermogravimetric and differential thermal analysis. Caloric measurements (DSC) however were not able to detect this type of secondary transition, although modulated-DSC showed a slight difference in thermal capacity at 180°C.

Coefficients of friction and wear rates for PET are summarized in Table 1, indicating the beneficial sliding properties of PTFE additives and lower friction in sliding against stainless steel counterfaces. The latter was previously also reported by [3], although the low friction in contact with stainless steel was attributed to lower surface roughness. Since present counterfaces have identical roughness Rₐ = 0.20 µm, the different friction is most likely attributed to lower surface energy (45 mJ/m² for steel and 39 mJ/m² for stainless steel) and the formation of a thick film on the polymer surface due to back-transfer in contact with stainless steel.

Table 1. Variation of friction and wear for PET with internal lubricant and different counterfaces under 25 MPa.

<table>
<thead>
<tr>
<th>Test material</th>
<th>Friction</th>
<th>Wear (mm/km)</th>
<th>Friction</th>
<th>Wear (mm/km)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PET</td>
<td>0.19*</td>
<td>6.9</td>
<td>0.09</td>
<td>1.3</td>
</tr>
<tr>
<td>PET/PTFE</td>
<td>0.08</td>
<td>2.2</td>
<td>0.07</td>
<td>0.9</td>
</tr>
</tbody>
</table>

* stick-slip
SURFACE ANALYSIS

The spectrum of SP surfaces as shown in Figure 2 contains absorption bands relating to the imide-structure (orientation effects) and the poly(amic) acid precursor (decomposition). From the increase in $I_{1788}/I_{1612}$ relative intensity, it reveals that the C=O in the imide ring is stretched through the combination of higher temperature and shearing stresses. Chemical reactions between 100°C and 180°C related to thermal imidisation from polyamic acid to polyimide [4] however restricts the molecular moveability in the 100°C to 180°C temperature range for 50 N tests. The orientation is also constrained under 200 N sliding (decreasing trend and lower intensity of $I_{1788}/I_{1612}$), where only at 260°C the molecular movement allows for reorientation of C-O parts along the sliding direction. The C-N-C orientation is given by $I_{1124}/I_{1612}$ intensity increasing under both 50 N and 200 N sliding. The orientation is more pronounced under high loads, pointing towards a concentration of the shearing stress on the C-N-C functional group rather than on the C-O positions. Also the $I_{1124}/I_{1788}$ confirms this trend. However, there is a transition from transverse to axial C-N-C orientation at 180°C, according to the observed transition in friction and maximum wear rates. Mainly for temperatures above 180°C the C-O-C related intensities (1272 cm$^{-1}$) sharply decrease, as the enhanced molecular chain motion allows for tilting of the ether structure anti-parallel to the sliding surface.

The PET and PET/PTFE surfaces, showing brown PTFE depositions after sliding against steel and a grey transfer film after sliding against stainless steel, were analysed by SEM/EDX showing that steel particles were incorporated after sliding against stainless steel (Fig. 3). This is ascertained by levelling of the roughness peaks on the stainless steel surface. Raman spectra in Fig. 4 show clear differences between the PET and the PET/PTFE sliding surfaces at the 713 cm$^{-1}$ band, characteristic for the PTFE depositions on the sliding surface: its relative intensity increases from 0.23 before sliding to 0.26 after sliding. Other absorption bands are analysed according to the trans (oriented) and gauche (non-oriented) structure relative to the reference band at 795 cm$^{-1}$, indicating an increase in $I_{996}/I_{795}$ (trans) intensities and decrease in $I_{857}/I_{795}$ (gauche) intensities after sliding. The amount of trans conformation for PET sliding against steel is larger than for PET/PTFE, indicating stronger interactions at the PET sliding surface as expressed by the high coefficient of friction. The trans conformation of PET after sliding against stainless steel is lower according to lower frictional shear forces at the surface.

CONCLUSIONS

Raman spectroscopy illustrates orientation on the polymer sliding surfaces correlating with the observed friction and wear behaviour. For polyimides, the 180°C transition temperature corresponds to reorientation of C-N-C groups and for PET/PTFE the trans conformation is favoured while internal lubricants are deposited on the polymer surface.

References