Effect of surface temperature on tribological behavior of PTFE composites

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Abstract

Tribological behavior of PTFE is highly affected by fillers used to improve its mechanical characteristics and depends on the ability of the material to maintain its integrity in the working conditions. Specifically, in the case under study, the heat generated by friction was modelled as a heat flow coming from a source at the contact surface in static condition. Considering that a heat flow is also supplied to the samples during a Differential Scanning Calorimetry (DSC) analysis, where crystallinity of material is evaluated, a correlation between thermal characteristics of the material, its structure and tribological behavior is presented.

Keywords: PTFE, friction, heating, wear, temperature rise.

1 Introduction

Polytetrafluoroethylene (PTFE) is well known for its low coefficient of friction in dry conditions even if it presents low carrying capacity, which is a reason why manufacturers have been trying to improve its mechanical characteristics by means of opportune fillers building a wide family of PTFE composites [1]. The results have been quite interesting but, at the end it has been seen that such fillers compromise PTFE’s attractive low friction properties (μ<0.1) even if wear of said composites in comparison with virgin PTFE is further reduced [2]. Furthermore, the disadvantage of using hard phases in soft matrix is well known, that is, the possibility of transfer film removal and the aggressive abrasion of the hard counterface if the hard phases are released to the interface as a third body due to loosening of the bond between the filler and the polymer matrix: it was found that the particles used as fillers were rubbed off during the test, highlighting the weakness between the transfer film and the countersurface [3].
The role of the transfer film has been also deeply investigated, but not too much importance has been given to the role of temperature at the contact surfaces and its effect on the characteristics of PTFE composites, probably due to understandable difficulties in experimental measurements. Frictional heating calculations in fact are quite difficult and imperfect because of the lack of knowledge about many of the underlying assumptions [4, 5]. Parameters like normal load and sliding velocity affect the presence of thermal energy from frictional resistance but material properties and friction coefficient are constantly changing, and if we consider that the latter enters the flash temperature computation to the first power, it is clear that its variation cannot be considered negligible, especially during the running-in period [6]. Aim of this work is the interpretation of the tribological behavior of PTFE and PTFE composites in relation to contact temperature and their thermal characteristics, and their structure.

2 Experimental setup and specimens

Friction and wear tests were carried out in the test rig represented in Figure 1 a PTFE sample (1) is mounted on a frame (2) and loaded by an axially sliding rod of CrVNiMo (3) supported and fixed by two holders (4) on which normal constant load \( W \) is applied and transmitted to the axel of the rod. The holders and a couple of screws avoid rotation of the rod around its axel. The system is located in a climate chamber in order to set temperature and humidity percentage. Normal load was set on 50 N for the firsts 30 s and then at 100 N, 60 Hz frequency and 2 mm stroke for each sample. Coefficient of friction (CoF) was recorded at regime condition for 30 minutes; each test was repeated 2–3 times.

Figure 1: Test rig configuration: PTFE sample (1), frame (2), sliding rod (3), holders (4). Normal load is set on 50 N for the firsts 30 s and then at 100 N.
Taking the virgin PTFE as reference, three commercial PTFE composites were tested in sliding contact against a CrVNiMo rod (Table 1). According to the provider’s communications, the PTFE samples come from a process of compression molding of the PTFE and filler powder mixtures, and subsequently sinterization and cooling. The PTFE dispersion has a median particle size of 0.25 μm; average carbon particle diameter is about 10-25 μm; average bronze particle size is about 25 μm; glass fibers are about 5 μm diameter and 90-120 μm length.

Table 1: Thermal characteristics of the samples.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Thermal conductivity K (W/mK)</th>
<th>Thermal diffusivity χ (m²/s)</th>
<th>Melting Temp. T_m (°C)</th>
<th>Heat of fusion (J/g)</th>
<th>Δm (mg)</th>
<th>E (MJ)</th>
<th>E_w (MJ/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 PTFE Virgin (REF)</td>
<td>0.24</td>
<td>9.24e⁻⁸</td>
<td>330</td>
<td>27.80</td>
<td>5.3</td>
<td>9.0</td>
<td>1.7</td>
</tr>
<tr>
<td>2 PTFE +25 wt% Carbon</td>
<td>0.45</td>
<td>2.04e⁻⁷</td>
<td>330</td>
<td>19.09</td>
<td>0.4</td>
<td>10.5</td>
<td>26.4</td>
</tr>
<tr>
<td>3 PTFE +60 wt% Bronze</td>
<td>0.46</td>
<td>1.86e⁻⁷</td>
<td>329</td>
<td>11.73</td>
<td>1.1</td>
<td>14.2</td>
<td>12.9</td>
</tr>
<tr>
<td>4 PTFE +25 wt% Glass fibers</td>
<td>0.44</td>
<td>1.88e⁻⁷</td>
<td>331</td>
<td>18.91</td>
<td>0.7</td>
<td>9.9</td>
<td>14.2</td>
</tr>
</tbody>
</table>

PTFE composites with Carbon, Bronze and Glass fibers fillers were chosen in order to evaluate the effect of their presence and their different ways of acting.

Optical microscopy was used for investigating the worn surface. Differential Scanning Calorimetry (DSC) was used to study the thermal transition of polymers and to evaluate the crystallinity of the semi-crystalline materials. The dimension of the crystals depends on the mobility of the polymeric chains, easier at higher temperatures, and is influenced by the content of fillers and their nature. The thermal traces in Figure 2: 2 can be interpreted beginning with the concept of the heat of fusion: the ratio between the total heat input, that is, the area between the melting peak and the linear extrapolation of the curve after the glass transition, and the mass of the sample. It represents the amount of heat absorbed per unit mass of the material during melting. The thermal traces in Figure 2 show no additional reaction between the filler materials and the matrix and no variation in the position of the transition-melting peak. On the other hand,
the heat of fusion of the bulk PTFE polymer is significantly greater than that of the bulk composites. This indicates a higher thermal stability for the pure polymer even if great importance has to be given to the slope of the samples 1), 2) and 3) between the glass transition phase and the starting of the melting transition phase (approximately between 30 and 290°C) and corresponding to a reduction of the supplied heat flow. After glass transition, in fact, polymers have high mobility increasing their temperature up to creating ordered dispositions called crystals and subsequently they release heat. Observing the behavior of the PTFE composite 4), it seems that glass fibers constrain the polymer chains more than carbon and bronze particles probably due to their bigger size and content in wt%, inducing a higher level of stability.

![Thermal transition of PTFE samples](image)

Figure 2: Thermal transition of PTFE samples and corresponding melting temperatures. Integration lines come from linear extrapolation from the end of the glass transition.

From the tribological point of view, sliding contact of two materials results in heat generation at the asperities and consequently in increments of temperature at the interface. It means that the wear resistance of the material to adhesion depends upon the ability of the material to maintain its integrity at the resultant temperature due to the heat generated by friction and the way this heat is dissipated. Thus, fillers material characteristics like thermal conductivity and thermal diffusivity have a significant effect on the tribological properties of the PTFE composites.

It should not show that the only way to crystallize is due to temperature, but that these kinds of materials show great propensity to crystallize under stretched conditions whereas they crystallize slowly under quiescent conditions.
3 Tribological tests and frictional heating calculations

When a surface contact experiences frictional heating an unsteady situation ensues because the temperature rise is a function of time and position. The transient behavior is determined by the geometry of the thermal source, the thermal properties of the materials and relative velocity. In the case under study, which is the conductivity and diffusivity of the rod much higher than the corresponding properties of the polymers, starting from the flash temperature rise calculation illustrated in [6], the following assumptions were taken: a linear contact area as thermal source; a steady state conductive heating thanks to the short stroke of the sliding movement in comparison with the contact length. The latter assumption permits to avoid the calculation of the Peclet number [6], parameter highly affected by the heat capacity variation of the polymer over temperature. Considering the work done by the friction force Q over the time as following:

\[ Q(t) = \mu(t) \cdot W \cdot v \]  

(1)

where \( \mu \) is the coefficient of friction, \( W \) the normal load and \( v \) the sliding velocity, the contact temperature can then be described also as function of time by:

\[ T_{fmax}(t) = \frac{2 \cdot Q(t)}{K \cdot A} \cdot \sqrt{\frac{2 \cdot \chi \cdot b}{\pi \cdot v}} \]  

(2)

where \( K \) is the thermal conductivity, \( \chi \) the thermal diffusivity, \( A \) the contact surface and \( 2b \) the contact width. The contact area considered for calculations in Equ. (2) is the cylindrical sector of the contact zone at the end of the test, which is not reliable to measure or to hypothesize its evolution over the time: it means that the calculated temperature was underestimated. In the case under study, the differences observed between the contact areas of the samples were so small that their variation did not affect the calculation and the value was approximately 9 mm².

Equations (1) and (2), thus, describe the progressive evolution of the work done by the friction force and the temperature evolution at the contact. In Figure 3, coefficient of friction and temperature are plotted over time: the curves are the same excepting the multiplication by the geometrical dimensions of the contact and the thermal characteristics of the materials. The importance of taking into account the effect of the fillers from the structural and thermal point of view becomes clear looking at the coefficient of friction of virgin PTFE and its maximum contact temperature (Figure 3a)) if thermal conductivity is half with respect to the PTFE composites, thermal diffusivity is an order of magnitude lower delaying the cooling of the polymer and resulting with increment of temperature.

Considering the thermal transition curves of PTFE composites in Figure 2 it is possible to see how the composites n. 1, 2 and 3 can be affected by the heat flux.
generated at the contact, as previously explained, it means that small crystals are formed in that range of temperature, that is, less stable crystals start wear processes. Presence of high wt% of bronze (composite n. 4) avoids the formation of bigger crystals (more stable) so wear resistance results are significantly affected.

![Figure 3: Coefficient of friction and calculated contact temperature evolution of the PTFE samples.](image)

1) Virgin PTFE
2) PTFE + 25 wt% Carbon
The energy that is transformed as a consequence of frictional contact can be dissipated (conversion to heat, vibration, material deformation, new surface creation) or stored into the tribosystem. Therefore, materials exhibiting the same friction coefficient can have different wear rates because the energy is partitioned differently between and within the materials. Both friction coefficient
and wear rate are needed for a good understanding of the test. Specific wear energy is a criterion, which takes both into account: it is the ratio of the friction work spent in the interface divided by the mass loss due to the wear:

\[ E_w = \frac{E}{\Delta m} = \frac{\nu \cdot W \cdot \int_{t_i}^{t_f} \mu(t) \cdot dt}{\Delta m} \]  

(3)

where \( E \) is the energy dissipated by friction, \( \nu \) is the mean relative sliding velocity, \( W \) is the normal load, \( \mu \) is the coefficient of friction, \( t_i \) the initial time, \( t_f \) the time at the end of the test, and \( \Delta m \) is the total mass loss.

In Figure 4 frictional energy vs. mass loss is shown in order to identify the best combination of low frictional energy, that is, low friction, and less mass loss, which is, low wear. PTFE composites 2) and 4) correspond to these criteria and present also the highest values of wear resistance.

Figure 4: Specific wear energy \( E_w \).

For the composites n. 1, 2 and 3, the small crystals formed at lower temperature are destroyed resulting in flakes separation being less stable: in fact, calculated contact temperature is around 60-80°C. PTFE fails along weak intermolecular bonds due to the minor temperature rise which involves slippage of crystalline formations of the bond structure. In other words, temperature rise is quite relevant as consequence of low thermal conductivity and the energy dissipated when the carbon-to-fluorine bonds, which have high bond dissociation energy, are broken.

In Figure 5 the worn surfaces of PTFE composites can be observed. As expected, the virgin PTFE (a) shows plucked marks due to the transfer film formation and subsequent adhesion, encouraged by temperature rise at the
running in stage. The smallness of the black carbon dispersed particles in the PTFE composite 2 (b), avoid abrasion of the countersurface due to their self lubricating properties. Bronze hard particle (c) and glass fibers (d) act removing the transfer film and abrading the hard countersurface.

Figure 5: Worn surfaces of a) Virgin PTFE, b) PTFE+25 wt% Carbon, c) PTFE+60 wt% Bronze, d) PTFE+25 wt% Glass Fibers.
4 Conclusions

The strengthening of the bulk PTFE is well known to be affected by the presence of fillers. On the other hand, tribological characteristics of various PTFE composites are affected by their thermal properties and their structure. Modelling of the heat flow generated by friction force permits the following considerations:

1. The presence of fillers increase the stability of the structure improving the wear resistance;
2. The increment in thermal conductivity and diffusivity improves wear resistance of the material to adhesion;
3. Bronze and glass fibers fillers can reduce the wear mass loss of PTFE under dry conditions significantly but their big size can affect the countersurface and the transfer film;
4. Carbon filled PTFE has good combination of thermal characteristics and structure due to the small size of carbon particles.

References