Tribological behaviour of epoxy based composites for rapid tooling

Pedro V. Vasconcelos a, F. Jorge Lino b, *, António M. Baptista b, Rui J.L. Neto c

a Departamento de Ciências da Engenharia, ESTG/IPVC, Viana do Castelo, Portugal
b Faculdade de Engenharia da Universidade do Porto, DEMEGI, Rua Dr. Roberto Frias, 4200-465 Porto, Portugal
c INEGI—Instituto de Engenharia Mecânica e Gestão Industrial, Porto, Portugal

Received 2 March 2004; received in revised form 1 November 2004; accepted 23 December 2004
Available online 19 February 2005

Abstract

Epoxy resin composites are frequently applied in moulds manufactured with rapid tooling technologies that are used for wax and polymer materials injection. With the propose of enlarging the application field of the polymer matrix systems, it is fundamental to select adequate dispersed phases and analyse their influence on the composite properties in order to reinforce the polymer matrix and tailor the properties according to the tools specifications.

Thermal conductivity and wear resistance are critical parameters for a good service performance and durability of the mould. Metallic fillers allow significant improvement in the resin thermal conductivity. In this work, it was possible to show that small amounts of milled fibres enhance the wear resistance, with little changes in the processability and in the allowed aluminium concentration in the resin matrix.

A tribological study of these materials was performed involving the neat resin, the aluminium filled resin and tri-phase composites composed by epoxy, aluminium particles and milled glass or carbon fibres. The study was focused on the role of the particles and fibres in the friction and wear at room temperature and at a typical plastic injection temperature of 160 °C.

© 2005 Elsevier B.V. All rights reserved.

Keywords: Epoxy resins; Composites; Wear; Milled fibres; Rapid tooling

1. Introduction

Liquid epoxy resins exhibit a good mixture and processing ability with reinforcement materials in granular or fibre form. The result of these mixtures is composite materials with intermediate properties depending, however, on the combined action of the components.

In rapid prototyping (RP) and rapid tooling (RT) applications, metallic filled resins are frequently employed in mould manufacturing for production of small series of plastic parts [1–4].

The injection of fibre reinforced thermoplastic polymers is in a process of great expansion. Moulds manufactured with metallic filled polymers [5–7] exhibit limited durability, due to the extensive wear to which they are submitted during the filling injection stage of abrasive thermoplastic polymers, making their use in this application not very attractive.

In this context, a detailed study was conducted to analyse the tribological behaviour of these composites, aiming to understand the effect of the particle and fibre addition on the epoxy matrix and, consequently, tailor the moulds properties to increase the total number of parts that can be injected.

2. Materials and experimental work

Epoxy resin based composites containing aluminium and milled carbon or glass fibres, with the compositions shown in Table 1, were used. The epoxy resin (E) was a commercial tetraepoxide grade based in an aromatic glycidyl amine, Araldite LY5210 (Vantico, UK) with a high molecular weight [8–10]. The epoxy resin/curing agent, aluminium powder (A-98.7% Al) and fibres (C: carbon fibres; G: glass fibres) were manually mixed and cured at room temperature for 48 h.
Table 1

<table>
<thead>
<tr>
<th>Designation</th>
<th>E</th>
<th>E + A</th>
<th>E + A + C</th>
<th>E + A + G</th>
</tr>
</thead>
<tbody>
<tr>
<td>Composition (%)</td>
<td>100</td>
<td>59</td>
<td>57.5</td>
<td>57.5</td>
</tr>
</tbody>
</table>
| E: epoxy; A: aluminium; C: carbon fibres and G: glass fibres.

Fig. 1. Polished surfaces of epoxy resins filled (grey colour) with: (a) aluminium (white particles) and milled glass fibre (dark filaments) – EAG composite; and (b) aluminium (white particles) and milled carbon fibres (white filaments) — EAC composite.

Table 2

<table>
<thead>
<tr>
<th>Dispersed phase</th>
<th>Manufacturer</th>
<th>Dimensions</th>
<th>Size</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aluminium powder PD 200</td>
<td>Hexcel (France)</td>
<td>99% &lt; 200 μm</td>
<td>–</td>
</tr>
<tr>
<td>Milled E-glass</td>
<td>PPG (USA)</td>
<td>215/11 μm</td>
<td>Polyvinyl acetate with silane</td>
</tr>
<tr>
<td>Milled carbon</td>
<td>Toray (Japan)</td>
<td>63/7 μm</td>
<td>1 wt% epoxy</td>
</tr>
</tbody>
</table>

* l/d: fibre length/diameter

Table 3

<table>
<thead>
<tr>
<th>Materials</th>
<th>Hardness</th>
<th>Elastic modulus (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>E</td>
<td>40 (Barcol)</td>
<td>2.7</td>
</tr>
<tr>
<td>A</td>
<td>58 (Barcol)</td>
<td>69</td>
</tr>
<tr>
<td>C</td>
<td>6 (Mohs) [12]</td>
<td>232</td>
</tr>
<tr>
<td>G</td>
<td>6.5 (Mohs) [12]</td>
<td>72.5</td>
</tr>
<tr>
<td>EA</td>
<td>53 (Barcol)</td>
<td>7</td>
</tr>
<tr>
<td>EAC</td>
<td>53 (Barcol)</td>
<td>7.3</td>
</tr>
<tr>
<td>EAG</td>
<td>53 (Barcol)</td>
<td>7.3</td>
</tr>
</tbody>
</table>

E: epoxy; A: aluminium; C: carbon fibres and G: glass fibres.

and at 40 °C for 14 h, and post-cured at 200 °C for 1.5 h. Fig. 1 shows micrographs of the polished surfaces of the tri-phase composites after this heat treatment cycle. Aluminium is seen as light grey round particles and glass and carbon fibres as elongated filaments in a grey epoxy matrix.

The technical and mechanical characteristics of the raw materials and respective composites are presented in Tables 2 and 3 [11,12].

Considering that it is difficult to simulate the erosive wear mechanisms present in an injection mould, two accessible tests were employed, which although not reproducing exactly the mould operation conditions, allow the assessment of the wear resistance and the integrity of these composites, both at room temperature and at a typical thermoplastics injection temperature of 160 °C [13]. A comparative study, between the results obtained with these conventional tests and the ones using an industrial injection-moulding machine, will be the subject of other publication.

For an extensive wear characterization, two wear tests were performed with different typologies and experimental conditions (see Fig. 2):

![Schematic diagram of the wear tests that were employed](image)
reciprocating tribometer (reciprocating wear type) [14] and metallographic polishing microabrasion (abrasive wear type) [15,16].

2.1. Reciprocating wear

In the reciprocating test, a flat surface of the sample is abraded against a steel sphere, involving sliding friction and wear at high pressure, giving information of the material integrity level. This tribological configuration decreases the tendency for the topography modification effect caused by polymer transfer, keeping the contact nature of the steel–polymer interface almost unchanged during the whole test. To determine the influence of the temperature on the friction and wear behaviour (dry conditions), a reciprocating tribometer, Cameron Plint TE67 (Budenberg, UK) was used. The following test conditions were established:

- pin—polished steel sphere (DIN-105Cr6) with 9.5 mm diameter;
- specimen—rectangular plate (dimensions: 60 mm × 40 mm × 5 mm);
- force = 25.4 N (pressure ≈ 25 MPa);
- amplitude motion = 10 mm;
- maximum linear velocity = 0.13 m/s;
- sliding distance = 82 m.

Three samples were used for each material and temperature (room temperature and 160 °C). Due to the presence of defects, such as scratches and cavities that can significantly influence the test results, the sample surfaces were polished with a P1200 SiC paper.

The volume of the material removed during the wear test was determined by contact profilometry (Hommel Werke LN-50, Hommel Werke-Thuissen, Germany). This volume was computed by multiplying the medium area of three wear track sections by the respective track length. For comparison analysis, the parameters of the test conditions of the two wear tests are indicated in Table 4.

The worn surfaces of the specimens were examined in a scanning electron microscope (Jeol JSM-6301F, USA) and the chemical X-rays spectra (SEM/EDS) obtained.

The reciprocating test allowed the determination of the wear coefficient evolution relatively to the sliding distance and the effect of the temperature on the tribological behaviour of the different composite materials, considering the neat resin as a reference. It was possible to apply a significantly higher pressure in dry conditions, which also allowed the material integrity evaluation under severe conditions. This severe wear is due to the existence of a mixed abrasive/adhesive contact condition [17,18].

2.2. Abrasive wear

This test was employed to determine the materials specific wear rate at room temperature and was only used to complement the information given by the reciprocating test. In each wear cycle of the metallographic polishing microabrasion test, three rectangular prismatic samples were simultaneously abraded against a SiC paper to assess the abrasive wear resistance. The samples were cut in rectangular prisms of 30 mm length with a square section of 10 mm. Prior to the test, the specimens were polished with a P1200 SiC paper and weighed before being mounted into the specimen holder. The three specimens were separated from each other in the holder by 120°. The wear apparatus was a semi-automatic grinding–polishing machine (Planopoli-3, Struers, Denmark), where a constant load of 60 N was applied for 2 min. The mean velocity of the specimens, mounted into the sample holder, relatively to the abrasive disk (P320 SiC paper), was 202.5 m/min. Water was used as lubricant with a constant 250 ml/min delivering rate. The sample holder and the disk rotate off-axis, which allows the samples to sweep a wide working area, keeping the wear rate practically unchanged during the test [14].

The mass loss was measured weighing the specimen before and after the test and the specific wear rate, \( W_s \), was calculated by [19]:

\[
W_s = \frac{\Delta m}{l \rho F}
\]

where \( \Delta m \) is the mass loss, \( l \) the sliding distance, \( \rho \) the density of the specimen and \( F \) is the normal load.

Six wear cycles were performed with each material.

3. Results and discussion

3.1. Reciprocating wear

3.1.1. Friction behaviour

Initially, at room temperature (see Fig. 3a), the neat epoxy resin exhibits a constant friction coefficient, \( \mu \), of about 0.16. Nevertheless, after about 30 m of sliding distance, \( \mu \) begins to increase at a slow rate. This behaviour is probably due to the thermal softening of the resin, as a result of the pressure and heat generated on the reduced contact area. Increasing the sliding distance, the sphere penetrates more deeply into the
epoxy surface, increasing the ploughing deformation zone and the real contact area and consequently raising the frictional force [19].

When the temperature rises to 160 °C, the neat resin behaviour is significantly affected. The initial friction coefficient increases abruptly, and after about 20 m stabilizes to a magnitude of about 0.65. After this period, the curve tends to reach a steady state. At this high temperature, the thermally affected resin layer increases rapidly producing a larger real contact area and high friction coefficients. The short-term fluctuations that are present at room temperature are similar at high temperature.

The addition of aluminium particles to the epoxy system improves the material stiffness and thermal conductivity by one order of magnitude [11,20]. The better thermal conductivity contributes to a more efficient dissipation of the heat generated on the contact area. Due to the presence of aluminium, the friction coefficient (µ) exhibits initial peaks for µ = 0.5. The initial stage is characterised by a high friction coefficient (tending to decrease with the distance) and irregular fluctuations, showing an unstable frictional behaviour (Fig. 3b). After 20 m of sliding distance, a steady state is reached.

At 160 °C, the behaviour is similar, but a slight increase in µ was detected after 20 m of sliding distance.

The incorporation of glass or carbon fibres to the previous material keeps the friction coefficient practically unchanged (Fig. 3c and d). At room temperature, the initial highly unstable frictional behaviour disappears after a short sliding distance. Both glass and carbon composites show similar friction behaviour with a slightly higher friction coefficient observed in the glass fibre composite. At 160 °C, the initial peak and the respective instability are also detected and a slightly higher steady state friction coefficient. At the end of the wear test, this value increases by 12% in EAC composites and about 9% in EAG composites, relatively to the similar material at room temperature.

3.1.2. Wear and topography of worn surfaces (reciprocating tribometer)

Compared with the composites, the neat resin specific wear rate is reduced, showing that the friction energy is dissipated in the deformation and in the heating up of the ploughing zone (Table 5). The spectra of characteristic X-rays (EDS) of the worn surfaces shows the presence of a significant iron concentration that is visible in the SEM images as a light grey region (Fig. 4). The steel sphere suffers wear and incorporates iron particles in the interfacial layer. Due to the test conditions, these iron particles are certainly oxidised. SEM image shows multiple parallel microcracks, approximately perpendicular to the sliding direction (vertical direction), indicating the presence of a fatigue mechanism (Fig. 4a) [21]. Table 5 shows that, at 160 °C, the wear rate increases significantly.

The highest wear, 99.8 × 10⁻⁵ mm²/Nm (Table 5), was obtained in aluminium filled epoxy with a large production of debris derived from the particle pullout during the test. This is due to the decrease of the material integrity, where the cohesion now depends basically on the aluminium/resin interface resistance. Wear track micrographs and EDS analysis show an aluminium loss. In the SEM image of Fig. 5a, a large plastic deformation of the aluminium particles is observed in the wear surface, masking the real aluminium loss. The approximately equiaxial aluminium particle geometry and its chemical nature produce a relatively poor adhesion
Table 5

Comparison of the specific wear rate results of epoxy (E), epoxy with aluminium (EA) and epoxy with aluminium and fibres (EAG and EAC) systems, at room temperature and at 160 °C, determined in the reciprocating tribometer

<table>
<thead>
<tr>
<th>Materials</th>
<th>Specific wear rate (10⁻⁵ mm³/Nm)</th>
<th>Percentage increase rate (RT → 160 °C)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Mean value</td>
<td>Standard deviation</td>
</tr>
<tr>
<td>E</td>
<td>1.82</td>
<td>0.22</td>
</tr>
<tr>
<td>EA</td>
<td>15.5</td>
<td>1.66</td>
</tr>
<tr>
<td>EAG</td>
<td>7.39</td>
<td>0.31</td>
</tr>
<tr>
<td>EAC</td>
<td>8.18</td>
<td>0.57</td>
</tr>
</tbody>
</table>

force to the epoxy matrix, as suggested in references [22] and [23]. This fact is responsible for the easy aluminium pull out under the high contact pressure of the pin. Furthermore, the aluminium particles are significantly harder than the epoxy resin (see Table 3), which means that when released from the composite, they can also act as hard third-body abrasives, increasing the composite wear rate [24]. This effect would be enhanced by the probable oxidation of the aluminium into alumina. Fig. 5b shows microcracks that are now concentrated in the particle/resin interface, contributing to the aluminium particles debonding. No iron traces were detected in the composite. Fig. 6 shows that the wear tracks are different in the initial and final stage of the wear test. It is observed that in the initial stage, the surface is more wrinkled, probably due to the severe wear conditions originated by higher aluminium concentration in the wear track.

When the temperature rises to 160 °C, the wear rate increases about 544% for the selected sliding distance (Table 5).

Similarly to what occurred with the abrasive wear test, in the reciprocating test the fibre addition to the aluminium filled epoxy also significantly improves the composite wear resistance. These tri-phase composites show more integrity, despite the low fibres concentrations that were employed.

The high aluminium thermal conductivity and fibre stiffness, combined with the good adhesive bonding between fibres and epoxy resin, substantially enhances the tribological behaviour of the respective composites. EDS analysis of the final wear track reveals loss of aluminium and resin and fibres enrichment relatively to the original material. The combination of these materials significantly improves the wear resistance.

At room temperature, the wear resistance of the carbon and glass fibre composites is very similar, but at 160 °C, the wear rate of the carbon fibre composite experiments a 214% increase, while the glass fibre composite only undergoes a 158% increase (Table 5). These particular changes of the tribological behaviour, due to the thermal effect, can be explained if one considers, as described below, the fibre and matrix properties.

Glass fibres display a homogeneous, amorphous and isotropic microstructure. On the other hand, PAN carbon fibres are composed by a heterogeneous stacking of fine crystalline layers of aromatic type (nanometric width) [25]. This intrinsic heterogeneity originates anisotropic thermal properties, such as thermal conductivity and coefficient of thermal expansion, CTE. The latter varies from −0.6
SEM images of the worn track of the EA composite. The left side shows the track in the initial wear stage (the surface is wrinkled due to the pull out of the aluminium particles), the right side shows the wear track in the final stage of the test. The asperities are now smaller (SE).

SEM images show an extensive carbon fibre fragmentation (Fig. 7). The wear track profile of the EAC composite is more irregular than in the EAG composite, which probably indicates that its surface is prone to suffer more damage and a more severe wear (Fig. 8).

Fig. 9 shows SEM images of the worn track of the EAG composite. In the initial wearing stage, an interface layer with a viscous mixture of resin and fine aluminium debris is observed. At the end of the test, the wear track exhibits lower aluminium content, resulting in higher resin and glass fibre concentrations.

Due to the longer friction action of the composite, the aluminium particles suffer a severe plastic deformation before its removal (Fig. 10). Some fragmented fibres appear stacked to the aluminium particles.

At high temperature, the EAC composites exhibit lower wear resistance than the EAG composites. This can be explained by the fact that carbon fibres are more fragmented, and probably more easily removed from the wear track, than the glass fibres, which are less brittle than carbon fibres [28].

The influence of the temperature on the mechanical behaviour of the epoxy-based materials was examined by dynamic mechanical thermoanalysis (DMTA) (Fig. 11). The results obtained show that, at 160 °C, the neat resin and the aluminium filled epoxy (EA) experiment a remarkable loss in their mechanical properties. The tan δ curve, at 160 °C, demonstrates that the epoxy systems are close to the glass transition temperature, detected at about 200 °C. EAC and EAG composites show DMTA behaviour similar to the EA composites.

The decrease of the matrix modulus with the temperature affects the fibre–matrix interfacial shear strength, as predicted by Cox and Cooke theory [29,30] and experimentally demonstrated by Rao and Drzal [31]. These researchers proved that...
Fig. 7. SEM images of the wear track of the EAC composite at 160°C: (a) the aluminium loss in the wear track (at the left side) is clearly visible (BE) and (b) the wear track shows deformed aluminium particles and fragmented carbon fibres (BE).

Fig. 8. Cross section of the wear track profile of: (a) carbon fibre composite, EAC and (b) glass fibre composite, EAG. The surface topography of the two composites, before and after wearing, is different, despite the same processing, surface finishing and wear conditions.

Fig. 9. SEM images of the worn track of the EAG composite: (a) on the left side, the wear track in the initial stage of the test (an interface layer with resin and fine aluminium debris is produced) and (b) on the right side, the wear track at the end of the test.
the fibre–matrix interfacial shear strength (determined by the fragmentation analysis), decreases nonlinearly with the matrix modulus. Considering this, the modulus decrease at high temperatures produces a softening effect, negatively influencing the matrix and interface properties, and consequently causing the weak tribological performance of all the studied materials.

3.2. Abrasive wear

The SiC particles of the abrasive paper act as multiple microtools that wear the material to be tested. This abrasive wear depends on the hardness of the two contacting materials, cutting properties of the hard particles and microcracking resistance of the softer material [17]. The test was performed at low pressure and water lubricated to avoid vibrations and excessive heating. When compared with the E neat resin, the aluminium addition to the resin yields about 25% decrease in $W_s$, as shown in Fig. 12.

As it was expected [18,32], adding reinforcement elements, like milled carbon and glass fibres (EAC and EAG
4. Concluding remarks

Mixtures of fibres and aluminium particles can be used to optimise mechanical and thermal properties of composites manufactured for rapid tooling applications. These type of tools, although less demanding in terms of technological requirements than the conventional tools, can exhibit an adequate performance in applications where a short number of parts is required, with the enormous advantage of being obtained in a short period of time.

The neat epoxy resin in the reciprocating test exhibits the lowest wear. SEM images show that the main mechanism for energy dissipation is located at the interface layer of the wear track, involving adhesion contact, plastic deformation, microcracking and iron transfer. These mechanisms also contribute to the constant increase of the friction coefficient with the sliding distance.

Due to geometric relations and surface chemistry, the fibres tend to adhere more strongly to the resin matrix than aluminium particles. Submitted to the high pressure of the pin, the aluminium particles are easily removed, while the fibres, staying longer in the tri-phase composite, increase considerably the load carrying capacity, reducing the friction coefficient, and consequently the composite wear rate.

High temperatures affect the mechanical properties of the composite, due to resin softening and reduction of the particle and fibre/matrix adhesion.

In the reciprocating test, EAG glass reinforced composites show lower wear rate than the EAC carbon reinforced composites, and a better tribological behaviour, especially at high temperature (160°C). Besides the high stiffness of the carbon fibres, their brittle nature makes them more prone to break under severe wear conditions than the glass fibres.

Considering the hardness and stiffness of the raw materials used in the composites, they can be sorted, from the lowest to the highest wear resistance between the reinforcing dispersed phase and the matrix.

Acknowledgements

Financial support from FEDER through the Project POCTI/EME/41199/2001, “Development of an Indirect Rapid Tooling Process Based in Polymeric Matrix Composites”, approved by the Fundaçãopara a Ciência e Tecnologia (FCT) and POCTI.


References