Cold, clean and green: improving the efficiency and environmental impact of a cryogenic expander

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Abstract.

The Dearman Engine is a cryogenic expander, utilised in the case of combined power and cooling, currently applied in truck refrigeration units. As the temperatures involved ($\sim 30^{{\circ}}$C) are significantly lower than those experienced in an internal combustion engine, there is scope for material replacement. These operating conditions open up the opportunity to employ polymers and exploit their tribological properties. A composite is often used to combine preferable properties of each material. It has been hypothesised that a composite could be replaced by a cheaper alternative: a laminate. Five materials were tested for friction and wear: PEEK, PTFE, PTFE-PTFE laminate, PEEK-PTFE composite and PEEK-PTFE laminate. The surfaces were also examined under an SEM/EDS post test in order to determine any defects and to detect any transfer layers. The results showed that the friction and wear for the PTFE-PTFE laminate were similar to that of pure PTFE and so the bonding of the material had no impact on the overall result. This was also the case in the PEEK-PTFE composite and laminate. The major difference was the presence of a transfer layer in the PEEK-PTFE laminate that was not present in the composite. These results suggest that lamination is a suitable alternative that warrants further investigation.

1. Introduction

With increasing restrictions on emissions and consumer awareness of environmental impact, there is a strong drive to reduce carbon footprint. One of the largest contributors to inner city pollution is refrigeration of food in the back of lorries destined for supermarkets [1]. This is an application where a combination of power and cooling is required.

Liquid nitrogen is a waste product produced by various industries and with its high thermal expansion index during the boiling process, could have many potential applications. The Dearman truck refrigeration unit (TRU) provides clean power and cooling powered by this waste resource. The TRU consists of a single piston engine connected to a vapour compression refrigeration unit. The engine piston is driven by either liquid nitrogen or liquid air, which expands 710 times when transitioning from liquid to gas [2]. The use of a heat exchanger fluid significantly increases thermal efficiency without the need for re-heating [3].

Polymers are rarely used in typical combustion engines due to the high temperatures involved [4] meaning that their weight and power saving advantages can not be exploited. However, the much lower operating temperatures of the Dearman engine ($\sim 30^{{\circ}}$C) mean that this technology
has many potential applications and one key material of interest is poly-ether-ether-ketone (PEEK) [5].

One of the major benefits of using polymers is the ability to combine two polymers to utilise the beneficial properties of the materials used [6]. Traditionally a stiff polymer is used in combination with a lubricious polymer in order to provide a component that is durable and reduces the coefficient of friction [7]. This combination tends to be produced by embedding the softer polymer into a stiffer matrix material. These tend to be more expensive compared to unreinforced polymers and the interfacial boundary between materials can adversely affect mechanical properties.

PTFE-PEEK composites have been investigated in a variety of different ratios. However when the PTFE percentage is larger than that of the PEEK, they do not perform favourably an undesirable phenomenon known as grooving occurs [6]. The tribological film produced during grooving also has a lower thickness resulting in lower lubricity.

Although composites are widely used to obtain properties of multiple materials, there is some evidence to suggest that using laminated materials can provide comparable friction with composites. Qi et al. investigated the tribological performance at elevated temperatures using a pin on laminated aluminium oxide with molybdenum, the friction was 60% lower than the monolithic material [8]. However, at ambient temperature the AlO$_3$/Mo composite gave better results than the laminate.

This paper aims to investigate the impact of laminated PTFE with PEEK to determine if its tribological performance is better than that of a composite of the same PTFE-to-PEEK ratio.

2. Materials and Methods

Five different material combinations were tested: PEEK, PTFE, PTFE-PTFE Laminate (PTFE L), 20% PTFE - PEEK Laminate (PTFE-PEEK L) and 20% PTFE - PEEK Composite (PTFE-PEEK C). All the materials were sourced from Direct Plastics (UK) other than the PTFE-PEEK C which was supplied by Solvay (Atlanta, Georgia, USA). These were machined to the dimensions as shown in Figure 1. Where the materials have been bonded for testing, the surfaces were initially primed with a polyolefin primer (Loctite 770) and then bonded with ethyl-cyanoacrylate (Loctite 496). PTFE-PTFE L was tested to investigate the effect of the bonding process on the sample. In order to ensure the samples were flat they were polished with an abrasive paper before they were run.

The samples were tested on a TE77 Reciprocating Tribometer (Phoenix Tribology, Hampshire, UK) in order to measure the friction and to generate wear. A bespoke upper specimen holder was produced for the rig to clamp the polymers in place. Table 1 shows the testing parameters used, they were selected to simulate the worst tribological condition in the Dearman Engine, start up. The upper specimens were weighed pre-and post-test in order to quantify wear. The samples were then also examined under a scanning electron microscope (SEM) and analysed using energy dispersive X-ray spectroscopy (EDS).

| Parameter          | Value          |
|--------------------|----------------|
| Test Frequency     | 4 Hz           |
| Stroke Length      | 12 mm          |
| Contact Pressure   | 33 MPa         |
| Test Time          | 1 h            |
| Sliding Distance   | 172.8 m        |
| Temperature        | Ambient        |
| Lubricant          | None           |

Figure 1: A schematic of the PTFE-PEEK laminated samples

Table 1: The test parameters used in this research
3. Results and Discussion

Figure 2 shows the median coefficient of friction as measured by the TE77. It can be seen that the PEEK sample had a significantly higher coefficient of friction than the rest of the samples tested. The rest of the samples had a very similar coefficient of friction and a Mann-Whitney U test showed that there was no significant difference between the four datasets at a 95% confidence interval. This is an exciting result for two major reasons. One is that the pure PTFE sample and the PTFE-PTFE sample having no significant difference suggests that the process of bonding two polymers together has no effect on the coefficient of friction under these conditions. Another interesting result is that a 20% PTFE-PEEK mix produces a coefficient of friction statistically similar to a pure PTFE sample.

Figure 2b shows the logarithmic gravimetric wear percentage after 1 h of testing. This graph shows why materials such as PTFE are commonly used as composites as the wear rate for PTFE is significantly higher than any other than the any other of the materials tested. As with the friction, it can be shown that the bonding has no significant effect on the wear. This can be surmised due to the fact that the pure PTFE and bonded PTFE as well as the PTFE PEKK composite and laminate both had no significant difference in their wear rates.

There is a wider spread of data in the PTFE-PEEK L cases, this error may have been caused by inconsistencies in the material preparation. Samples not being perfectly flat or layers being perfectly parallel may cause variation in the friction and wear. These errors are not of major concern as the purpose of the paper is to investigate if the process will worsen the performance which is not the case here.

Figure 3 shows the SEM Images of the polymer upper samples. Subplots a) and b) were sliding vertically and c) was sliding horizontally.
As shown in Figure 3a, PEEK showed very little damage to the surface. There were areas of fatigue and areas of scoring. The scoring was due to the scratching of the stiffer aluminium into the PEEK surface. The areas of fatigue are small in comparison to other samples and after one hour did not appear to produce any pitting within the surface. The composite surface as shown in Figure 3b looks remarkably similar to the bulk of PEEK again scoring and fatigue cracks are seen on the surface. There are areas in which the fatigue cracks have led to a small amount of pitting.

Figure 3c shows an overall view of a laminated upper specimen it can be seen that the surface has been subject to a large number of imperfections. Only one of the bonding lines can be seen clearly as on the other bonding line the PTFE is smeared across the top of the surface. Around the bonding surface, there does not appear to be an increase in the intensity or frequency of the fatigue cracks the scene surface. The bonding line itself does not appear to be damaged and would suggest that the adhesive was suitable for the application and did not fail during testing. Again scoring can be seen on the surface parallel to the direction of reciprocation. It is difficult to separate damage produced during sample preparation and damage ascertained during testing, however, all of the samples were treated in the same manner and so it is possible to compare between samples.

Figure 4a shows a bar chart of the intensity of the F$^-$ ions detected by the EDS on the lower aluminium specimens. The scan was taken in the middle of the wear track where the velocity was highest, shown in Figure 4b. It can be seen the pure PEEK and the PTFE-PEEK-C demonstrated either low or no intensity of F$^-$ ions. This is expected for the PEEK as there is no material present that contains F$^-$. However comparing the PTFE-PEEK-C and PTFE-PEEK-L it can be seen that significantly more PTFE is transferred onto the aluminium from the laminate. This transfer layer has been shown by Dearn et al. to promote a low coefficient of friction and potentially a more stable contact [9]. However, in both a transfer of PTFE occurs. These results would suggest that the hypothesis that laminating makes no difference to the tribological properties of the sample compared to a composite is in part true. Whilst the friction and wear are not effected the mechanism by which the PTFE spreads across the surface appears to be different for the laminate and composite PEEK and PTFE samples. This is difficult to examine but in a composite, PTFE is spread evenly assuming that the composite is homogeneous and therefore the PTFE is supplied to the contact from an evenly distributed source. In the laminate, PTFE is at either end of the sample and so is very easy to identify where the PTFE has come from. As it has been shown that PTFE has a higher wear rate than the PEEK this would suggest that the edges of a laminated sample would wear quicker than the centre. One solution to this is to reduce the contact pressure incident on the PTFE by reducing the thickness of the laminates and increasing number of laminated layers.

4. Conclusion

This paper described a study, aiming to ascertain whether combining the polymers in a laminated material would produce similar tribological properties to composite polymers. A 20% PEEK PTFE composite under the conditions tested demonstrated a wear resistance consistent with PEEK and a coefficient of friction consistent with PTFE. It was shown that bonding PTFE together changes neither the friction or wear properties of the material.

Most significantly it was also shown that a 20% PTFE PEEK laminate produced statistically similar results to the equivalent composite. A comparison of the surfaces demonstrated that smearing of the PTFE across the surface occurred in the laminate material. This is important as a PTFE layer will reduce the coefficient of friction. Similar levels of fatigue cracking and scoring occurred between the composite and the laminate.

The PTFE encompassed within the laminate may have worn at a higher rate than the PEEK due to it being located on the leading edges of the samples. However, increasing the number of
PEEK, PTFE, PTFE-PTFE L, PTFE-PEEK C, PTFE-PEEK L

| Material     | Intensity of F⁻ Ions (%) |
|--------------|--------------------------|
| PEEK         | 0                        |
| PTFE         | 0.2                      |
| PTFE-PTFE L  | 0.4                      |
| PTFE-PEEK C  | 0.6                      |
| PTFE-PEEK L  | 0.6                      |

(a) A bar chart of the intensity of F⁻ ions as detected by the EDS for each material

(b) A schematic of the position of the EDS analysis

Figure 4: The EDS Analysis of the Aluminium Samples

Laminating layers would reduce the contact pressure in these areas.

In conclusion, the presence of a stiff component and a lubricious component within a specimen is more significant than whether the PTFE is evenly distributed across the surface or not. This leads to the conclusion that it is possible to use lamination as an alternative to composite materials.

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