November 2015

FAKUMA: OUR PICK OF THE SHOW
DEVELOPMENTS IN CARBON BLACK
ADDITIVES FOR WEAR RESISTANCE
INNOVATIVE MIXER TECHNOLOGIES
Surface modification | additives

Whether to reduce long term wear or to ease one-off activation, tribological modification of plastics is an increasing demand. Jennifer Markarian reviews the latest additive and compound developments.

Formulating to reduce friction and wear

Wherever moving parts come into contact, friction and wear can be a concern. Polymeric materials used in applications such as gears, bearings, conveyors and seals must resist wear, sometimes under high temperatures and pressures, for extended service periods. And the trend toward lighter-weight and thinner parts only intensifies this need for improved management of wear. But surface properties are not only a concern in long term applications. Wear many not be an issue in short-term or single-use applications such as medical devices, but low surface frictional properties can be vital.

A wide variety of polymers are used in wear applications today. While certain polymers display inherently better tribological properties than others (see Table 1 on page 42), lubricating additives also play a significant role in differentiating compounds and in enhancing compounds for specific application needs.

There are certain key basics to take into account when designing a part where tribological properties (wear and friction) are a concern. These include consideration of the two materials that will be in contact, the surface roughness of the parts, the usage parameters (continuous or intermittent, sliding speed, contact pressure), ambient conditions (temperature and humidity), and other application-related factors (such as whether foreign debris will be present and whether external lubricants will be used), explains Cliff Watkins, marketing director at distributor PolySource.

The most demanding applications are those with the highest pressure-velocity (PV) load, which is a measure of the contact pressure multiplied by the sliding speed. Frictional heat generated during use can be a concern that must be managed, says Watkins. High friction can also cause energy losses, so a low coefficient of friction is desired for applications such as bearings or gear wheels.

Common anti-friction additives that are compounded into a polymer to act as internal lubricants include those that act immediately by migrating to the surface (such as perfluoropolyether [PFPE] synthetic oil and silicone) and those that are distributed throughout the polymer and begin to lubricate when they are exposed after a "wear in" period, such as polytetrafluoroethylene (PTFE), fibres (aramid, carbon, and glass, for example), and other solid additives (such as molybdenum disulfide and graphite powder). RTP Company also offers its all-polymeric wear additive (APWA), which is an
olefin-based additive designed for immediate lubrication and for improved wear resistance compared to particulate-based alternatives and that does not exhibit the plateau associated with PTFE, according to the company.

Laurel Products, headquartered in Pennsylvania in the US, specialises in fluoropolymer additives to enhance wear performance, friction, and other properties. The company’s fluorinated mica additive, Thor-FPz, imparts both the properties of a mica (hardness and abrasion resistance) and of a fluoropolymer (low coefficient of friction, low surface energy). The additive has been used in various engineering polymer matrices (for example, PTFE, PA, and POM) in applications including gears, ball-valve seats, and slide pads. “Laurel has quadrupled its production and sales of this unique additive since it was commercialised in 2014, and wear-reducing applications and opportunities continue to emerge in the compounding marketplace,” says James Downing, business director at Laurel.

Laurel’s Marzon fluoroadditives are said to be specially processed to improve specific properties, including a heat-treatment to improve thermal stability, thermal-vibratory processing to improve particle morphology and flowability, and the addition of hydrophilic molecules to optimise polarity and dispersability. The company’s latest addition is Marzon 638, a polysiloxane-infused PTFE additive that is claimed to feature silicone/fluoropolymer chemistry within each discrete particle that provides both chemical and mechanical benefits.

Solvay Specialty Polymers produces PTFE micronised powders [Polymist and Algoflon L] and PFPE fluids [Fomblin, Fluorolink, and Galden]. “PTFE leverages the hydrophobicity and low surface tension of the material to impart enhanced tribological properties to the matrix,” says David Gibala, global business development manager at the company. The powder additive can be compounded directly or using a masterbatch of up to 40% to produce formulated compounds, which typically contain 10-20% PTFE, in a range of engineering and high-performance polymers. Special grades of micronised PTFE are optimised to withstand the high temperatures needed to compound PEEK and other high-melting specialty polymers. The company says PTFE does not migrate from the polymer, and its lubricating effect is most efficient following a short “wear in” period.

PFPE fluids, on the other hand, are used at low levels (less than 1%) and bloom quickly to form a thin lubricating layer at the surface. Solvay’s fully fluorinated material can be compounded at temperatures up to 280°C. The company also offers PFPE with hydrogenated end groups that allow better compatibility in the matrix. The polarity of the end groups can be designed to modulate blooming rate for a specific matrix, according to Antonio Puppo, technical marketing for functional fluids at Solvay Specialty Polymers. These grades have a maximum compounding temperature of 250°C. PFPE oils should be added to the compounding process as a masterbatch, suggests Puppo.

Colloids, a UK masterbatch producer that opened a manufacturing facility in Chanshu in China in May of this year, offers high-end, friction-modifying masterbatches for engineering resins under the brandname PACE. “Graphite is the preferred type of low-friction additive in aqueous applications, whereas molybdenum disulphide is the material of choice where the component parts are in contact with metal surfaces,” says Bob Thomas, technical director at the company. The company also produces a range of low-friction masterbatches containing silicone oil, erucamide or oleamide fatty acids. Silicone oil offers high temperature resistance making it suitable for use in engineering polymers. Erucamide and oleamide are only suitable for polyolefin applications.

“Choosing the correct additives and the correct level

Table 1: Typical polymers used in wear-resistant applications

<table>
<thead>
<tr>
<th>High-performance [higher temperature resistant] polymers:</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polyetheretherketone (PEEK)</td>
</tr>
<tr>
<td>Polyphenylene sulfide (PPS)</td>
</tr>
<tr>
<td>Polyphthalamide [PPA]</td>
</tr>
<tr>
<td>Polyethersulfone (PES)</td>
</tr>
<tr>
<td>Polyimide [PI]</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Technical or engineering polymers:</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polyketone (PK)</td>
</tr>
<tr>
<td>Polyamide (PA)</td>
</tr>
<tr>
<td>Acetal or Polyoxymethylene (POM)</td>
</tr>
</tbody>
</table>

Table 2: Tribological test results of PC versus POM

Source: RTP Company
is highly dependent on the application requirements,” according to Thomas Collet, global product manager at Lehmann&Voss&Co. For example, aramid fibres, although more expensive than carbon or glass fibres, provide high wear resistance and reinforcement and are softer than carbon or glass, so they are better for contact with soft metals such as aluminum. Various tribological tests (including the pin on disk, pin on roll and thrust washer test) can be used to evaluate formulations. Customer-specific testing that simulates an application’s temperatures and speeds, for example, is also crucial.

**Measuring friction**

Recent research at RTP Company yields new insight into friction behavior, which is important for choosing materials for contact parts. Although initial studies were designed for single-use medical device applications, the concept can be applied to any other friction applications, says Josh Blackmore, global healthcare manager at the company, and tribological engineer Ben Gerjets.

Common friction-related problems include high “start up” force (which makes it difficult to initiate movement of a plunger through a barrel, for instance) and “stick-slip” or “stiction,” where a material will start to slide but will “stick” rather than a consequence of stick-slip occurring at a fast rate. External lubricants may solve these problems, but manufacturers (especially in the medical sector) prefer to avoid wipe or spray-on lubricants for many reasons, not the least for friction can present particular challenges in syringe production, contributing to high injection force requirements and preventing smooth operation.

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the difficulty in applying and controlling these products, explains Blackmore. Part designers would instead prefer to choose materials, possibly formulated with internal lubricants, that will slide smoothly. Identifying tests that can predict behavior is more efficient than trial-and-error methods.

Key tribology measurements include the static coefficient of friction ($\mu_s$), which describes the force required to initiate motion of one surface past another, and the kinetic coefficient of friction ($\mu_k$), which describes the force needed to sustain motion. RTP developed a new measurement—the “Glide Factor”. It defines this as the difference between $\mu_s$ and $\mu_k$ measured with a modified ASTM D3702 thrust washer test measuring oscillating friction.

The researchers found that pressure or load can dramatically change the Glide Factor. After experimenting with several loads, the studies were performed at 50psi to simulate the force found in a typical drug-delivery device. "Materials with a low $\mu_s$ will slide easily past one another at start-up, and materials with a low Glide Factor are less likely to experience stick-slip. The Glide Factor concept can be used to establish thresholds for performance that will aid formulation development," says Gerjets.

Friction is a complex phenomenon that is affected not only by the materials in contact with each other and the applied force, but also by environmental factors (such as temperature) and use factors (such as human-skin oil on the surface or changes to the material surface over time), says Gerjets. Part designers want to choose a material pair that will work consistently, no matter what the external factors.

“We identified thresholds for both static coefficient of friction and Glide Factor using field data, and we worked with customers to verify our findings. A good formulation will be well below the thresholds so that the parts can tolerate variation in temperature or surface defects without problem,” says Blackmore. For example, a typical medical-device combination of PC-POM without internal lubrication meets the static friction threshold, but not the Glide Factor threshold. When an internal lubricant is added to either material, however, the Glide Factor drops below the threshold. With lubricant in both materials, the Glide Factor is significantly below the threshold. A manufacturer of insulin auto-injector pens, for example, can choose lubricant in both materials to have greater assurance that the device will work well, and could even use this information to redesign the device with a smaller spring, says Blackmore. RTP is also developing correlations of their friction data with other critical factors for medical device design, such as the force needed to start an injection or to inject a drug at the correct rate.

Dealing with wear
While friction is a concern for short-term use, wear is the concern for long-term applications such as gears or seals. Some sealing applications, such as automotive transmission seals, pump seals, and offshore oil and gas gaskets, must resist wear under high temperatures and high pressure and velocity (PV) ratios. RTP

<table>
<thead>
<tr>
<th>Speed</th>
<th>rpm</th>
<th>1,600</th>
<th>1,600</th>
<th>1,600</th>
<th>1,600</th>
<th>1,600</th>
<th>1,600</th>
</tr>
</thead>
<tbody>
<tr>
<td>Torque</td>
<td>Nm</td>
<td>5.5</td>
<td>5.5</td>
<td>5.5</td>
<td>5.5</td>
<td>5.5</td>
<td>5.5</td>
</tr>
<tr>
<td>Loading period</td>
<td>min</td>
<td>91</td>
<td>58</td>
<td>53</td>
<td>72</td>
<td>25</td>
<td>61</td>
</tr>
<tr>
<td>Breakage behaviour</td>
<td>-</td>
<td>Melt at hub</td>
<td>Tooth breakage tip abrasion</td>
<td>Melt at hub</td>
<td>Tooth breakage tip abrasion</td>
<td>Melt at hub</td>
<td></td>
</tr>
</tbody>
</table>

Source: Akro-Plastic
Company’s UltraWear compounds were introduced in 2013 for these extreme applications that have conventionally used thermosets. UltraWear compounds using synergistic wear additives in PEEK, PPA, and PPS have been tested at PV ratios up to 100,000 and temperatures up to 205°C (400°F), says the company.

Additives used in the UltraWear compounds include combinations of carbon fibre/ceramics, carbon fibre/graphite/PTFE, and proprietary packages. Ceramics have been found to provide the best performance in very severe wear environments (high pressures, velocities, and temperatures) and are used synergistically with other additives in RTP’s highest performance selection.

Collet at Lehmann & Voss also notes an increasing demand for materials that function in high pressure and elevated temperature applications. The company, a compounder of high-performance specialty materials, introduced its Luvocom XTF family of high-performance compounds modified with a proprietary PTFE formulation designed for extreme wear applications in March this year. The first compounds in the series are based on PEEK; compounds based on other high-performance polymers are currently in development. “By substituting standard PTFE additives with our proprietary lubricant and by optimising our processing technology, we have been able to substantially elevate wear resistance performance with these new compounds,” says Collet.

The 3M Dyneon Compound New Sealing Technology (NST) 1111R incorporates a 3M Dyneon PTFE matrix and a 3M microsphere filler system to improve properties (including friction and wear) for polymeric seal applications, such as shaft seals and transmission seal rings where low friction and wear resistance are key. Compared to a standard PTFE compound (Dyneon PTFE Compound TF 4105 with glass fibres) used for this application, the new compound offers a 17% improvement in friction coefficient. In addition, optimised friction and wear behavior leads to longer service life and less fuel consumption, according to 3M.

Celanese introduced a tribologically modified acetal copolymer called Hostaform SlideX POM in October last year. The compound is designed for use in manufacture of injection molded parts with good mechanical properties and a very low coefficient of friction and wear rate. The company claims it can help reduce energy loss, heat generation and noise in mechanical systems.
such as gear shift systems, stabiliser joints, roller shutter devices, furniture slide systems, or speed masters.

**Opportunities for polyketone**

Polyketones (PKs), which were available up until 2000 until Shell Chemical discontinued production, have recently become available again from South Korea’s Hyosung, which started up a 50,000 tonne (110 million lb) commercial plant in June of this year. The company announced plans in August for a second plant expected to start up in 2020. Although PK is limited to temperatures under 220°C, it offers an unusual combination of mechanical properties, barrier properties, broad chemical resistance, and low water absorption, in addition to wear resistance.

This performance combination gives PK an edge over POM and PA in some applications and several compounders, including A. Schulman, Lehmann&Voss, Ensinger, and Akro-Plastic, introduced PK compounds in 2014 and 2015. Early in 2015, PolySource became an authorised distributor for PK in North America.

In addition to its previously mentioned property combination, a further unusual feature of PK is that PK-PK material pairs show much lower wear than other like-paired materials, according to Oliver Frey, head of the compounding department at Ensinger. Although it is a common principle to avoid having like materials in contact for wear applications, it can’t always be avoided, and in such cases PK might present a solution, he says. At the upcoming Compounding World Forum in Philadelphia (8-9 December) Frey will give a presentation on the properties of tribological materials, different material classes, and the use of PK in these applications.

Akro-Plastic reports that in a test of combinations of materials in gears, PK-PK gears without lubrication lasted longer (91 minutes at 1600 rpm and a maximum torque of 5.5 Nm) than the user’s existing combinations of POM mated with lubricated PA 6.6 (72 minutes) or POM mated with lubricated POM (58 minutes). See Figure 1 on page 46 for full results.

According to Thilo Stier, head of sales and innovation at Akro-Plastic, PK is a sensitive material to compound and is prone to crosslinking if the residence time in the extruder is too long. Akro-Plastic uses a compounding extruder from its sister company Feddem that is specially designed with no kneading blocks. It also uses a die-head design that eliminates dead areas. Extremes in pH can also cause crosslinking, he adds. Stier says that temperature control during compounding is also crucial for PK but that, with care, Akro-Plastic is able to compound up to 60% glass fibre.

Carbon fibre is desirable for wear applications because of its combination of lower wear and higher mechanical strength compared to glass fibres (plus carbon fibres are lighter in weight). The limiting factor, however, is typically their high cost. Akro-Plastic is currently working with BMW on a process that allows compounding of post-industrial, pre-treated carbon fibre that is a residual material from BMW’s production process. “Using post-industrial recycle brings the price of carbon fibre down to only two to three times more than glass fibre,” says Stier.

**Click on the links for more information:**

- [www.polysource.net](http://www.polysource.net)
- [www.rtpcompany.com](http://www.rtpcompany.com)
- [www.laurelproducts.com](http://www.laurelproducts.com)
- [www.solvay.com](http://www.solvay.com)
- [www.colloids.com](http://www.colloids.com)
- [www.lehvoss.de](http://www.lehvoss.de)
- [www.dyneon.com](http://www.dyneon.com)
- [www.celanese.com](http://www.celanese.com)
- [www.poly-ketone.com](http://www.poly-ketone.com) (Hyosung)
- [www.ensinger-online.com](http://www.ensinger-online.com)
- [www.akro-plastic.com](http://www.akro-plastic.com)
Zeppelin Systems has launched the Henschel CMS (Container Mixer Series) for compounds and master-batches. These are exchangeable, static, non-rotating high-intensity mixing containers with tip speeds of 10 to 60 m/s. R&D manager Henning Kreis says the series has been designed for very easy handling and gives “excellent” dispersing results.

“The outstanding container handling is a real novelty on the market,” claims Kreis. “By using the latest design of tilting brackets, the container docking is very easy, even with larger machines,” he says. “The container clamping to the mixing head is carried out by a centring fork and spindle stroke gear at the container head. This leads to very high tensioning forces and additional safety by means of self-retention of the spindle stroke gear and motor brake.”

Container movement, driving-in and centring into the mixer is carried out by this automatic centring fork. “No matter which position the container is entered, it will be centred automatically to the precise position for lifting,” Kreis says. He adds that no additional guidance units or centring rails on the floor are required.

Zeppelin has also developed what Kreis describes as a special multiple round bar-profile style tool to achieve best mixing quality based on the vertical mixing position. He says this significantly improves homogenisation and dispersion. “The quite common build-ups and caking [that can occur with] difficult materials are minimised or even eliminated,” he says.

**Optimised for cleaning**

This lightweight mixing tool, which is claimed to generate less heat than earlier types, has been optimised for assembly and cleaning. Kreis says operators will appreciate the considerably easier cleaning and overall handling of the entire mixing system.

**Above:** A Mixaco CM Multi Tool container mixer shown in the mixing (left) and loading position.

**Below:** The multiple round bar-profile tool in Henschel’s mixer is said to provide high mix quality in vertical mixing positions.