LUBRIZOL

GLOBAL PRESENCE

Our polymers bridge the gap between flexible rubber and rigid plastics, with physical and functional properties that make them valuable in industrial, sports, apparel and consumer goods applications. We collaborate with customers to solve some of the industry’s toughest challenges, making products safer, stronger, more sustainable, better-performing, more appealing, and longer-lasting. With local sales and technical support and a global supply chain, we offer a convenient, single-source solution for customers across the world.

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Lubrizol Engineered Polymers offers an amazingly broad TPU offerings to the adhesives industry.

When considering thermoplastic polyurethanes (TPUs) for use in adhesives, Lubrizol Engineered Polymers product offering can be found in the following segments:

- **Solvent-based adhesives**
- **TPU for hot melt adhesives (powder and film)**
- **TPUs for inks, binders, lacquers and other end-uses**

**Amazing Benefits/Properties**

The addition of low melting point Pearlbond™ and Pearlstitch™ TPU to the high melting point Esilane® TPU product offering, uniquely positions Lubrizol to satisfy customers’ melting range needs across a wide crystallization range. This combined adhesive product line can be applied in a variety of end-uses: automotive, furniture, wood structures, apparel, medical garments, footwear and construction.

Lubrizol offers an amazingly broad TPU offering to the adhesives industry. Available in pellet and/or powder form, our products meet customer requirements for high-performing properties and benefits including:

- Low to high melting point (60-150°C)
- Slow to very fast crystallization rate
- Broad processing window: heat activation across a wide range of temperatures
- Good adhesion to polar substrates (e.g., polyester textiles) and materials such as PVC, ABS...
- TPUs that can be dissolved into solution (solvent-based adhesives)
- TPUs that can be added to polyurethane pre-polymers as a property modifier (NMPUR)
- TPUs that can be converted into hot melt film via flat die and/or blown film extrusion
- TPUs for inks, binders, lacquers and other end-uses

**A PORTFOLIO OF INNOVATIVE POLYMER SOLUTIONS**

Customers choose Lubrizol Engineered Polymers’ innovative solutions for the outstanding physical and aesthetic properties they provide in many industrial, sports, recreational and consumer goods applications.

Our polymers bridge the gap between flexible rubber and rigid plastics, with a wide variety of physical and functional property combinations. We help customers solve some of the industry’s toughest challenges, making products safer and stronger for better end-use performance, often while simultaneously improving aesthetics and sustainability measures.

Advancing materials, elevating performance – it’s both our mission and our passion.

**AMAZING PRODUCTS**

- Pearlstick™: TPUs for use in solvent-based adhesives
- Pearlbond™: TPUs for use in hot melts and
- NMPUR (R-M) adhesives
- Pearlbond™ ECO™: Bio-based TPUs for hot melts adhesives such as NMPUR (R-HM)

To learn more, visit www.Lubrizol.com/Engineered-Polymers
KEY FEATURES OF PEARLSTICK™ TPUS FOR USE IN ADHESIVES

CRYSTALLIZATION RATE AND THERMOPLASTICITY

The crystallization rate is the measurement of the time needed by a film of a TPU adhesive to reach its maximum values in the cooling period that follows its heat activation (measured by Lubrizol’s Standard MQSA N° 12 A). The thermoplasticity is the property of softening or melting under the effect of temperature. It is measured in terms of modulus of deformation (MPa) in relation to temperature - in accordance to Lubrizol’s Standard MQSA N° 69 A.1, and is obtained by a “Modulus of dynamic mechanical tests”. The graphic to the right shows crystallization rate and thermoplasticity of different Pearlstick™ TPU families.

HOT TACK

By means of the Tack Tester we can reproduce this property very well (for instance, the bonding of a shoe sole to the upper) by adjusting and studying production variables, such as: activation temperature, time allowed before bonding, material, bonding temperature and pressure.

Hot-Tack (PVC/Split leather) (Pressure: 2 kg/cm², Contact time: 4 sec)

In sole bonding, the adhesive used should have high hot tack so as to guarantee a perfect initial bonding, even at relatively low temperatures. Studies performed with some Pearlstick™ TPU grades are shown in the graph.

PEEL STRENGTH VERSUS ACTIVATION TEMPERATURE

Pearlstick™ TPUs stand out for their high initial strength obtained at a fairly low temperature. The graphic below shows peel strength and activation temperature of different Pearlstick™ TPU families.

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To learn more, visit www.Lubrizol.com/Engineered-Polymers
HMPUR (RHM) IS A TWO-STEP REACTIVE SYSTEM

The polyurethane prepolymers (RHM), when applied at a relatively low temperature (90-140°C), flow well and can adequately wet the surface of the adhering material. They act in two clearly different phases:

- In a first phase, also called physical crosslinking (Figure 2), the green strength develops, as a result of the cooling process (as also happens with a conventional hot-melt), together with the crystallization of the soft segments that can be found in the polymer component.
- In a second phase, or chemical crosslinking (Figure 3), the isocyanate groups start to react with the ambient moisture and/or the moisture of the materials.

As a result, an increase in the molecular weight is produced and a fully reacted polymer is obtained after some time, where urethane and urea groups alternate. This allows stronger and lasting adhesive bonding, which cannot be melted again as happens with conventional hot-melts.

**Figure 1.** Formation of a HMPUR (RHM)

\[
\text{H}_2\text{O} + \text{R} - \text{OH} + 2\text{OCN} - \text{R} ' - \text{NCO} \rightarrow 2\text{R} - \text{ON} + \text{OCN} - \text{NCO} + \text{H}_2\text{O}
\]

**Figure 2.** Physical crosslinking

- a: Open time
- b: Setting time
- c: Curing time
- d: Green strength
- e: Ultimate strength

**Figure 3.** Chemical crosslinking

- a: Open time
- b: Setting time
- c: Curing time
- d: Green strength
- e: Ultimate strength

Generally speaking, the benefits offered by the HMPUR (RHM) as a result of their structure, versus the conventional hot-melts can be summarized as follows:

- Lower application temperature.
- Immediate green strength and rapid increase of the cohesive strength (crosslinking).
- The cross-linked adhesive has an excellent resistance to heat and ambient conditions.
- Better adhesion to a variety of substrates.

To learn more, visit www.3M.com/Engineered-Polymers
PEARLSTICK™ TPUS FOR USE IN SOLVENT-BASED ADHESIVES

EASY SOLUBILITY

The mechanism by which a linear TPU changes from solid to liquid form in the presence of a solvent when a solution is prepared, can be described as follows:

Firstly, the TPU swells and then, progressively, due to the absorption of the solvent by the solid, it takes the aspect of a viscous solution, and a homogeneous solution is eventually formed. The swelling corresponds to the penetration of the solvent in the TPU molecules, followed by the absorption and combination of the TPU with the solvent. Such a combination results in a progressive separation of the macromolecules, breaking the intermolecular bonds (hydrogen bridges) and destroying the forces that form the initial structure. Such forces are much weaker in the soft segments than in the hard segments. When all the links are broken, the macromolecules can move easily, and a homogeneous solution is then obtained.

Depending on the needs of our customers and end-users, Lubrizol grades can offer the following key features:

- Good wash and/or dry cleaning resistance
- Food compliance
- Adhesion to tight fabrics
- Low to high hardness
- Chemical, fungus and hydrolysis resistance
- Low to high heat activation
- Short to long heat tack time
- Transparency, glossiness
- Sprayability

Depending on the grades, the following solvents can be used:

- Acetone
- MEK
- THF
- Cyclohexanone
- Ethyl Acetate
- Butyl Acetate
- Methylene Chloride
- Trichloroethylene
- 1,1,1-Trichloroethane
- Xylene
- Acetone/Toluene (70:30)
- MEK/Toluene (90:10)
- MEK/ Ethyl Acetate (90:10)

Lubrizol recommends the following equipment and dissolution conditions as explained at the right:

A typical TPU to be dissolved at a dry content of 18% is Pearlstick™ 45-60/18.

To learn more, visit www.lubrizol.com/Engineered-Polymers
**TYPICAL HMPUR (RHM) FORMULATION**

**Production Process:**
- Melt the polyester polyol at 100 °C
- Charge the polyester polyol and add Pearbond™ TPU
- Start agitation and elimination of moisture by N₂ at ≤ 10 mbar and 120 °C, (time = 1-2 hours)
- React with excess diisocyanate at 120 °C under N₂ atmosphere (time = 1 hour)
- Filter the melt (depending on application)
- Fill into sealed containers
- Quality control (% NCO, etc.) at 24 hours

<table>
<thead>
<tr>
<th>Component</th>
<th>OH / NCO ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>Crystalline Polyester (High Crystallinity)</td>
<td>11.95</td>
</tr>
<tr>
<td>Polyester (Amorphous Solid)</td>
<td>30</td>
</tr>
<tr>
<td>Polyester (Amorphous Liquid)</td>
<td>32</td>
</tr>
<tr>
<td>Pearbond™ TPU</td>
<td>16.80</td>
</tr>
<tr>
<td>MDI</td>
<td>10.00</td>
</tr>
<tr>
<td></td>
<td>13.20</td>
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<tr>
<td></td>
<td>100.00</td>
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</tbody>
</table>

The basic purpose of the Pearbond™ TPU grades is to modify some of the properties which are inherent to HMPUR (RHM) that are based on urethane pre-polymers. These crystalline TPU grades are typically used in the following industries: automotive (e.g., automotive interior parts), bookbinding, furniture (profile wrapping or edge banding), textile and footwear, as well as in various fixing adhesive applications.

**PEARLBOND™ TPUS FOR HOT MELT ADHESIVES (HMAS)**

Lubrizol TPU grades for hot melts are available with the following properties:
- Low to high melting point (50-150 °C)
- Slow to very fast crystallization rate
- Closely-textile compliant grades available upon request

**FILM & WEB ADHESIVES**

Lubrizol has a broad offering of TPUs that can be processed via extrusion process for making film and/or web adhesive. Lubrizol TPU grades are available in different hardnesses, across a wide range of melting points (50-150 °C), and crystallization rates (slow, medium, fast and extremely fast).

**Powder:** Lubrizol TPU grades are typically supplied in the form of pellets. These can also be made available in powder form. Depending on the TPU grades and order sizes, various average particle sizes can be made available such as < 100 μm, < 355 μm, < 500 μm and < 800 μm.

**CRYOGENIC GRINDING**

**THERMOBONDING**

Lubrizol has developed a range of TPUs that are specifically adapted to Thermobonding and more specifically to processes such as: scatter, paste dot, powder dot, double dot, screen coating and engraved roller coating to name the most commonly used processes.

To learn more visit www.Lubrizol.com/Engineered-Polymers