



ELASTOMERS

A guide to thermoplastic polyurethanes (TPU)

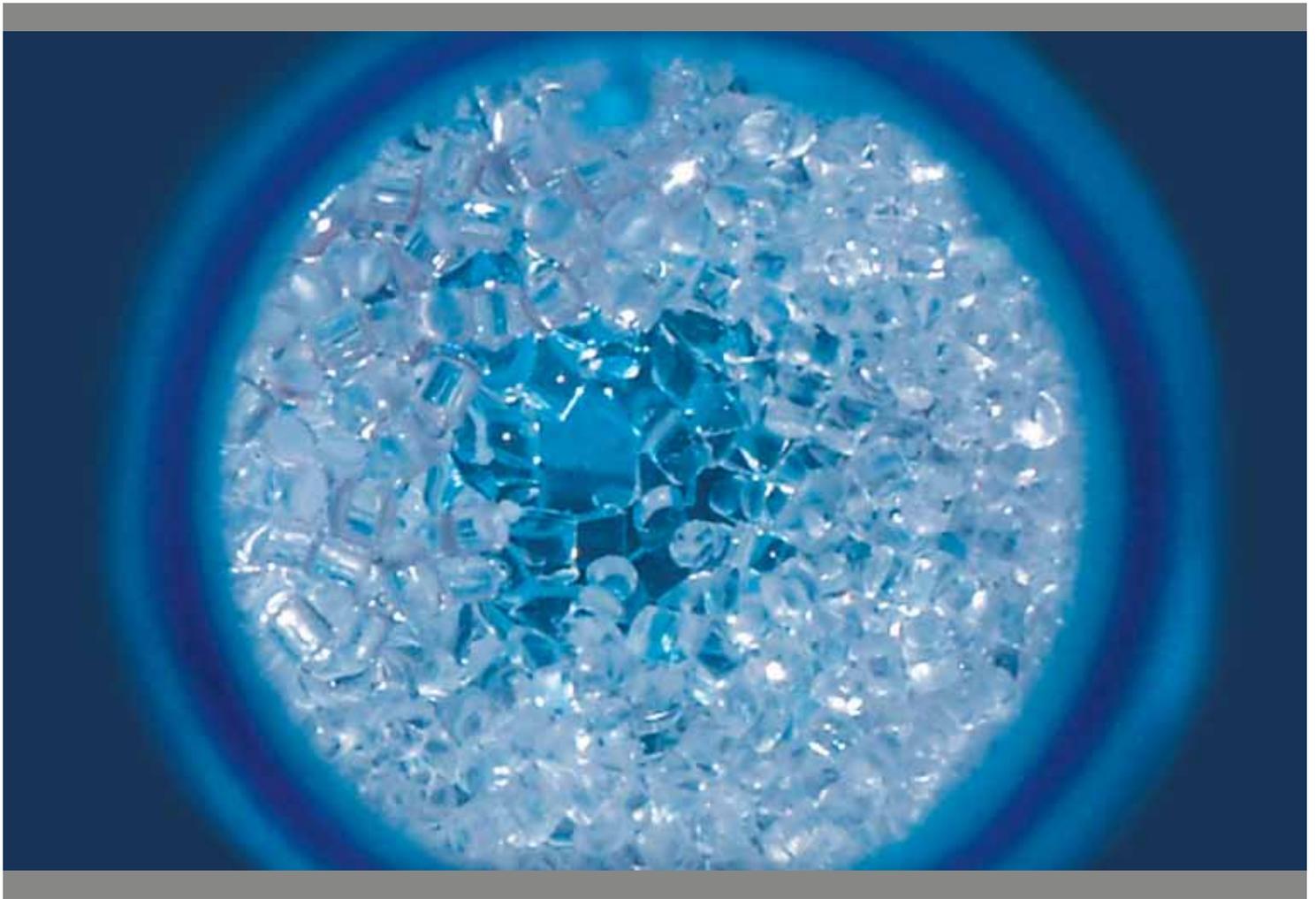


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A guide to TPU

Thermoplastic polyurethanes (TPUs) offer exciting possibilities for meeting the manufacturing challenges of a fast-changing world.

Well-known for their outstanding versatility, Huntsman's TPUs can improve the production and enrich the performance of anything from shoes, seals and films to filters, conveyor belts and cables.

Building on years of experience, we have developed a large number of TPUs with limitless potential to meet adhesive, coating, injection molding, extrusion, film and compounding application requirements.

- **Innovative solutions that can be customized to individual needs**
- **Ideally suited to a wide range of processing technologies**
- **Global supply chain plus excellent technical support**



1. What is TPU?

Thermoplastic polyurethane (TPU) is a unique category of plastic created when a polyaddition reaction occurs between a diisocyanate and one or more diols.

First developed in 1937, this versatile polymer is soft and processable when heated, hard when cooled and capable of being reprocessed multiple times without losing structural integrity. Used either as a malleable engineering plastic or as a replacement for hard rubber, TPU is renowned for many things including its: high elongation and tensile strength; its elasticity; and to varying degrees, its ability to resist oil, grease, solvents, chemicals and abrasion.

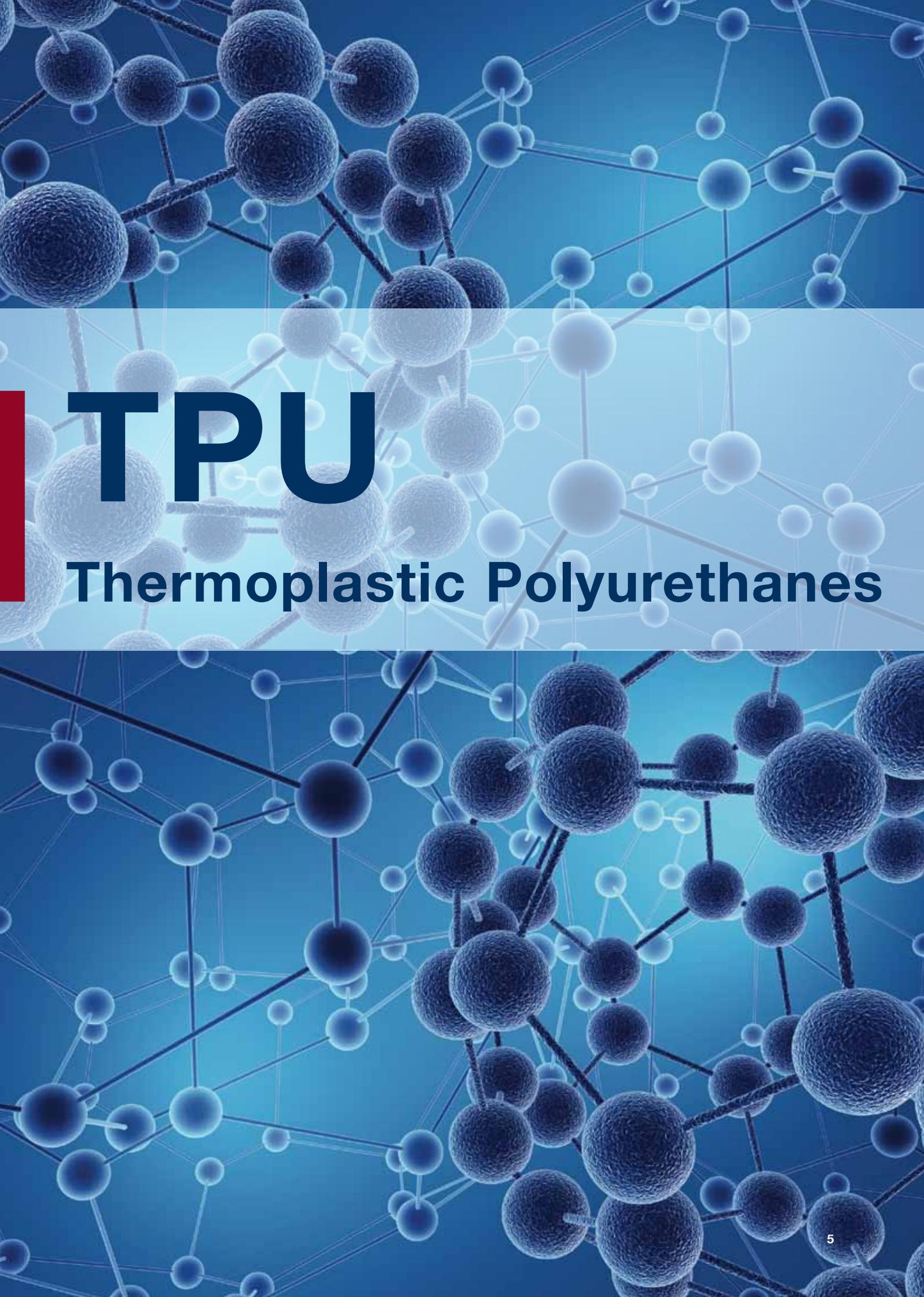
These characteristics make TPU extremely popular across a range of markets and applications. Inherently flexible, it can be extruded or injection molded on conventional thermoplastic manufacturing equipment to create solid components typically for footwear, cable & wire, hose and tube, film and sheet or other industry products. It can also be compounded to create robust plastic moldings or processed using organic solvents to form laminated textiles, protective coatings or functional adhesives.

There are three main chemical classes of TPU: polyester, polyether and a smaller class known as polycaprolactone.

- **Polyester TPUs** are compatible with PVC and other polar plastics. Offering value in the form of enhanced properties they are unaffected by oils and chemicals, provide excellent abrasion resistance, offer a good balance of physical properties and are perfect for use in polyblends.
- **Polyether TPUs** are slightly lower in specific gravity than polyester and polycaprolactone grades. They offer low temperature flexibility and good abrasion and tear resilience. They are also durable against microbial attack and provide excellent hydrolysis resistance – making them suitable for applications where water is a consideration.
- **Polycaprolactone TPUs** have the inherent toughness and resistance of polyester-based TPUs combined with low-temperature performance and a relatively high resistance to hydrolysis. They are an ideal raw material for hydraulic and pneumatic seals.

TPUs can also be subdivided into aromatic and aliphatic varieties:

- **Aromatic TPUs** based on isocyanates like MDI are workhorse products and can be used in applications that require flexibility, strength and toughness.
- **Aliphatic TPUs** based on isocyanates like H12 MDI, HDI and IPDI are light stable and offer excellent optical clarity. They are commonly employed in automotive interior and exterior applications and as laminating films to bond glass and polycarbonate together in the glazing industry. They are also used in projects where attributes like optical clarity, adhesion and surface protection are required.

The background of the entire page is a complex, three-dimensional molecular structure. It consists of numerous spheres of varying sizes, some with a textured, almost crystalline surface, connected by thin, dark lines representing chemical bonds. The overall color palette is a gradient of blues, from light sky blue to deep navy blue, with a prominent red vertical bar on the left side of the text area.

TPU

Thermoplastic Polyurethanes

2. TPU chemistry

A TPU is a multi-phase block copolymer that is created when three basic raw materials are combined together in a specific way. The individual components required to produce a TPU are:

- A polyol or long-chain diol
- A chain extender or short-chain diol
- A diisocyanate

Figure 1.0 depicts the basic chemistry of TPU. The soft block, built out of a polyol and an isocyanate, is responsible for the flexibility and elastomeric character of a TPU. The hard block, constructed from a chain extender and isocyanate, gives a TPU its toughness and physical performance properties.

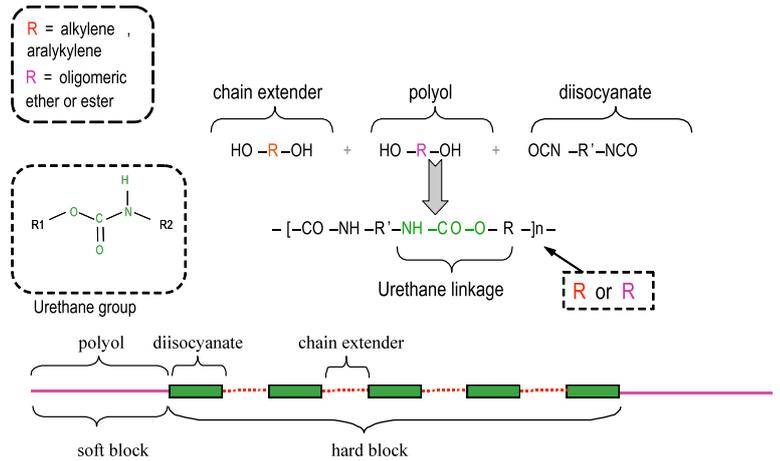


Figure 2.0 highlights the cross-linking structure of a thermoplastic elastomer versus a thermoset rubber. It shows that there are no chemical cross-links in TPUs unlike thermoset rubbers or casted polyurethane systems.

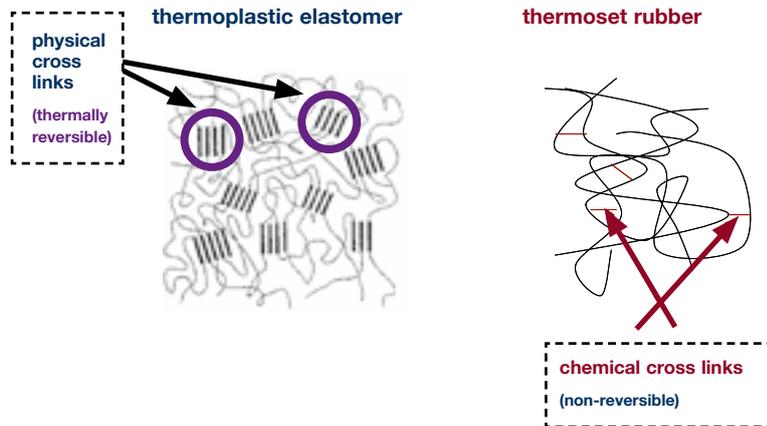
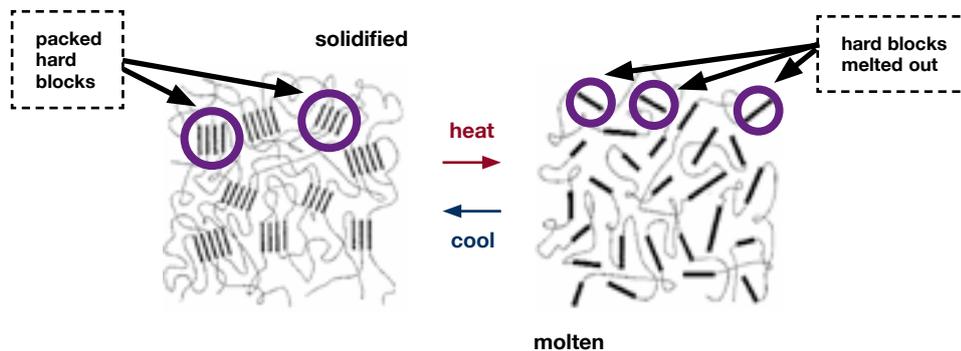


Figure 3.0 provides a graphic illustration of the morphology of a TPU. It shows how physical cross-links melt out under heat and repack when the material is cooled.





TPU chemistry

3. TPU from Huntsman

IROGRAN[®], AVALON[®], KRYSTALGRAN[®] and IROSTIC[®] are the four main TPU brands produced by the polyurethanes division of Huntsman. Available in an array of different grades, each has its individual characteristics and can be tailored for either basic plastic product applications or more complex engineering projects.

Regardless of brand, all TPU grades have some common performance traits that set them apart from other plastic materials. These typically include:

- High abrasion resistance
- High elasticity across the entire hardness range
- Excellent low-temperature and impact strength
- Resilience to oils, greases and numerous solvents
- Good flexibility over a wide temperature range
- Robust weather and high-energy radiation resistance
- Pleasant tactile properties
- Suitability for bonding and welding
- Ease of coloring
- Recyclability

For applications with specific requirements, it is possible to change a TPU's physical attributes and production values. Distinct performance properties can be achieved by:

- Varying the type of polyol used
- Adjusting the ratio of other raw materials
- Changing the reaction conditions under which processing takes place
- Using additives like UV stabilizers, mold release agents and flame-retardants.



A young girl with dark hair, wearing a light-colored top, is smiling and looking towards the camera. She is standing in a field of tall, golden-brown grass. In the background, a large white wind turbine is visible against a clear blue sky. The overall scene is bright and sunny, suggesting a rural or agricultural setting.

About Huntsman

Huntsman is a global manufacturer and marketer of differentiated chemicals. Its operating companies manufacture products for a variety of global industries, including chemicals, plastics, automotive, aviation, textiles, footwear, paints and coatings, construction, technology, agriculture, health care, detergent, personal care, furniture, appliances and packaging.

Originally known for pioneering innovations in packaging and, later, for rapid and integrated growth in petrochemicals, Huntsman today has more than 11,000 employees and operates from multiple locations worldwide. The Company had 2009 revenues of approximately \$8 billion.

4. Physical Properties

Material Resistance

The mechanical properties of a TPU can be evaluated in a number of different ways. Detailed below are some of the standard assessments used to measure a TPU's characteristics and define what can be expected in terms of physical performance and longevity.

Shore hardness

Shore hardness is an empirical measurement used to test a TPU's resistance to indentation or penetration under a defined force. Two letters are used to categorize the type of TPU being appraised: 'A' denotes a flexible type of TPU while 'D' refers to more rigid varieties. These two categories can sometimes overlap. On both scales measurements range from zero to 100 with zero being very soft and 100 very hard.

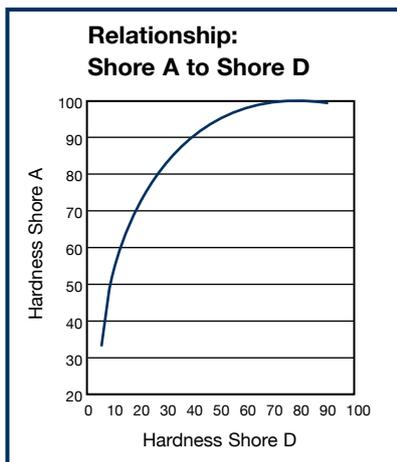


Figure 4.0 shows the correlation between Shore A and D. For material comparison, the Shore A scale is recommended for flexible grades (best below 92A). The Shore D scale is more appropriate for rigid grades (best above 92A).

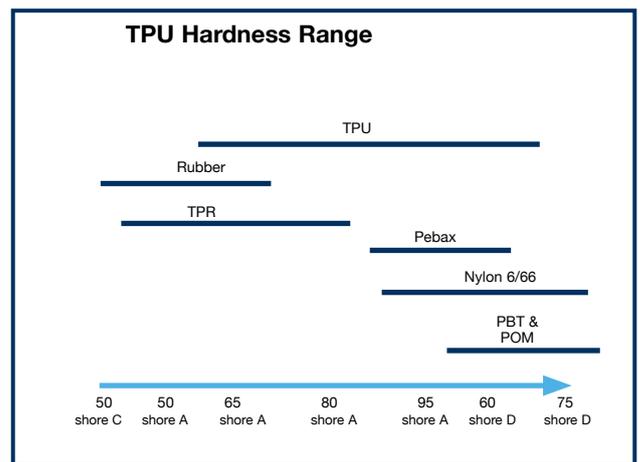


Figure 5.0 highlights the diversity of TPU chemistry and the broad spectrum of materials that can be created ranging from soft rubbers to rigid thermoplastics.

Tensile strength

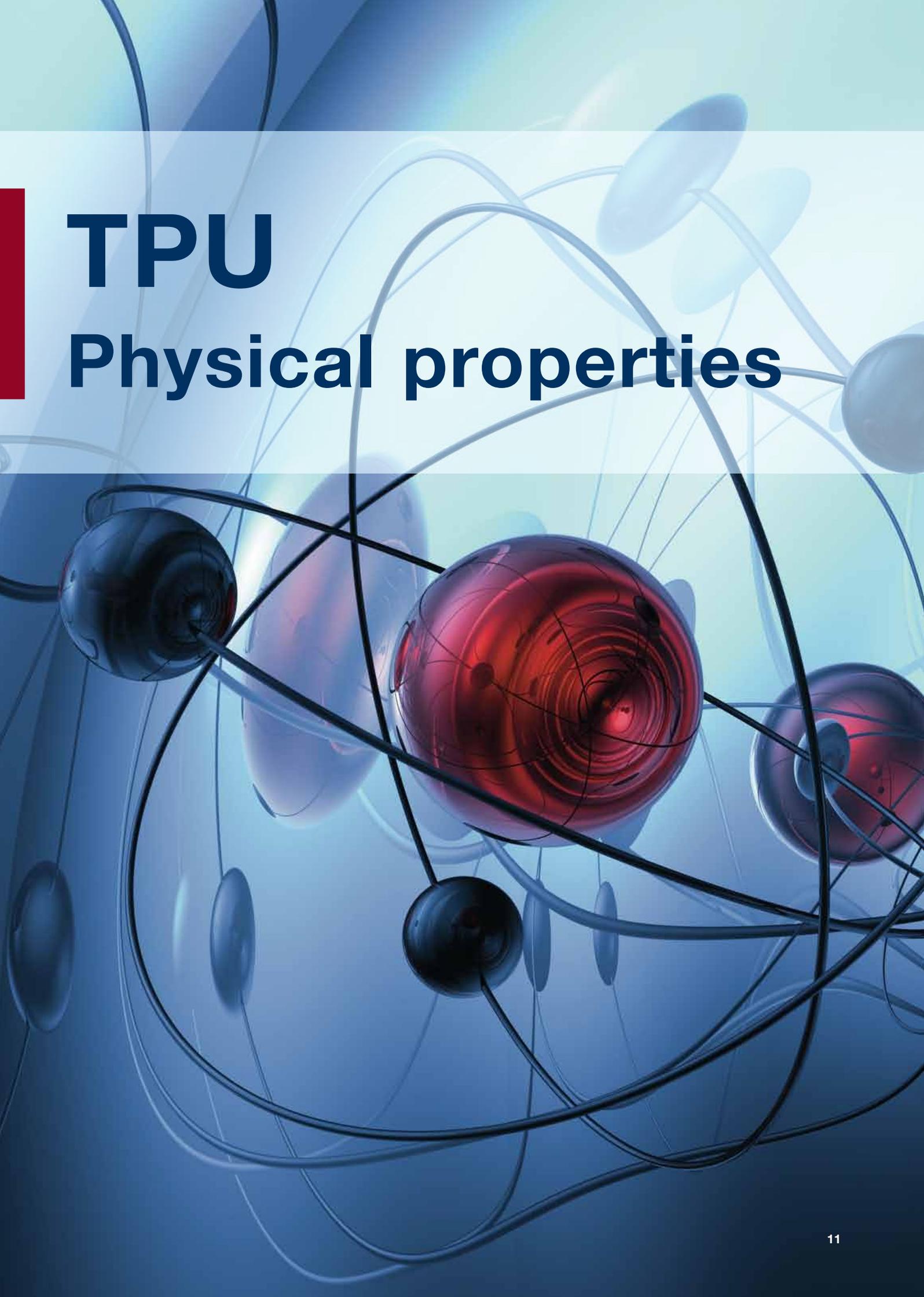
Tensile strength is an indicator of TPU behavior and the tendencies that will be exhibited when a specimen cross section is placed under short-term, uniaxial stress. In other words, the strain it will endure before any sort of deformation starts to occur. Guidelines for undertaking tests are specified in the standard DIN 53504 or ASTM D412. Results are usually documented in a stress strain diagram. See Figure 6.0 as an example.

Strength characteristics:

- **The yield stress** σ_y is the tensile stress at which the slope of the stress-strain curve becomes zero
- **Tensile strength** σ_{max} is the tensile stress at maximum force
- **Tear strength** σ_{xy} is the tensile stress at the moment of rupture of the specimen

Deformation characteristics:

- **The yield strain** ϵ_y is the elongation corresponding to the yield stress
- **Maximum force elongation** ϵ_{max} is the elongation corresponding to the tensile strength
- **Elongation at break** ϵ_{xy} is the elongation corresponding to the tear strength



TPU

Physical properties

Tear strength

Tear strength denotes a TPU's ability to counter break and distortion. The higher the tear strength, the greater the number of utilization options there are likely to be.

Compression set

A TPU's compression set can be defined as the permanent deformation that remains after compressive stress has been released. It is calculated as a percentage of the original deflection after the material has been allowed to recover at standard conditions for 30 minutes.

The compression set of a TPU is normally tested over a period of 24 hours at a specified temperature. Guidelines for standard deformation tests are defined in DIN ISO 815 or ASTM D395. For rigid grades of TPU, compression should ideally not exceed 5%. For more flexible grades, 10% is the upper acceptable limit. To ensure that TPU materials can offer the very best compression resistance, heat treatments like annealing can be helpful.

Abrasion

The abrasion resistance of plastic materials like TPU is measured by applying coarse paper to a substrate under pressure via a rotating cylinder. This sort of test typically takes place as per DIN 53516 (ISO 4649) guidelines. The weight of the TPU specimen is measured before and after the abrasion assessment to gauge how much wear has occurred. The original density of the material is considered alongside the roughness of the paper with results typically expressed in terms of volume loss of the substrate in mm³.

Shrinkage

The shrinkage of TPU moldings is influenced by a number of parameters including part design, wall thickness, gate design and processing conditions. Melt and mold temperature as well as injection and holding pressure are also important factors. Total shrinkage is a result of molding shrinkage and post-shrinkage. This can occur during annealing and also during the longer-term storage of parts. For this reason it is difficult to predict shrinkage with any great accuracy.

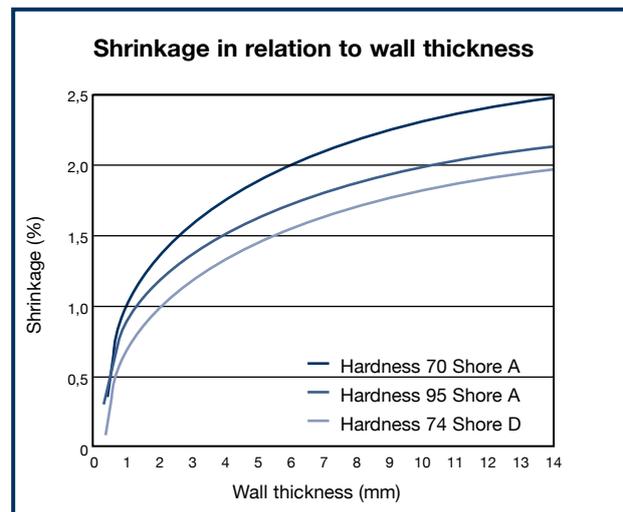
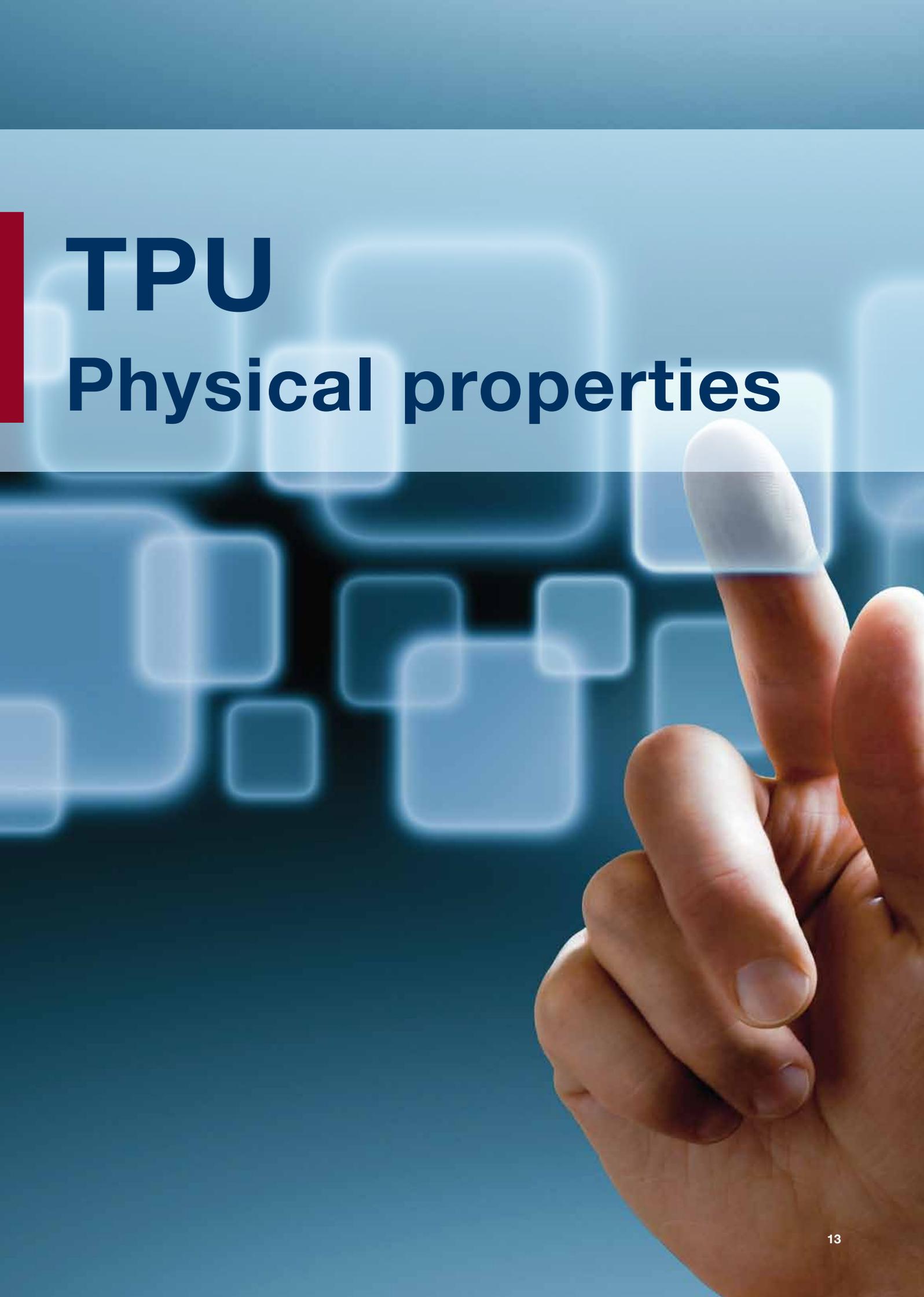


Figure 7.0 shows total shrinkage for TPU grades in relation to wall thickness and Shore hardness.

A hand is shown in the lower right corner, pointing upwards with the index finger. The background is a dark blue gradient with several glowing, semi-transparent blue squares of various sizes scattered across it. A horizontal white bar is positioned across the upper third of the image, containing the text.

TPU

Physical properties

5. Chemical properties

A TPU's chemistry will dictate its behavior in certain environments. It is therefore, important to choose the proper grade particularly if exposure to high temperatures, water and / or outdoor elements is a consideration. The degree to which any changes occur is dependent on the nature of the solution, compound or element involved; its concentration; the formulation of the TPU; and processing and application temperatures.

Acids and alkaline solutions

TPU has limited resistance to acids and alkaline solutions. It can only withstand diluted acids and alkaline solutions at room temperature for short periods of time.

Saturated hydrocarbons

When exposed to saturated hydrocarbons, TPU may expand slightly. Moderate swelling is known to occur with diesel oil, isooctane, petroleum ether and kerosene. While only temporary, this change can lead to an interim reduction in a TPU's tear resistance. Please note: flexible grades are more prone to swelling under these circumstances than rigid alternatives. Once the hydrocarbon is removed, swelling normally subsides and mechanical properties should return to normal.

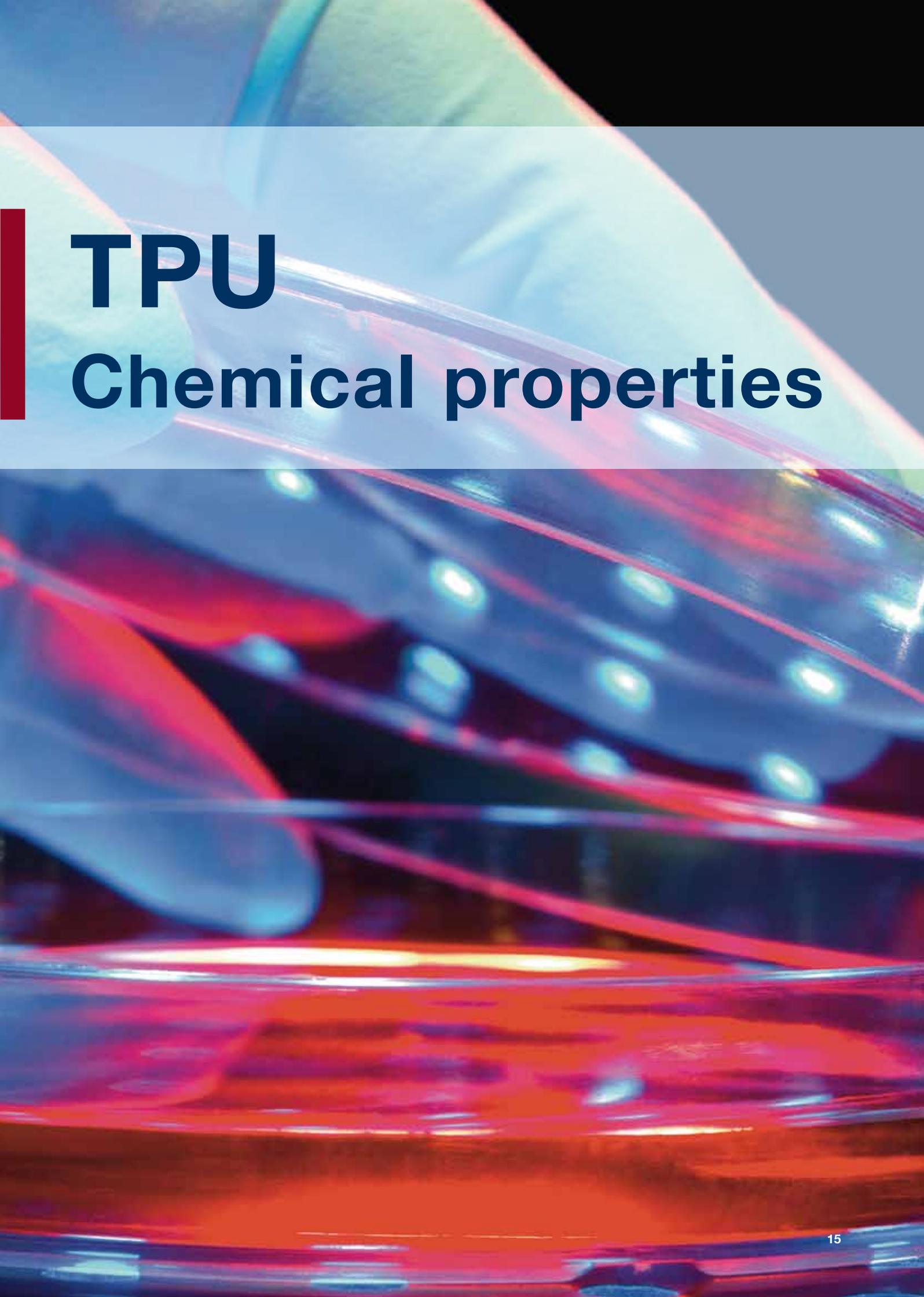
Aromatic hydrocarbons

As with saturated hydrocarbons, contact with aromatic hydrocarbons such as benzene and toluene can cause TPU to swell – resulting in a reduction in mechanical performance. Depending on the hydrocarbon in question, the scale of swelling will vary. In some cases it could be prominent with the material increasing in weight by up to 50%.

Chemical resistance

Recognizing that certain applications require TPUs that demonstrate chemical resistance, Huntsman offers a technical service that can help gauge the resistance of its TPU grades in relation to specific substances – particularly those employed in industrial, laboratory and medical projects. These can take place at Huntsman R&D facilities on request.

For other more general projects involving TPU, the following sections serve as a guide to chemical resistance. They include a glossary of terms, tests and standards explaining how TPU is likely to conform. Basic information can also be found in the comparison table – see page 16.



TPU

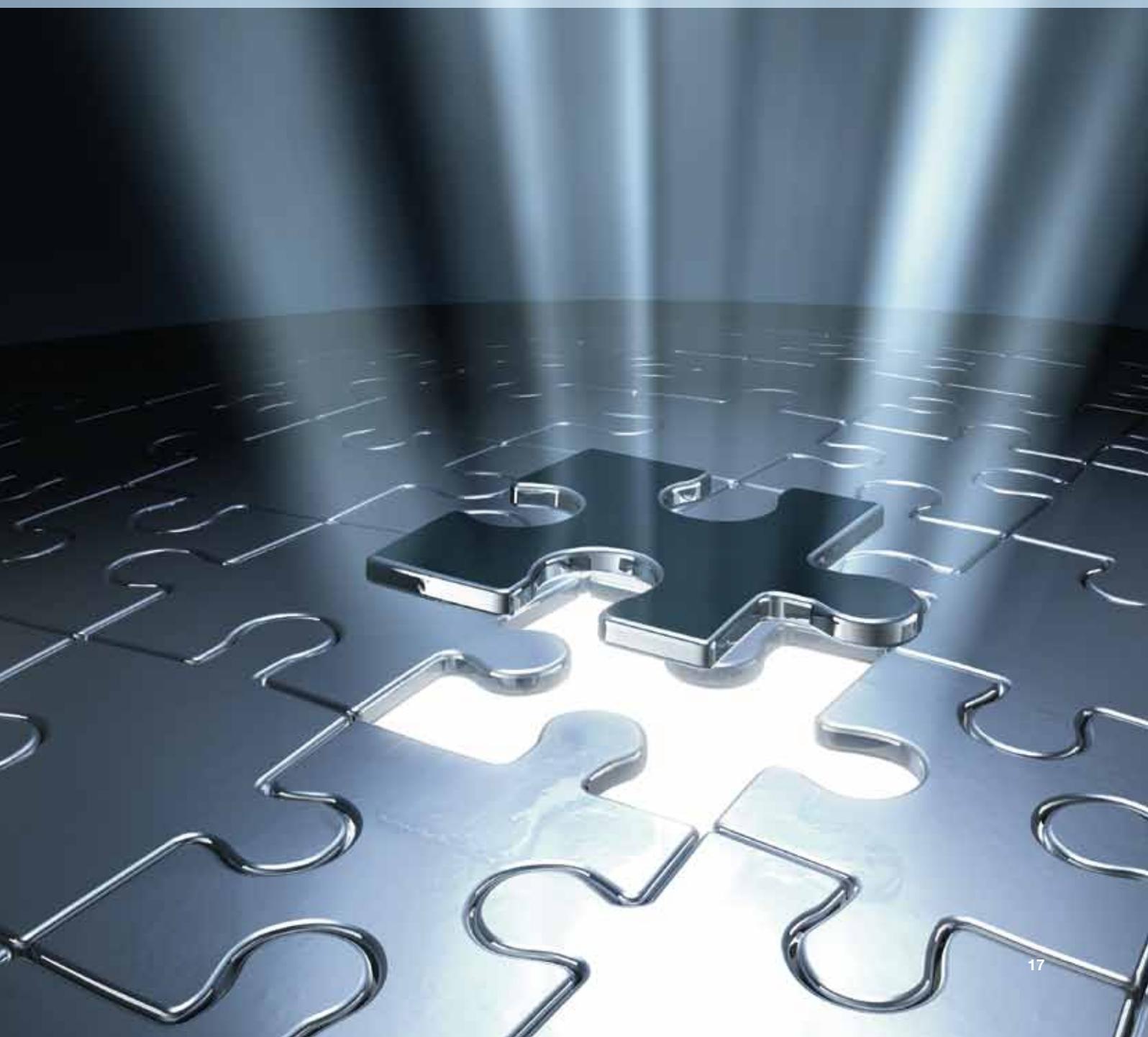
Chemical properties

IROGRAN[®] resistance properties

Medium	Temperature °C	IROGRAN Ether grades	IROGRAN Ester grades	max. volume increase %
Acetone	RT	-	-	40
AL-chloride, aqueous, 5 %	RT	++	++	1
Ammonia, 10 %	RT	++	++	1
Aniline	RT	--	--	
ASTM Fuel A	RT	++	++	4
ASTM Fuel B	RT	++	++	10
ASTM Fuel C	20°C	+	+	18
ASTM oil 1	80°C	++	++	
ASTM oil 2	80°C	++	++	3
ASTM oil 3	80°C	++	+	6
Ethanol 96 %	RT	+	+	11
Petrol, standard grade	RT	++	++	10
Petrol, premium grade	RT	-	-	17
Benzene	RT	-	-	
Butanol	RT	-	-	
Butylacetate	RT	-	-	40
Cyclohexanol	RT	+	+	5
Dibutylphthalate	RT	+	+	40
Diesel oil	RT	++	++	5
Dimethylformamide	RT	0	0	
Acetic acid 3 n	RT	-	-	2
Acetic acid, 20 %	RT	+	+	
Ethylacetate	RT	-	-	40
Ethylether	RT	+	+	
Fe chloride, aqueous, 5 %	40°C	+	+	
Glycol	RT	++	++	2
Glystantin / water 1:1	20	+	+	
Glystantin / water 1:1	80°C	+	-	
Isopropanol	RT	+	+	12
Kerosine	RT	++	++	3
Sodium chloride solution, conc.	RT	++	++	
Methanol	RT	+	+	10
Methylen chloride	RT	--	--	
Methylethylketone	RT	-	-	45
Mineral oil	80°C	++	++	
Soda soap fat	RT	++	++	
Sodium hydroxide solution 1N	RT	+	+	
Nitric acid, 20 %	RT	--	--	
Hydrochloric acid, 20 %	RT	+	+	
Sulphuric acid, 20 %	RT	+	+	
Sea water	RT	++	+	
Carbon tetrachloride	RT	-	+	
Toluene	RT	-	-	35
Trichloro ethylene	RT	-	-	
Water	100°C	-	--	
Water	RT	++	++	1
Water	80°C	+	-	2

TPU

IROGRAN[®] resistance properties



6. Chemical resistance

Solvents

Depending on the type of alcohol-based solvent used, the effect on a TPU may differ. Aliphatic alcohols such as ethanol and isopropanol can trigger slight swelling. More obvious levels of distortion can occur with exposure to aliphatic esters and ketones including acetone, methyl ethyl ketone (MEK) and cyclohexanone. Strong polar organic solvents like dimethyl formamide (DMF) and dimethyl sulfoxide (DMSO) can dissolve TPU altogether.

Microbial resistance

In applications where a TPU is in regular contact with soil in either hot or humid environments, its ability to resist microbial attack will need to be considered.

Polyether-based TPU grades – often used in the cable industry – are resistant to microbial degradation. The saponification value according to DIN 57472 (VDE 472-804) is below 200mg KOH/g for ether grades meeting VDE 0282-10 requirements.

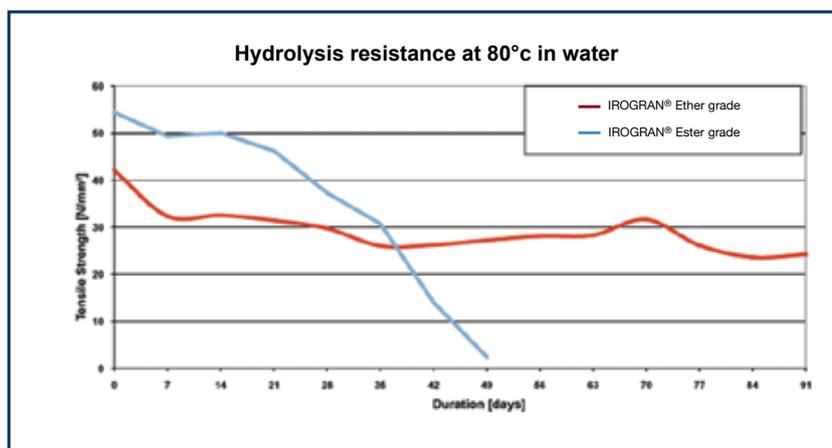
Flexible polyester-based TPUs can be vulnerable to damage from fungi and bacteria. The enzymes present in microorganisms can split ester bonds causing the TPU to discolor and crack – thereby affecting load-bearing capabilities.

Hydrolysis resistance

Polyester-based TPU may be put at risk by hydrolysis when exposed to high temperature levels and in humid environments. Problems typically start to occur when water molecules cause ester groups to split.

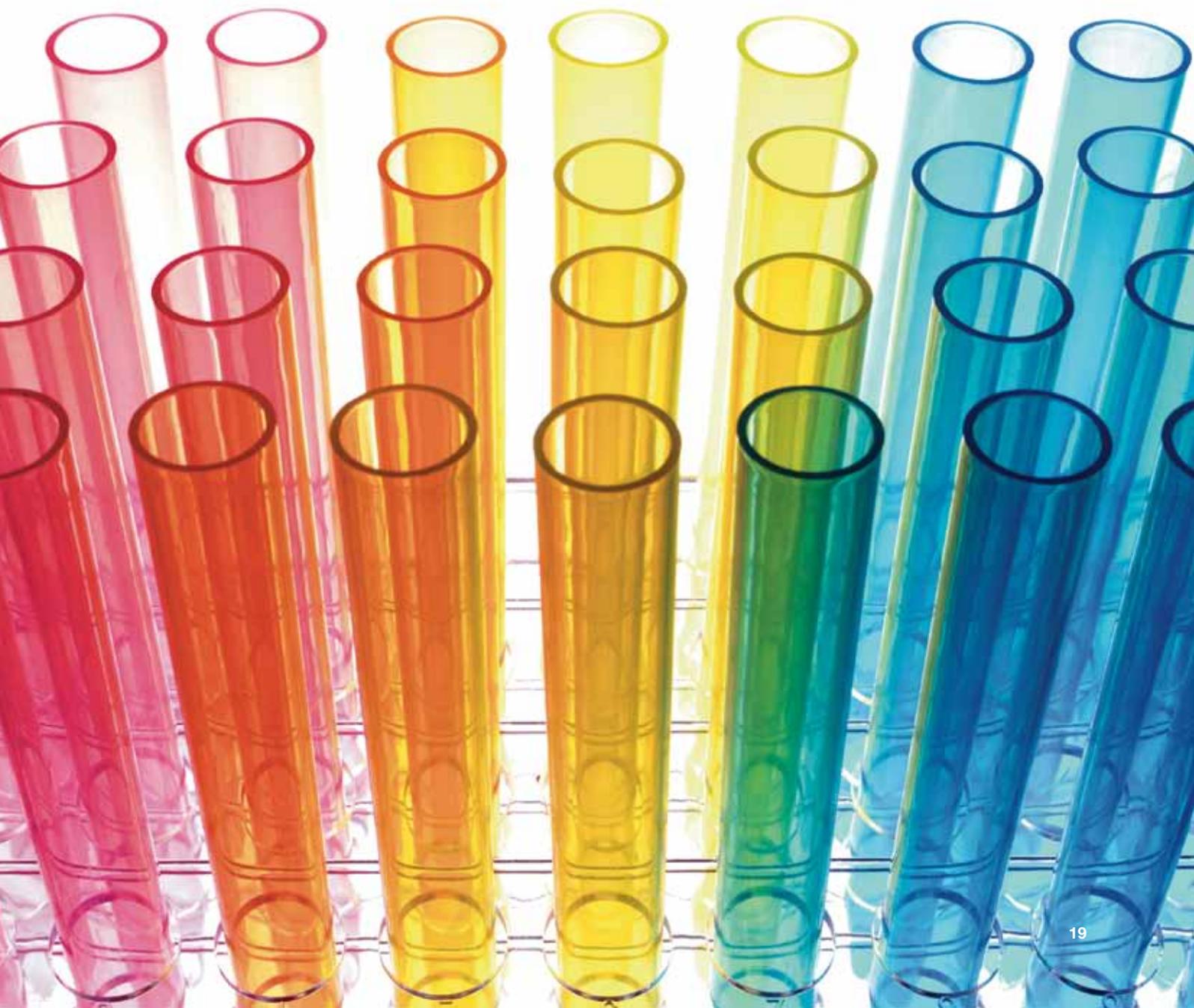
With hydrolysis resisting abilities, polyether-based TPU can be used in underwater applications as well as humid and damp situations. Where increasing temperatures would normally cause hydrolytic degradation, the graph indicates good hydrolysis resistance at a high temperature.

This makes polyether-based TPU a good solution for applications including ABS cables located on the anterior of automobiles, which come into constant contact with dirt and water.



TPU

Chemical resistance



Oil, grease and lubricant resistance

As a general rule, TPU remains stable when it comes into contact with greases, lubricants and test oils in tests like ASTM 1, IRM-902 and IRM-903. This is true even at high temperatures up to 100°C and over a period of several weeks. However, some oil-based fluids may be prepared with additives that could damage TPU. Compatibility testing is therefore recommended.

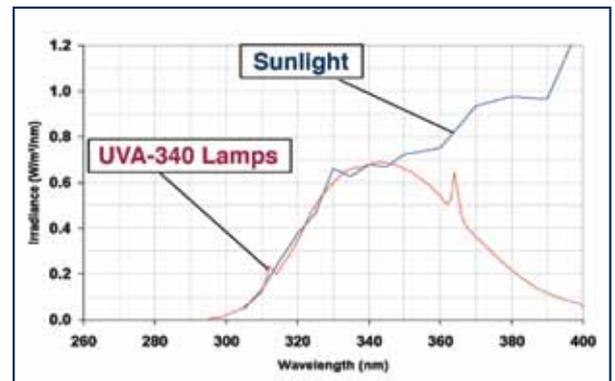
UV radiation resistance

Aromatic TPUs can yellow with exposure to UV radiation. In applications where a TPU will be exposed to sunlight, the best course of action is to employ an aliphatic TPU, which will not yellow or degrade with outdoor exposure. Huntsman has several grades of aliphatic TPU based on polyether, polyester and polycaprolactone polyols that cover a wider range of hardnesses. (See KRYSTALFLEX® PE 399 as an example).

Krystalflex PE 399		Accelerated Weathering - QUV Exposure				
Properties	Exposure hours					
	0	500	1000	1500	2000	
Tensile strength @ break, psi	4000	4000	3900	3500	4300	
100% Tensile modulus, psi	400	380	440	420	370	
300% Tensile modulus, psi	3500	2800	2500	2400	2000	
Ultimate elongation %	300	300	280	280	360	
Tear resistance, pli	140	125	125	125	170	
Yellowness index	0,42	1,73	2,08	1,86	2,52	

Conditions:

Extruded Film Thickness: 25 ± 5mils., Test methods: ASTM G-53; D-412; D-624
Light source: UVA-340 bulb, Cycle: 4 hours UV light @ 60°C,
4 hours condensation @ 45°C, Specimen Preparation: without glass



Ozone Resistance

Ozone is a powerful oxidizing agent that can break down the double bonds present in some elastomers. All grades of TPU from Huntsman are ozone resistant and meet VDE 472-805 requirements.

Fire behaviour

There are numerous compliance standards that document the behavior that can be expected of a TPU in the event of a fire. One of the most important from an international perspective is UL (Underwriters Laboratories) 94 – see section 7 for further details. Other specific criteria exist for individual markets. For example, in the cable & wire sector, evaluation according to VDE 0472 part 804, test B (IEC 60332-1) is often applicable. And in the automotive industry, all grades have to comply with FMVSS 302 – the Federal Motor Vehicle Safety Standard. As an example, the flame retardant grade IROGRAN® A 78 P 4766 has been yellow card listed by the UL. It reaches, at a thickness of between 1,5 – 3,0mm, the UL 94 VO classification for all colors.



TPU

Chemical resistance

7. Specific quality classification

The following sections provide information about the specific standards that Huntsman adheres to when manufacturing and testing TPU materials for a variety of end uses.

VDE specification (=Verband der Elektrotechnik/Elektronik&Informationstechnik e.V.)

TPU is specified in the VDE 0282-10 standard of 1995 "EPR insulated flexible high voltage power line with polyurethane jacketing". This standard conforms with the Cenelec harmonization document HD 22.10 S1 (Cenelec = European committee for electronic standards). The letters TPU are printed on these cables to indicate that the jacketing is made from TPU.

UL 94 (Underwriters Laboratories®)

Underwriters Laboratories® is an independent product safety certification organization that has been testing products and writing standards for safety for more than a century.

TPU grades that are not flame-retardant can meet HB classification. Flame retarded grades can reach V0 or V2 – see section 6 for further information.

Thermomechanical analysis (TMA)

Thermomechanical Analysis (TMA) measures the changes that occur in the dimensions of a product while it is subject to temperature fluctuations. TMA measuring is often used to analyze a TPU's performance where the expansion coefficient, melting and softening points can be assessed.

Toxic substances control act (TSCA)

The Toxic Substances Control Act (TSCA) is a US law passed in 1976. It authorizes the US Environmental Protection Agency (EPA) to gather information about the potential risks to human health and the environment posed by chemicals and mixtures which are manufactured (including import), distributed in commerce, processed, used or disposed. Generically known as "core" TSCA, Title I includes the major provisions listed below.

Compliance with TSCA is the responsibility of persons involved in manufacture, distribution, processing, usage and disposal who are obliged to know and meet TSCA requirements. EPA monitors compliance with core TSCA requirements through record reviews, other non-reporting sources and on-site inspections.

- If you manufacture, process or import a new chemical or mixture you may be subject to Section 5 pre-manufacturing notices. This includes not just new chemicals but also significant new uses of a chemical.
- If you manufacture, process or import an existing chemical or mixture, you may be subject to Section 8 reporting and record keeping requirements. A 'new' or 'existing' chemical may be determined if the chemical is listed on the TSCA Inventory.
- In addition, chemicals and mixtures that are manufactured, processed or imported may be subject to Section 4 test rules if there is thought to be unreasonable risk.
- If you are involved in importing and exporting chemical substances, additional requirements apply.
- TSCA exempts certain chemicals or mixtures that are manufactured, processed or imported in small quantities or batches for the purpose of scientific experimentation or analysis.



TPUs

Specific quality classifications

GMP (EC 2023/2006)

Following its implementation in August 2008, the Good Manufacturing Practice quality standard introduced strict guidance regarding the production of materials intended for contact with food. These regulations impact on each stage of the TPU manufacturing process from the selection of raw materials to the point at which the final product comes into contact with consumables.

Huntsman Polyurethanes has three grades of high performance IROGRAN® TPU designed specifically for use in food industry conveyor belts. These meet European Union GMP regulations (EC2023/2006). NB: All Food Contact Materials (FCM) are labeled with an illustration of cutlery to ensure customers can easily identify relevant products.

ISO

The Huntsman TPU team is committed to operating a quality management system to support the continuous development of its business. The target is to continuously improve the products and services delivered to customers through the optimization of all activities.

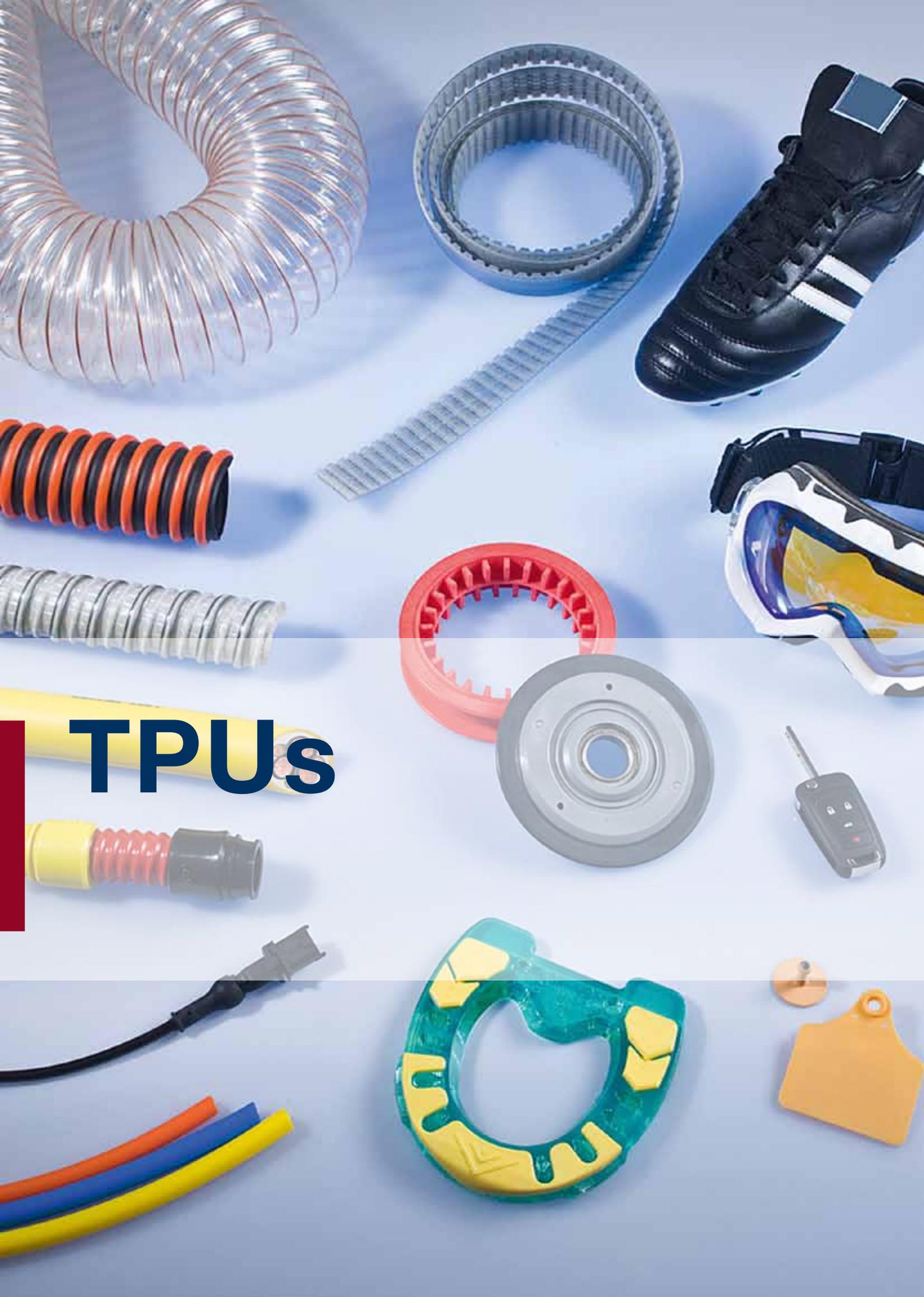
The Huntsman system is based upon ISO 9001. You will find a copy of the company's latest certificate at: www.huntsman.com/tpu

REACH

REACH is the European Regulation for the Registration, Evaluation, Authorization and Restriction of Chemicals. It came into effect on 1 June 2008 to streamline and improve the former legislative framework on chemicals of the European Union (EU)*. REACH places greater responsibility on industry to manage the risks that chemicals may pose to human health and the environment. Huntsman is well prepared for REACH and welcomes its objectives of ensuring adequate protection of human health and the environment, which are consistent with our own corporate philosophy. More information can be found at: www.huntsman.com

Restriction of hazardous substances directive (RoHS)

The directive on the restriction of the use of certain hazardous substances in electrical and electronic equipment 2002/95/EC, (commonly referred to as the Restriction of Hazardous Substances Directive or RoHS), was adopted in February 2003 by the European Union. The RoHS Directive took effect on 1 July 2006 and is enforceable and law in each member state. This directive restricts the use of six hazardous materials in the manufacture of various types of electronic and electrical equipment. Huntsman fulfills these compliances and is pleased to confirm certain products upon request.



TPUs

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HUNTSMAN

HUNTSMAN

Enriching lives through innovation

Huntsman Polyurethanes is committed to working closely with its customers and can offer a fast and flexible response to your needs. We offer direct links to our laboratories with full technical backup. Commercial support and dedicated customer service is available throughout Europe, the Middle East, Asia-Pacific and the Americas.



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About Huntsman:

Huntsman Corporation is a publicly traded global manufacturer and marketer of differentiated chemicals with 2012 revenues of over \$11 billion. Our chemical products number in the thousands and are sold worldwide to manufacturers serving a broad and diverse range of consumer and industrial end markets. We operate more than 75 manufacturing and R&D facilities in over 30 countries and employ approximately 12,000 associates within our 5 distinct business divisions. For more information about Huntsman, please visit the company's website at www.huntsman.com

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