design steps
polyurethanes for footwear
Huntsman is a pioneer and innovator in footwear. It was the first to supply polyurethanes to the footwear industry. You too can benefit from this heritage, and there’s more to come.

One of the immediate attractions of polyurethanes for shoe-making is that they allow manufacturers to produce lighter and more comfortable footwear. However, the introduction of polyurethanes to the footwear industry was not without its challenges.

In the late 1960s shoe producers had little experience with ‘reaction polymerization’ (the process whereby polyurethane materials are produced) and their favored materials required completely different equipment, manufacturing processes and raw materials handling.

For those who did make the ‘leap’ into new technology, the tremendous advantages were soon apparent. With relatively low capital investment, they could achieve high output and reduce unit costs. And the consumer benefited too. The technology generated a range of unique and almost limitless properties that could be manipulated to meet specific needs.

Huntsman was the first to introduce polyurethanes to the footwear industry. It built on this lead with the first water-blown polyether systems which completely eliminated the use of CFCs.

In the middle of the 1990s, Huntsman’s ‘rolling technology’ program broke new ground with the first universal prepolymer for use with both polyester- and polyether-based systems.

At the turn of the century, Huntsman pioneered the dual soling TPU/PU concept and the most recent innovation was the launch of AVALON® Lite, a new generation of lightweight high performance thermoplastic soling.

First Steps for Polyurethanes

In the Middle Ages, men and women wore ‘poulaines’, also known as ‘crackowes’. These shoes had a long pointed toe that curled upwards at the end. The left and right shoe were the same and the length of the toe denoted the wearer’s social status.

The ‘chopine’ rose to prominence with ‘society’ women during the early 16th century, and featured a tall platform sole and uppers made of kid leather or velvet. It fell from grace during the Baroque period, when men led the way in adopting the heeled shoe.

In the 20th century, technological innovation and social change have accelerated the evolution of footwear. Sport and leisure activities liberated women and heralded the age of ‘femme fatale’ heels and practical leisure shoes.
A polyurethane footwear system is the product of a chemical reaction between an engineered polyol resin-blend and a specific isocyanate (prepolymer) to obtain a microcellular structure. Huntsman Polyurethanes is recognized as the innovator for tailoring products to achieve the desired flexibility, softness, look, durability and lightness.

These unique properties give designers and manufacturers the freedom to create innovative designs that are in step with fashion and technological change. Polyurethanes can be made light, tough, comfortable, flexible, insulating, waterproof, slip-resistant, hardwearing and shock absorbent as required, simply by varying the formulation. They can have an almost endless variety of shapes, surface textures and colors and incorporate voids, inserts or dual-densities for extra comfort and support. Furthermore, PU bonds very well to any type of uppers (leather or textile).

Polyurethanes are either polyester- or polyether-based depending on the physical and mechanical properties required and can be injection- or pour-molded. They are easy to process, require relatively low tooling and manpower costs, offer flexibility for long and short production runs and are in line with environmental standards.

Add together the extra scope they give to be creative and fast off the mark with new designs, production advantages and user benefits of comfort, abrasion-resistance and durability, and you have a material that outperforms all others.

° Thermoplastic, rather than microcellular polyurethanes offer footwear manufacturers a material with high impact resistance. This is especially suitable for applications such as sports plates for soccer, golf and baseball shoes; skates and ski boots; top pieces for lady’s fashion shoes; and molded heels for women’s shoes. Utilizing Huntsman’s new soft grade of TPU, you can create unique designs for high performance casuals soles.

Huntsman is the only major global supplier that has developed a range of TPU dedicated to the footwear industry. This premium shoe soling material is marketed under the AVALON brand.

Patent leather was invented in the 1790s. Before this, shoes were made shiny by painting them with linseed oil.
Huntsman is committed to remaining the innovator in PU-based materials for footwear, offering manufacturers tremendous flexibility in meeting the needs of their market. Huntsman Polyurethanes was a pioneer of MDI* technology and is now one of the world’s leading producers of advanced material used in performance soling.

Polyester-based prepolymers are at the heart of the Huntsman offering to the footwear industry. However, to help producers differentiate, novel polyether-technology is being developed based on a new family of prepolymers like the ‘Suprasec®’ 2444 prepolymer. This material combines the traditional strengths of both polyether and polyester-materials without the use of CFCs.

Shoe soles made using the new ‘Suprasec’ technology achieve particularly good aesthetics with a natural look and feel and excellent surface definition. The material also provides superior flex life and high hydrolysis resistance. Other benefits include low temperature characteristics and better slip resistance (‘Suprasec Rubberlike’).

‘Suprasec’ polyether technology simplifies production logistics: only one prepolymer is needed for both polyester and polyether applications. The material is suitable for use in all types of footwear production from unit soles, midsole wedges and sock-liners to direct injection of single and double density soles.

AVALON Duo combines the outstanding wear and flex properties of a soft TPU for the outsole with the comfort and lightness of polyurethane for the midsole. It represents a superb alliance of design, performance and comfort.

Benefits

Design
- Perfect surface definition
- Matt, shiny and glossy effects
- Wide color range

Performance
- Excellent abrasion resistance
- Cold flex properties
- Slip resistance

Comfort
- Shock absorption
- Lightweight
- Thermal insulation

Plus
- Good adhesion to upper
- Anti-static optional

Applications
- Unit soles
- Casual shoes
- Safety footwear
- Hiking boots
- Sports shoes

The AVALON Duo technology has been designed to ensure perfect adhesion with polyurethane to offer robust and cost-effective processing.

Test AVALON Duo on your site or use our dedicated footwear prototyping facility.
**Working feet**

Whether they are cowboy boots, wellington boots, or boots for the construction site, working feet require footwear built to withstand very specific environments. International standards for safety shoes are very precise and polyurethanes meet the requirement for resistance to abrasion, oil and solvents, while providing excellent resistance to slip and flexural fatigue.

In recent years, the work shoe has become more sophisticated with aesthetics providing a user-friendly balance to the primary consideration of function. The expanded structure of microcellular polyurethanes means that they are almost three times lighter than other elastomer soiling materials and molded soles can be produced in a wide range of colors. Today’s working man and woman can now enjoy softer grades of shoe soles with a higher level of comfort, thermal insulation and energy absorbing properties.

In the manufacturing process, shoe soles can be direct molded onto uppers. If the bottom of the sole requires enhanced mechanical properties, a thin layer of almost compact polymer is molded in combination with a midsole to create a dual density sole which is light, comfortable and hard-wearing.

A recent development has been the introduction of AVALON TPU to further improve durability for demanding applications (AVALON Duo concept). This option even allows for release agent free manufacturing.

<table>
<thead>
<tr>
<th></th>
<th>Rubber</th>
<th>Suprasec PU</th>
<th>AVALON 65 AE</th>
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<tbody>
<tr>
<td><strong>Electrical resistance</strong> MΩcm</td>
<td>ca 70</td>
<td>ca 70*</td>
<td>ca 90*</td>
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*ESD optional

**Wellington boots made from polyurethane save energy!**

If you walk a mile in the lighter polyurethane boot, you will save enough energy to haul up a 10 litre bucket of water from the bottom of a 30 meter well.

**AIMED PRIMARILY AT THE CONSTRUCTION, AGRICULTURAL AND COLD STORE WORKER, POLYURETHANE WELLINGTON BOOTS OFFER GOOD FLEX PROPERTIES RIGHT DOWN TO LOW TEMPERATURES; TOUGH, HARD-WEARING, IMPROVED ANTI-SLIP OUTSOLES; OIL, MICRO-CHELAR AND HYDROLYTIC RESISTANCE; AND INSULATION OF BOTH FOOT AND LEG, WHICH IS PARTICULARLY IMPORTANT IN THE COLD STORE SECTOR. WELLINGTON BOOTS ARE PRODUCED ON PURPOSE-DESIGNED HIGH OR LOW PRESSURE MACHINERY WITH SEPARATE INJECTION OF LEG AND SOLE.**
For leisure shoes, which have become more comfortable and colorful over the years, polyurethanes have developed as the material of first choice because of the range of colors and design effects that can be achieved using them. Manufacturers can also meet the demand for soles that are very soft, flexible, and elastic, using polyether-based formulations to produce soles with hardness values down to 40 Shore A.

When elegance is a prime requirement, such as the production of women’s shoes, polyurethanes assure superb finishes—mainly self-skinned foam, based on polyether polyols—and smooth or leather-like surfaces, coupled with excellent ‘paintability’ using spray technology. Thermoplastic polyurethanes provide an added dimension, being ideal for ‘pin top’ and ‘autolok’ top pieces, heels and inserts for leather units. Superior durability and perfect surface definition of softer TPUs are leading to an increased usage in high quality casual shoes as alternatives to rubber.

The original shoe obsessive was Marie Antoinette who had a pair for every outfit; so many in fact that they had to be catalogued to allow servants to find a particular pair. She, and all the other shoe enthusiasts, bear testimony to the art of the shoemaker and reflect people’s eternal desire to leave a very individual footprint in the sand of today’s society.

In today’s society, with its broad range of lifestyles, quality footwear ranges from the classic to creative; from tooled leather brogues to translucent plastic sandals. High quality men’s shoes, women’s shoes and general leisure shoes all benefit from the versatility of polyurethanes.

Quality men’s shoes require high mechanical properties like elongation, tear strength, abrasion and flexural fatigue resistance. All of these properties are attained using polyurethanes and their resistance to flexural fatigue down to sub zero temperatures has made the technology a favored soling material for cold climates.

Huntsman Polyurethanes offers ‘top level’ technology combined with polyester and polyether-based systems. Personalized formulations can be developed to suit the required application.
THE FORERUNNER OF TODAY’S HIGH-TECH SPORTS SHOE WAS THE GYM PLIMSOLL, INVENTED IN THE LATE 18TH CENTURY WHEN RUBBER WAS FIRST INTRODUCED AS A SOLEING MATERIAL WITH A CANVAS UPPER. THESE TWO MATERIALS WERE SEALED WITH A CONTRASTING STRIPE REMINISCENT OF THE SAMUEL PLIMSOLL LOADING LINE ON SHIPS – HENCE THE NAME. SINCE THOSE DAYS, SPORTS SHOE CONSTRUCTION HAS COME ON BY LEAPS AND BOUNDS TO THE EXTENT THAT, TODAY, YOU CAN BUY A SHOE THAT HAS BEEN SPECIFICALLY DESIGNED TO MEET THE REQUIREMENTS OF YOUR PARTICULAR SPORT. WITH ADDED FUNCTIONALITY, HAS COME GREATER AESTHETICS, AND THE HOP, SKIP AND JUMP OF THE SPORTS SHOE FROM THE ARENA TO THE HIGH STREET.

In this footwear sector, competition focuses on performance, fashion and cost. Polyurethanes provide a competitive advantage to the manufacturer through their unique capacity to be reformulated to meet the exact application requirements of each sport.

Serious sports enthusiasts and professionals require footwear which will both protect and enhance performance. Microcellular polyurethanes are the ideal material for producing high quality midsoles, which reduce the risk of leg joint and muscular injury without impeding performance. In addition, the ability to encapsulate inserts within the mold has allowed leading sports shoe manufacturers to enhance cushioning by inserting energy return devices into the midsole.

Unlike alternative materials for midsoles, polyurethanes can be adjusted to suit the application, and offer the best compromise between damping and elasticity. Outsoles made from polyurethanes are also widely used and new formulations are being developed to improve abrasion resistance and provide better grip on wet surfaces.

Using the direct injection process, the shoe maker can also adjust the color, density and hardness of the sole and produce multi-layer soles (three colors and densities) in one step, on a single machine.

An area of special application is the field of ski boots and in-line skates. Here, thermoplastic polyurethanes are used to mold the entire shell to provide a flexible and high impact resistant structure. Another major outlet of TPU is in sports plates, primarily for soccer and golf shoes. A special formulation ensures that it retains its properties at low temperatures.

In today’s highly competitive sports shoe environment, the adaptability of polyurethane materials for automated production gives the shoe manufacturer improved output and reduced labor costs.
Global offer with local support

Wherever our customers are located, they will benefit from our global strengths in research and application development.

Long term research activities are based in Belgium, where scientists liaise closely with marketing teams and customers to ensure that technological developments keep pace with market needs. Base products from Research and Technology are developed by strategically located Regional Centers to create new formulations meeting industry-specific requirements.

At a local level, Huntsman Polyurethanes works in partnership with customers through dedicated footwear teams, whose specialists visit factories regularly to advise on ways of improving system performance and reducing manufacturing costs.

Huntsman Polyurethanes has set itself rigorous targets for improvement in all environmentally-sensitive areas of polyurethane production. It is implementing CFC-free technology for polyurethane foams globally, managing its processes more efficiently, developing recyclable materials to reduce waste and taking steps to reduce CO2 emissions in production processes.

As a supporter of Responsible Care, the international chemical industry initiative, the company is committed to improving all aspects of environmental, health and safety activities.

Expert scientific and technological support is available free from Huntsman Polyurethanes to help designers and manufacturers select the chemical components, formulations and processes best suited to achieve specific physical and mechanical characteristics in footwear.

email footwear@huntsman.com

GLOBAL PROTOTYPING FOOTWEAR CENTER

The global development center for footwear applications is located in Everberg in Belgium. The headquarters houses some of the most advanced research and prototyping facilities, enhanced by a proven expertise in PU and TPU.

The facility highlights the versatility and breadth of the ‘Suprasec’ PU and AVALON TPU portfolio with a range of processes, including PU injection and casting and all TPU/PU combinations.

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Most shoes take 25 days to make and involve more than 25 people in the process.
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