

*Two-density PU boots.*

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Footwear Fundamentals

Versatile PU

Polyurethane is a remarkable material; it can be found in the mattresses we sleep on, the chairs we sit on, the cars we drive, the lap-tops we work with and the shoes we wear. To almost everyone it is just another plastic and, to a certain extent, this is probably true in regard to most people working in the footwear industry unless directly involved with it on a day-to-day basis. So, just how much do you know about this versatile material?

BACKGROUND

Polyurethane is the result of a polyaddition (step-growth) reaction between diisocyanate and diols discovered by Otto Bayer in the late 1930s, who is now regarded as the father of the polyurethane industry. The first commercial applications of polyurethane polymers appeared after the end of World War II and were millable elastomers, coatings and adhesives. By the late 1950s, both flexible and rigid foams were available

leading to the use of the material in the huge range of products and applications we see today.

It is produced commercially by creating a chemical reaction between molecules which contain two or more isocyanate groups with polyol molecules having two or more hydroxyl groups. The vast number of polyurethanes now used are created by combining a relatively small number of basic isocyanates with a much broader range of polyols possessing different molecular weights and characteristics. This simple fact is why polyurethane can be regarded as the most versatile of all plastic materials.

A further strength is that, unlike most other plastic compounds, the properties of the final product can be controlled or changed during the actual production process. This is made possible by the nature of the process itself whereby the component chemicals are mixed and then allowed to react. Changes in the balance of these components or the introduction of additives enable varying

end polymers to be produced.

Further fine tuning is made possible by altering mixing conditions and ratios such that colours, for instance, can be quickly changed as required. The fact that the final polymerisation process then immediately takes place is what gives the material its versatility and, coupled to its excellent physical characteristics, has directly led to its use in so many industrial applications and products.

SOLING

Since its introduction in the late 1960s, polyurethane has established itself as a major alternative to traditional soling materials such as leather and rubber. Here it competes against other plastics such as thermoplastic rubber, polyvinyl chloride, ethylene vinyl acetate, nylon, thermoplastic urethanes and other polymers. Its big advantage however is that it combines excellent physical properties with light weight to produce footwear that is both extremely durable

and comfortable to wear. It now accounts for over 7% of all soling materials used and, while this may appear surprisingly small, it must be remembered that a major proportion of global footwear output is still low cost sandals and flip flops.

The principal footwear application is as microcellular compounds used to produce single or dual density soling, either as unit soles or by direct moulding onto the lasted upper. The compounds used can be based on either polyester or polyether polyols, with the former being dominant. They are also used to produce midsoles, which can be made as a separate unit for subsequent bonding to the sole and upper in a two-stage operation or by direct moulding to attach a vulcanised rubber or TPU outsole to the shoe bottom.

POLYESTER PU

Polyester PUs offer the best physical properties but are more difficult to process and handle due to the fact that most urethane grade polyester polyols are either solid or highly viscous at room temperature and therefore require thawing and preheating prior to use. The moulding process itself involves similar steps and needs special processing equipment, adding to an high material cost. Polyester products are also hydrolytically unstable and, under some conditions, subject to microbial degradation.

Polyester PU is therefore more susceptible to deterioration due to hydrolysis (the chemical action of water) whereby it gradually loses physical properties if stored or used in moist conditions. This water does not need to be in liquid form and the culprit is more usually water vapour present in humid air. The process causes breakage of the polyurethane molecular chain and, in seriously affected material, may show obvious weakening and softening, or to even crack and crumble (*Figure 1*).

The degree of deterioration depends on temperature, humidity, exposure time and whether the soles are in contact with any materials that can act as catalysts and accelerate the reaction. In temperate conditions it can be several years before a sole deteriorates to a critical level. Breakdown is much quicker in warmer

climates or under more challenging usage when a sole can be significantly weakened within 12 months. Even in temperate climates, soles may suffer if stored in warm conditions, particularly in confined spaces without ventilation if still damp from use. While more hydrolysis resistant polyether PU would be less affected, its inferior abrasion and oil resistance render it less suitable for industrial footwear which is where the problem is most prevalent.

The reason this deterioration occurs lies in the chemical reaction used to create the material in the first place, where a diacid reacts with a hydroxyl-containing compound to produce hydroxyl-polyester and water. These are held in balance, so the water must be removed in order to produce the final compound. Exposing it to moisture for a prolonged period simply causes a reverse reaction.

Polyester PUs were traditionally stabilised against hydrolysis by adding from 0.5-2.0% carbodiimides and/or polycarbodiimides. The main disadvantage of this approach was that it is essentially a temporary solution where the effect is limited to the volume added which, in turn, is controlled by cost and impact on the properties of the PU itself. The past ten years have seen new polyester systems where, instead of containing additives, the building blocks forming the backbone of the polyol have been modified so that the steric effect (spatial arrangement of atoms in each molecule) and reduced hydrophilicity (capacity to absorb

water) of the polymer chain protects the ester bonds from water attacks. The resulting materials are more hydrolysis resistant and generally also have enhanced tensile, tear and flex fatigue properties.

The quest to use renewable materials wherever possible has led to another approach to the hydrolysis problem where dimerised fatty acids are used in the formulation of the polymers. Based on soya bean oil or tall oil (a by-product of timber pulping), they have an irregular structure consisting of a large number of isomers and carbon atoms that makes them extremely hydrophobic. When dimer-based polyester polyols are used instead of conventional esters in PU systems, the hydrophobic nature, closed cell structure and high molecular weight of the dimerised fatty acid result in greater hydrolytic stability, microbial resistance and increased sole life. Being plant derived, the technology is also safe, sustainable and not directly influenced by oil prices.

POLYETHER PU

Polyether PUs, on the other hand, are typically low viscosity allowing easier handling and processing, and makes them equally suitable for both low and high-pressure processing equipment. They are also hydrolytically stable and not subject to microbial degradation. In general, the material and processing costs of polyether technology are considerably lower compared to polyester. Its main disadvantage,



Fig 1 – Serious deterioration of a sole due to hydrolysis.

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Figure 2: Typical Physical Properties of Polyether versus Polyester Soling Materials

Type of PU	Blowing Agent	Molded Density (gr./cc)	Tensile (psi)	Elongation at Break (%)	Die "C" (pli)	Hardness Shore A	Taber Abrasion mgr. loss
Polyester	Water	0.50	900	600	150	55	40
Polyether	FREON 11	0.50	540	410	100	55	75
Polyether	Water	0.50	500	400	90	55	150
Polyether	HFC 134a	0.50	450	425	55	75	190

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however, is that it provides inferior physical properties compared to polyester (Figure 2).

While the data shown here indicates that the physical characteristics of polyether are typically lower than polyester, they do appear to meet the basic requirements for the majority of applications as far as footwear soling is concerned. The exception is the abrasion resistance of its outer skin which, unless enhanced through additives or other techniques, is barely sufficient even for casual footwear. The problem has always been how to bring it up to an acceptable level for more demanding footwear applications.

Chlorofluorocarbons (CFC) and hydrochlorofluorocarbons (HCFC) used as blowing agents did, before they were banned, increase surface density enough to give an acceptable level of abrasion resistance. Legal alternatives such as hydrofluorocarbons (HFC) and hydrocarbons provide similar characteristics but, due to cost (HFC 245fa), flammability (pentane) or solubility (HFC 134a), their scope is limited. A further concern is that as soon as the skin is abraded, the core still lacks the desired durability. The advantage of water-blown polyurethane is that the core is almost as tough as the outer surface, which results in more uniform wear.

Abrasion resistance can also be improved by the use of solid fillers and waxes, such as fine particles of alumina and silica. However, a relatively high content is needed and this has a negative impact on other physical properties. Synthetic waxes including polyethylene (PE) have produced better results but their relatively low density, melting point and poor slip resistance also proved limiting.

A better solution was found in polyethylene/polytetrafluoroethylene (PE/PTFE) copolymers that have density ranges closer to the resin blends themselves. The combination of higher density and small particle size with PE/PTFE powder (typically less than 10 microns) allows fine dispersions to be produced that are dimensionally stable and do not require special handling or processing. The amount of PE/PTFE copolymer required has proved to be remarkably small as an addition of only 1% by weight based on total system composition improved abrasion resistance by over 75% (Figure 3).

By gradual developments such as these, polyether systems have become a viable alternative to polyester ones in many more soling applications and enabled manufacturers to exploit the lower cost, easy handling and processing, and hydrolytic and

microbial stability of this polyether technology. The sheer diversity of potential for PU polymers continues to be exploited in footwear and this has brought them into use for more than just their hard wearing properties.

PU FOOTWEAR

The microcellular nature of blown PU makes it lightweight and the lower the density, the lighter it obviously becomes. Indeed, the maximum density at which blown PU can be effectively processed is 280kg/m³. The same microcellular structure also means it is an excellent insulator that is particularly effective in cold conditions down to as low as -30°C. Technical advances in recent years by moulding machine manufacturers have now enabled complete boots or shoes to be moulded using two densities of PU (Figure 4).

The first application has been to produce Wellington boots for industrial and agricultural workers required to spend the whole of their working day in cold, wet and otherwise adverse conditions. Increased comfort is obviously beneficial as it reduces fatigue and helps to improve performance. At the same time, it is of course essential that safety standards are not jeopardised. PU boots can do this in several ways.

Figure 3: Physical Properties of Polyether Polyurethane with and without Additive

Blowing Agent	PE/PTFE Additive (%)	Molded Density (gr./cc)	Tensile (psi)	Elongation at Break (%)	Die "C" (pli)	Hardness Shore A	Taber Abrasion mgr. loss	Ross Flex KC to Fail (-20 F)
HFC 134a	1	0.50	475	550	85	55	45	>100
HFC 134a	0	0.50	450	425	75	55	190	>100
Water	1	0.60	610	420	110	63	37	>100
Water	0	0.60	600	400	100	63	153	>100

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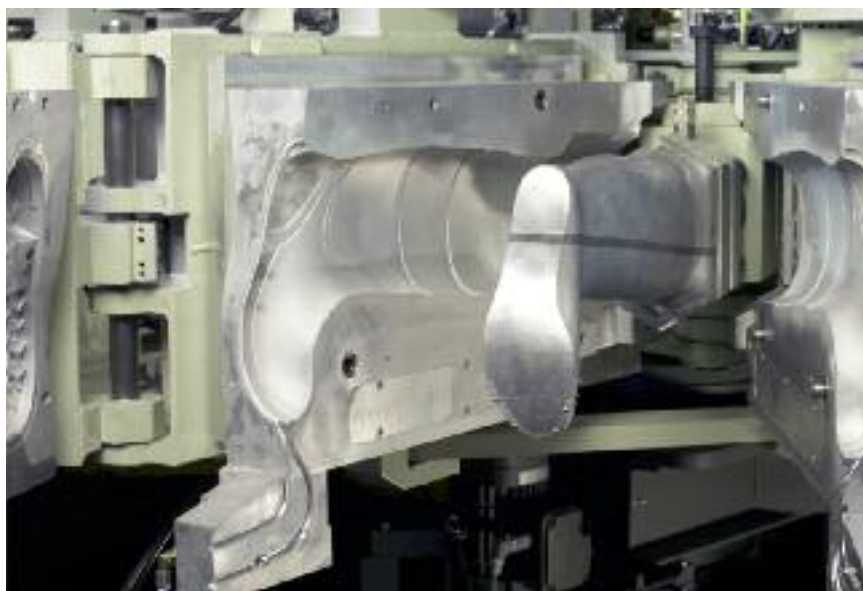


Fig 4 – Four-part mould mounted horizontally are used to produce PU boots.

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To begin with, they are at least 40% lighter than conventional PVC or rubber boots. PU's excellent thermal properties also enable them to be worn in a much wider range of environments. Due to further

developments in PU systems, they can also have excellent resistance to all the normal chemicals, oils or acids found in industry. As regards safety, the key factor is slip resistance in wet conditions. Combining a correctly

formulated PU and a good tread pattern on the outsole gives excellent results, particularly if the latter is designed such that any dirt comes away quickly and easily. There is also the possibility to produce them in limitless colour combinations so that they can be matched to company overalls.

Wellingtons can now be produced entirely from PU in a one step process which uses one density for the main body of the boot and another for the sole. Alternative outsole materials, such as pre-moulded rubber inserts for very wet conditions or TPU where a higher abrasion resistance to that of standard PU is required, can also be incorporated. This multifunctional ability has opened new possibilities for boot producers to widen their ranges and at the same time lower manufacturing costs. The extraordinary versatility of polyurethane appears to have no limits and the material will doubtless find further applications in footwear manufacture in the future. 

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 Not making a style - setting a standard
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Lace Designer, 2011/12

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