



Polyurethane has high performance capabilities for footwear

CREDIT: BAYER MATERIALSCIENCE

POLYURETHANE HAS SO MUCH TO OFFER

In his address to the 2009 CPI Conference, leading soling material consultant Steve Lee of Steve Lee Associates remarked that polyurethane has failed to increase its market share beyond the six percent it has held for the past few years. Clearly, the global economic downturn has hit footwear product overall but, considering all the plusses that polyurethane has as a soling material, this still comes as something of a surprise.

Two things could be starting to move in its favour however. First, there is the growing need for smaller batch production of more extensive ranges, with ultra-fast delivery times. The second is the increasing consumer awareness of the carbon footprint resulting from producing goods in low labour cost countries and then shipping them halfway round

the world. The answer to both is flexible automated production systems closer to the selling point, allied to a careful choice of the materials used.

DESMA of Germany has already pointed the way forward as far as automation is concerned with its amir system which produces good quality shoes consistently at a minimal labour cost. Other companies are developing ever more 'greener' polymers and colourants. The ideas put forward by some of them at this Center for the Polyurethanes Industry conference show just how versatile polyurethane is in terms of footwear manufacture. A better understanding of the potential benefits that this versatile material has to offer for manufacturers and consumers will hopefully help it to increase its market share sooner rather than later. 

Green colour carriers for PU soles

Giorgio Rolla and Donato Bargigia, REPI SpA, Italy

Pigment dispersions are the most common way to add colour to polyurethane elastomers and phthalate plasticisers, the carrier used. Unfortunately, phthalates are endochrines which can be harmful to the body (especially children) and, as a result, are likely to become subject to strict legislation in the future. There is an urgent need to find an equal and economical alternative, so REPI has carried out a programme of laboratory tests to compare the performance of conventional phthalate-based dispersions with a range of potential 'green' carriers.

Phthalate plasticisers have been popular due to the fact that their very low viscosity combined with a suitable dispersing agent allows a good addition and dispersion of colour pigments over a viscosity range of 500-2500 cps (centipoise or metric unit of dynamic viscosity) at 20°C. This low viscosity makes the dispersion method particularly suitable for direct dosing into the mixing head on standard casting machines. Direct injection machines need a slightly higher viscosity and this can also be achieved by simply reformulating the dispersion.

Furthermore, phthalates have provided a cost effective method that also maintains a high level of quality provided the correct phthalate carrier is chosen. They are also inert components, so no particular formulation adjustments are necessary, which makes them easy to use.

PHTHALATES AND REACH

Recent years have seen increasing concern regarding the toxicity of certain phthalates. Some are now considered unacceptable and a number of companies have begun to avoid these types of products fearing that sooner or later all phthalates could be banned.

The major drivers that have led REPI to develop an effective alternative have included improving environmental aspects and REACH (Registration, Evaluation and



ALL CREDITS: REPI SpA

Authorization of Chemicals) requirements. REACH is a system created in the EU to monitor chemical products throughout their life cycle. In addition, there will soon also be GHS (Global Harmonised System) in place to examine all Substances of Very High Concern (SVHCs).

VEGETABLE OIL BASED DISPERSIONS

The meaning of the expression 'green' has been exhaustively covered already in various articles and publications and many meanings have been listed. Our definition is 'materials derived from natural products that reduce the use of petroleum-based raw materials and, in the end,

result in less global emissions'. REPI has succeeded in developing two lines of green colours. While one is still based on a phthalate-free plasticiser, the other is based on vegetable oil (BIO).

The major chemical difference between using a vegetable oil-based carrier rather than a phthalate is represented by the presence of OH (hydroxyl radical*) groups that can vary with the type of oil used and so merely require small formulation adjustments. The molecular weight of vegetable oil is also higher than that of phthalate plasticiser, so VOC (volatile organic compounds as defined by the EC Solvents Emissions Directive) emissions are minimal.

DEVELOPMENT

These BIO-based dispersions required specific chemical developments in order to create the three main colour groups – black, white and the full range of all other colours. Black and white comprise the largest volume used in PU footwear either as single products or when blended with primary colours to create specific shades.

While REPI as a manufacturer of pigment dispersions needs to cover the entire colour range, the greatest attention

Figure 1: UV TESTS

CIE LAB	REFERENCE	50 h UV EXPOSURE (SUN TEST)	
		BIO BASED	PHTHALIC PLASTICISER
L	62.51	75.83	77.7
a	-0.66	-1.75	-1.93
b	-0.56	15.77	17.31
Yellow index (db)		16.33	17.86

was initially paid to black. This is not only the most frequently used colour but is often also the most critical pigment as the right choice of carbon black is essential in maintaining all the various grades of black that are involved. These grades must all be pourable and pumpable whatever the various carbon black concentrations.

White pigment dispersions, on the other hand, generally have a higher viscosity. The level of titanium dioxide used to produce white pigment can be as high as 70% of the total formulation while still maintaining good flow characteristics. Having successfully formulated black and white, the development of a full colour range presented few extra problems and the same ample range of shades available in phthalates is now also available BIO-based.

One particular challenge that did arise was when UV stabiliser blends were incorporated in the same formulation of pigment dispersion. The table in Figure 1 shows the comparative results obtained from exposing a UV stabilised phthalate-based white dispersion and a BIO-based version.

The important value to note is the Yellow Index where the Bio-based dispersion is shown to give a slightly better performance compared to the phthalate version.

PERFORMANCE

Shoe soles coloured with BIO-based products have been evaluated for physical mechanical properties. Figure 2 shows

Figure 2: EVALUATION OF VEGETABLE OIL BASED BLACK

Test	Neutral	Black 99350	Black 99672
Addition rate %		3%	3%
Hardness ShA°	44	44	45
after hydrolysis 7 days	44	45	42
Tensile Strength (N/mm ²)	5.6	5.7	4.8
after hydrolysis 7 days	5.8	5.7	5
Elongation at break (%)	394	391	365
after hydrolysis 7 days	419	428	406
Flex test 30 kC thick 8 mm (mm)	3.3	2.8	2.4
after hydrolysis 7 days	2	2	2
Tear strength (N/mm)	4.7	4.6	5
Abrasion (mg)	141	224	51
Loss of Hardness 7 days	0	0	0
Tensile Strength Retention 7 days	104%	100%	104%

typical values under hydrolytic ageing conditions where no significant differences are noticed with the ester formulation. Abrasion resistance results did however show a dramatic improvement.

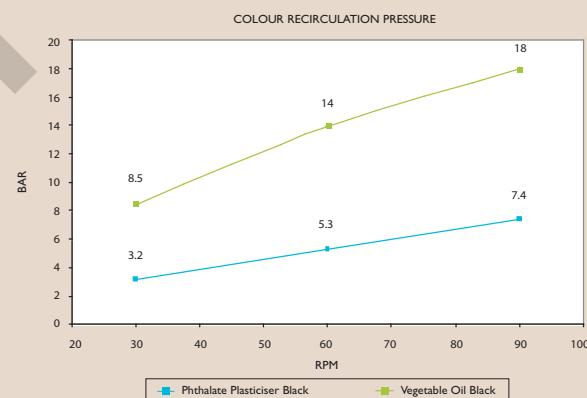
As PU-soled shoes are used in many different work environments, a particularly difficult one, automotive, was selected, where specifications on fogging emissions are tight and VOC must be held below 200 ppm (parts per million).

The test safety shoes passed VW, BMW and Mercedes fogging tests. Black Remap paste in fact showed 47 ppm when this dispersion was used at 3% addition to the polyol, the total emission contribution being just 1ppm.

PROCESSABILITY

It is important to keep a stable pressure in the colour circuit of a direct injection machine for PU footwear. Here, viscosity plays a key role. BIO-based dispersions have a viscosity of around 4000 cps so the pressure needed in the circuit has to be double that of a standard phthalate of 2000 cps. That in turn is equal to the pressure of the main components, which results in reduced turbulence when the colour meets the polyol and isocyanate components in the mixing head. This is perhaps best explained by a graph (Figure 3).

Figure 3: PROCESSABILITY



BIO-based colour dispersions offer a number of advantages to footwear manufacturers. They can be used with both polyether and polyester systems on conventional dosing equipment. They improve material flow characteristics and create a good foam structure. They are easy to store and handle. They are also free from harmful phthalate carriers, non-toxic, derived from a renewable raw material resource and are environmentally friendly.

In the steady 'greening' of industry, they can help the footwear industry in particular to play its part. 🌱

* Radicals (or free radicals) are atoms, molecules or ions with unpaired electrons. These are usually highly reactive and so form an important part in many chemical reactions.



DESMA TPU processing unit. ALL CREDITS: DESMA

Innovative colour dosing for TPU

Christian Decker and Bjoern Dorman, DESMA, Germany

The market trend towards 'Mass Customisation' for almost all consumer goods means bigger ranges, smaller unit volumes and higher production costs. This has created problems for footwear manufacturers using direct injection moulding systems where the larger the volume, the greater the efficiency. The process of colouring TPU for this type of soling construction is one of the most expensive processes in modern shoemaking, so a way to speed it up and reduce waste would be a welcome development.

The new DESflow TPU colour dosing unit has been developed to do just that. It overcomes these problems by injecting liquid colour into the TPU during the plasticising phase immediately prior to the mould being filled and removing the need for pre-coloured granules. Quantity is metered at a constant percentage and up to four different colours can be interchanged. It also offers good material distribution within the mould cavity, optimal colouring of the finished sole and considerable cost savings:

- One neutral colour base TPU stock as against four separate ones
- Five to ten minute colour changes rather than 15 to 60 minutes
- 0.5-4.5kg waste per colour change compared to 10-50kg

TPU TECHNOLOGY

The standard DESMA injection system is the DESflow process shown in the header image. It works by pouring hot liquid TPU on the bottom plate of the mould cavity and then pressing it into the edges of the mould. This avoids the use

of runner channels which can create frictional heat and affect the heat-sensitive TPU compound. It also reduces the amount of waste they create as well as the clamping required, making it possible to use cheaper aluminium moulds. Flow marks are also lessened due to the improved pre-distribution of material within the mould.



Casting by the DESflow process.

PROCESSING COLOURS

The traditional method has been to use pre-coloured granules for direct processing on the machine without any further additive. This involves buying in pre-mixed masterbatches from a supplier or making them in-house with tumbler or big mixing bins. A more recent improvement has been to colour the material directly at the machine with either solid or liquid colours, using different types of pump.

Colour intensity depends on the amount of pigment added and the amount of additional colour, and on the type

used. The following standard values can be taken as a general guide:

- Colour granules 1.0 to 4.0 %
- Colour pastes 0.5 to 1.0 %
- Colour pigments 0.2 to 0.5 %

All existing techniques waste time and material due to the fact that the feeding units containing the coloured material have to be emptied before the process can be restarted with a new colour. If the masterbatch method is used with liquid or solid colours, the whole injection unit must be cleared from the feed hopper via the screw to the injector nozzle. This in turn requires special clearing granulates to guarantee that the edges of the screw and nozzle are really clean. Any small amount of pre-used colour will contaminate the next colour run in the form of thin stripes or shading and expensive rejects.

The average 30 minutes needed to make a colour change has also been a clear argument for less or optimised colour changes. Any interruption of production costs money. Today's thermoplastic injection machines do not need an operator but, for colour changes, they become essential. Changing colours is therefore expensive.

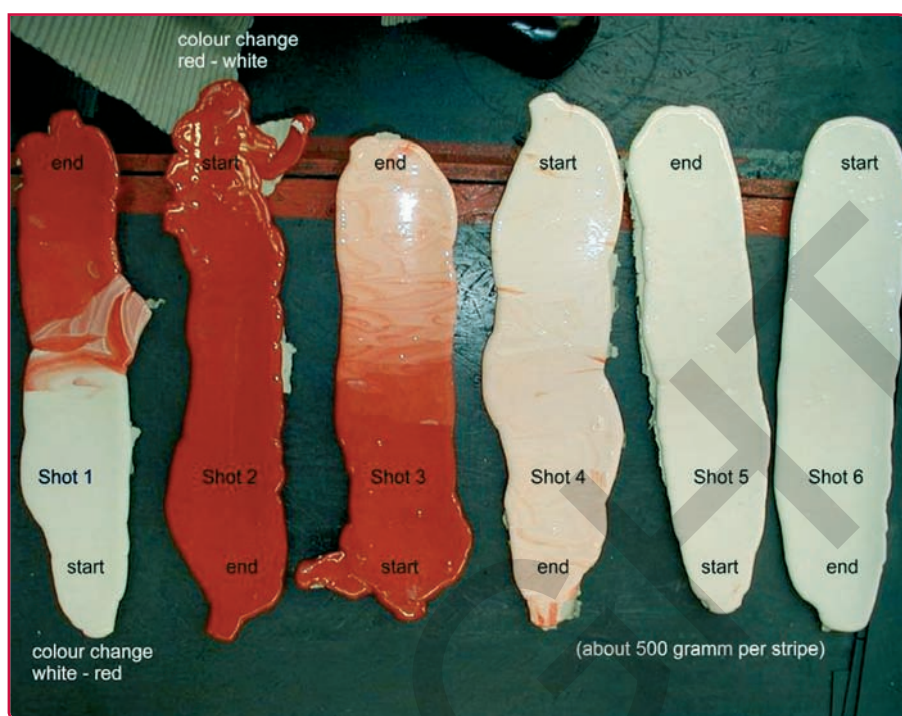
TWO INJECTORS

One way round this is to use a second injector. This is a good solution if colours are strictly limited and production is scheduled such that either injector has a regular injecting time. If this cannot be guaranteed, the properties of the TPU will vary due to different heating and waiting times between individual shots. If it can, smooth two-colour production will be achieved but at the cost of a second injector.

DESFLOW METHOD

The principle is to dose the colour at a point nearest the mould cavity. Neutral TPU granules are plasticised in the normal way but using a special 24D/65mm screw for smoother heating up and plasticizing. Liquid colour is injected by a specially designed and patented device which delivers the exact dose required into the hot liquid thermoplast where it is thoroughly mixed in.

Up to four colours can be installed at each injector and they are recirculated to maintain stable conditions within the pipes and hoses. The colours used are slightly modified to have a higher viscosity than would normally be used with liquid polyurethane. Even so, the actual colour injector has to withstand the pressures involved as the TPU is injected. The actual dosing stroke is coupled to that of the TPU so



Examples of colour change.

that there is always a precise amount of colour added.

With an accurate calculation of the necessary part volumes, material loss can be reduced to between 250 and 400 grams depending from which colour the change starts. Let us take a colour change from white to red and then from red to white as shown in the above image. From white to red, experience suggests around 350 grams, while the other way round, it is likely to be nearer 1500 grams. The time taken depends on the capacity of the injector; a standard DESMA injector with a screw diameter of 65mm takes between 20 and 240 seconds.

Each strip weighs about 500 grams and needs about 15 seconds to be poured. Changing colours such as red and white is therefore extremely critical. Standard colours such as black, brown and dark green will be faster and less wasteful. The following table compares existing TPU colour change possibilities. Results for the DESMA TPU colour system in the final column show that there are some significant advantages to be gained with this new system. 🔄

	Pre-coloured thermoplastics	Liquid or solid masterbatch	Twin TPU	DESMA TPU
Low material usage	--	--	+	+
Changing time	--	--	++	++
Machine investment	+	-	--	-
Maintenance cost	+	-	--	-
Material cost	--	-	-	+
Material storage cost	--	-	-	+
Colour quality	+	-	-	++
Cleaning time	--	--	--	++
Labour cost/change	--	--	--	++



Examples of colour change.
CREDIT: US ARMY

Marching on PU

David Schulte, Kurt Walter, Ulrich Holeschovsky
BayOne Urethane Systems, USA

Performance is paramount in military footwear, so nothing can be left to chance. One reason why all military equipment is so expensive is the amount of research and development that goes into design, materials, construction and the search for new and improved technologies.

The performance of the outsole on a military boot, for example, is clearly critical in regard to traction, wear and overall efficiency. While the days of studded leather soles and simple direct vulcanised rubber soles have long since gone, the latter in the form of highly sophisticated compounds has remained the soling material of choice. Could this be about to change?

One drawback with rubber soles is the degree of work involved in both producing them and then attaching them securely to the lasted upper. The latter in particular involves careful preparation by the roughing or chlorination of the moulded surface of the sole followed by application of adhesive and by attaching under strictly controlled pressure and dwell parameters or manual loading into a sole mould to be bonded to the upper by direct injection of a PU midsole.

The more processes involved, the higher the cost, the greater the chance of a quality issue occurring and, as a result, even more cost due to additional quality controls. An alternative material that equalled or excelled rubber in terms of performance and was also easier and cheaper to process would clearly have much going for it.

FINDING AN ALTERNATIVE

BayOne decided to approach this challenge by tackling one of the toughest military soling applications going, specifically the hot weather combat boot as specified under Milspec MIL-DTL-32237 [1] with a new polyether urethane system called Bayflex 3017. The reason for choosing this system was that the properties of urethanes made with 3017 are significantly better than more conventional polyether systems through having superior physical properties, higher abrasion resistance and greater resistance to chemicals. It is in fact very similar to a polyester urethane in this respect. However, unlike polyester, it has all the advantages of a polyether urethane's lack of hydrolysis, resulting in good

“...as a matter of fact...”

MilSpec specifications for US military footwear are as tough as the troops who will wear it. A typical example is that for Hot Weather Combat Boots which come in two types: type 1 for wet conditions and type 2 for dry environments. Both are covered by thirty-six full pages of materials specifications

and construction details. In addition, all boots made under US Department of Defence contracts are held to strict military specifications adhering to ASTM, ISO and Satra standards. Furthermore, quality assurance representatives separately inspect, approve and purchase each part order.

storage stability and better retention of physical properties under humid conditions.

ADVANTAGES

One of the most important aspects of a military boot outsole is abrasion resistance. Rubber outsoles are generally tested using an NBS Abrasion tester according to ASTM D1630 where a 40 grit sanding wheel grinds 0.10 inches (0.254MM) from the surface. The higher the number of revolutions needed, the better the abrasion resistance. The density of the material used in an outsole also affects overall performance and a lower density urethane would allow the manufacturer to produce a lighter and more comfortable boot.

COMPARATIVE PERFORMANCE

Characteristics	ASTM/SATRA Test	RB outsole spec.	Test results
NBS abrasion	D1630	150 min	>500
Hardness shore A	D2240	70-80 A	79A
Stitch tear dry	D4786	180 lb min	277 lb
Stitch tear Fuel B	D4786	50 lb min	160 lb
Die C tear strength	D624	300 lb min	338 lb
Ross Flex, Oil #3	D1502	250% max @ 50K flexes	0% @ 50K flexes
Volume swell, Fuel B @ 46hrs 1/	D471	30% max	28-38%
Non-marking	SATRA MTM-223	Pass	Pass
Tensile	D412	2,100 lb min	2169 lb
Elongation	D412	400% min	602%

*Tests conducted at room temperature with ASTM test slabs

Another advantage gained by using a urethane rather than rubber is simplification of the shoemaking process. Both the outsole and the midsole can be produced on conventional direct injection urethane moulding machines of the type supplied by DESMA. The outsole is produced first and, once it has reached sufficient cure, the mould top plate is raised, the lasted upper brought down into the mould and the foam urethane midsole injected to join it to the outsole. There is no need for any complex preparation or adhesives, so it is simpler, faster and cheaper than traditional rubber soling and, also important, everything is done in-house.

The Bayflex 3017 based urethane tested was developed with the express intention of having much better abrasion resistance than the current [1] specification. It in fact recorded an NBS Abrasion of >500 compared to the >200 of the current rubber outsole. Life expectancy for soles made with this urethane system should therefore be more than twice that of the existing rubber ones.

The rubber compound used for the current sole has a density of 1.34 g/cm³. The 3017 urethane was moulded at only 1.08 g/cm³ so a urethane outsole the same size and with the same tread design would weigh approximately 20% less than a rubber one. A combat boot could therefore be made considerably lighter to improve comfort and also reduce foot fatigue.

The only test where the results were not well above the required specification was Volume Swell Fuel B @ 46 hrs.

Military boots are big business - US production alone exceeds two million pairs a year

CREDIT: COVE FOOTWEAR

“...and it should be noted...”

Polyester PUs offer superior physical properties but are more difficult to process and handle due to their high viscosity. They are also hydrolytically unstable and, under some conditions, subject to microbial degradation.

Polyether PUs are low viscosity, allowing easier handling and processing. They are hydrolytically stable and not subject to microbial degradation. Their physical properties are generally inferior particularly in terms of abrasion resistance.

This test gave a wide range of values on samples cut from the same quarter inch test slab. For example, some pieces gave an initial reading of 28% and, when re-tested, one of 32.5%. Lowering fuel swell unfortunately causes other properties to suffer. However, it is unlikely that boots would be exposed to fuel under combat conditions for so long a period and Bayflex 3017 would pass if it was shortened to 24 hours. Furthermore, the cold weather specification only requires a maximum swell of less 70%, so why is the hot weather boot specification that much more stringent?

Milspec MIL-DTL-32237 [1] currently only covers rubber soles and, even though Bayflex 3017 might well

meet all its rubber requirements in terms of performance, it would still need to be formally approved as an acceptable material. Considerable lobbying will need to take place as changing something as fundamental as a Milspec does not happen overnight, particularly if areas such as fuel swell were to be altered. On the positive side, abrasion properties are so much better combined with the fact that the soles are so much lighter provides useful ammunition to justify the relaxation of one small part of the overall specification. Should Bayflex 3017 prove successful, tomorrow's soldiers will have more of a spring in their step. 🇬🇧



PURE 1.0 concept shoe

ALL CREDITS: BASF

Imagine the possibilities

Limei Lu and Martin Vallo, BASF, Germany

Thermoplastic polyurethane (TPU) is well known for its excellent abrasion resistance, very good mechanical and physical properties and easy processing by injection moulding or extrusion. From late 1990 up until now, polyurethanes, including PU foams and TPU elastomers, have shown strong growth in footwear applications. Also up until now, nobody has tried to bring together a variety of thermoplastic polyurethanes to produce a shoe made completely out of PU.

Elastogran's 'PURE1.0' concept shoe has been developed to show just what might be possible for shoemaking in the future by combining TPU non-woven, TPU foam, soft TPU (plasticiser-free grade) and high moisture/vapour transmission TPU all in shoe.

CONSTRUCTION

Many different materials are used in today's footwear industry—rubber, EVA, PVC, polyurethane, leather and polyester fabrics to name but a few. Polyurethane is one that is still developing. It is also one of the materials that covers two families of plastics, thermosetting and thermoplastic, which means it can be adapted to a wide number of applications.

Polyurethane flexible foam, for instance, is a 'chemically' cross-linked material that provides comfort and flexibility. TPU, on the other hand, is a 'physically' cross-linked material that, unlike PU, can be recycled and reprocessed.

The 100% polyurethane Pure 1.0 concept shoe shown at the heading of this article has been developed using different grades of Elastopan PU foam and Elastollan TPUs to create

the non-woven, thin film, foam and super soft elastic TPU materials from which it is made.

INSOLE TOP-LAYER

The insole is in constant contact with the sole of the foot so comfort is a very important factor when selecting materials. The insole top-layer in PURE 1.0 is constructed from three layers of unique TPU materials. The top and bottom ones are from TPU non-woven produced by a special melt blown process that is breathable, flexible and elastic.

These two TPU non-woven layers are bonded together by a thin layer of TPU film made from a special high moisture vapour transmission (HMVT) grade of TPU called Elastollan LP9286. This combination provides high breathability throughout the entire insole top-layer to keep the foot feeling dry and comfortable. This top-layer is tough and flexible, can be removed for washing to keep it clean and fresh, and has a textile feel to its surface which can also be coloured and embossed as required. The same three-layer construction is also used in the heel cushion area to provide the same degree of comfort and durability.

FOREPART OUTSOLE

Weight reduction has been a popular theme in modern shoemaking. Elastollan Light was developed by adding blowing agent concentrate to regular TPU pellets and then processing on conventional injection moulding machines. The blowing agents themselves can be a physical agent, a chemical agent or a combination of the two. A physical blowing agent provides a more uniform cell structure with a nice surface. A chemical blowing agent typically results in a

“...as a matter of fact...”

Melt Blown non-woven is a one-step extrusion process in which high-velocity air blows a molten thermoplastic resin from an extruder die tip onto a conveyor or takeup screen to form a fine fibrous

and self-bonding web. The process is not only capable of producing different grades of material but also different weights of fabric web ranging from 52 to 500 grams per square metre.

more irregular cell structure and, the lower the density, the weaker the structure. It does however result in a ‘softer’ touch to the material.

These blowing agents are suitable for various TPUs in different Shore hardnesses. The average aromatic polyester TPU has a density of around 1.22 g/cm³. By adding a blowing agent, the density can be reduced to around 0.4 g/cm³. Elastollan Konz V2882—a physical blowing agent—has been used to produce the outsole for Pure 1.0 in order to demonstrate how lightweight TPU foam can provide both the comfort and durability needed for everyday footwear.

OTHER COMPONENTS

The lace system is made from Elastollan LP9316, a soft and elastic TPU which is plasticiser-free and has a hardness of 54 Shore A. This new soft TPU has good mechanical strength and physical properties coupled to high tear and tensile strength. It also offers excellent flexibility and, since it is plasticiser-free, there is no risk of plasticiser bloom.

The shoe also features a chassis to provide support and structural stability. This is made from Elastollan B60D11 because of its high physical and tensile properties. It is a harder grade of TPU but, nevertheless, still possesses excellent low temperature flexibility.

IMPLICATIONS

The PURE 1.0 concept shoe has been a valuable exercise in that it has shown just how versatile polyurethane can be in regard to footwear. The innovative TPUs involved can all be processed by various existing technologies, such as injection moulding, extrusion and melt blown, into different formats including moulded components parts, thin films and non-wovens which can be applied to different areas of shoemaking.

While this concept shoe has essentially been a technical rather than design exercise, it is quite conceivable that with the continuous innovation occurring in TPU technology, it will be possible to produce commercially viable 100% TPU shoes that are comfortable, durable and recyclable. This will in turn open the door to further developments in automation that will make the manufacture of competitively priced footwear anywhere in the world an increasingly practicable proposition. 



Every component in the Pure 1.0 concept shoe is made using TPU