

PU, a highly versatile soling material for footwear, and in particular polyester-based footwear material, has characteristics that make it suitable for many types of application. Unfortunately, it has always suffered from hydrolysis and poor resistance to ageing under humid conditions. This extract from a paper presented by Giuseppe Vairo of Dow Italia s.r.l. at the last API Polyurethane Conference reveals a new solution to the problem.

Polyester PU with enhanced hydrolysis resistance

Up to 90% of the PU elastomers used for footwear soling are based on polyester polyols, with the remainder being polyether-based.

Panel 1: Polyester vs. Polyether

Properties	Polyester	Polyether
Hydrolysis resistance	-	++
Microbial resistance	-	++
Oil/solvent resistance	+	-
Elongation, tensile & tear strength	+++	+
Flex fatigue resistance @ +20°C	++	+++
@ -20°C	+	+++

Polyether would seem to be the right choice for hydrolysis resistance and polyester to combat oil and solvents. The footwear industry, however, tends to be oriented towards modified polyester-based systems with anti-hydrolysis additives as these systems are easier to process.

WHY DOES HYDROLYSIS IN PU OCCUR?

Hydrolysis is the chemical decomposition of a substance by water. The reason for this lies in the chemical reaction used to create the material, 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. The reverse reaction, therefore, is hydrolysis of the ester bond through humidity. Polyester PUs for footwear have been traditionally stabilised against hydrolysis by adding 0.5-2.0% carbodiimides and/or polycarbodiimides.

Dow has developed a new family of polyester polymers with enhanced hydrolysis by using proprietary building blocks in the backbone of the polyol, whereby the steric effect and a reduced hydrophilicity of the polymer chain protects ester bonds from water attacks. The resulting material is thus more hydrolysis resistant and, as it doesn't require additives, offers advantages in terms of cost, processing, reliability and durability compared with additive-based technology. In addition, tensile, tear and flex fatigue properties are both better and longer lasting.

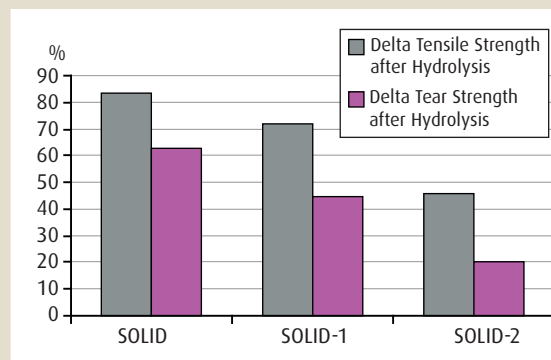
The addition of polycarbodiimides does improve hydrolysis

resistance as can be seen by comparing three solid PU elastomers—SOLID (no additives) SOLID-1 (+ 0.6% of polycarbodiimides) and SOLID-2 (+ 1.8% of polycarbodiimides).

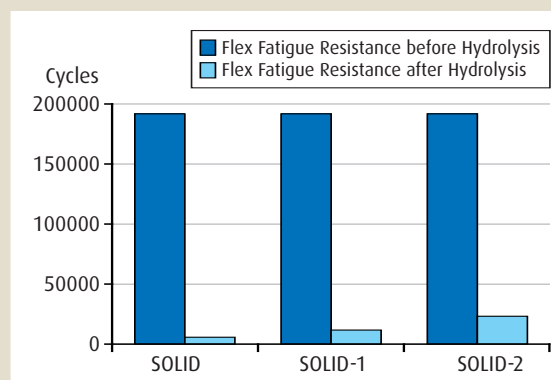
Retention of tensile strength can in fact be increased by 16 to 51%, tear strength from 44 to 77% and flex fatigue resistance from 5,000 to 30,000 cycles (respectively for SOLID-1 and SOLID-2 as shown in *Panels 2 and 3*).

The main disadvantage of the additive approach is that it is essentially a temporary solution where the effect is limited to the volume added, which, in any case, is controlled by cost and the impact on the properties of the PU before hydrolysis.

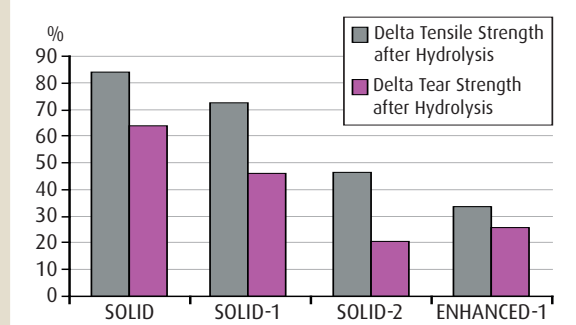
Panel 2: Percentage loss of tensile and tear properties after hydrolysis



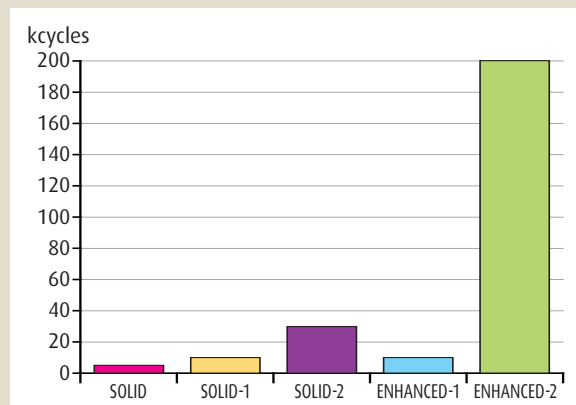
Panel 3: Drop of flex fatigue resistance after hydrolysis



Panel 4: Percentage loss of tensile and tear properties after hydrolysis



Panel 5: De Mattia flex fatigue resistance after hydrolysis



A DIFFERENT APPROACH

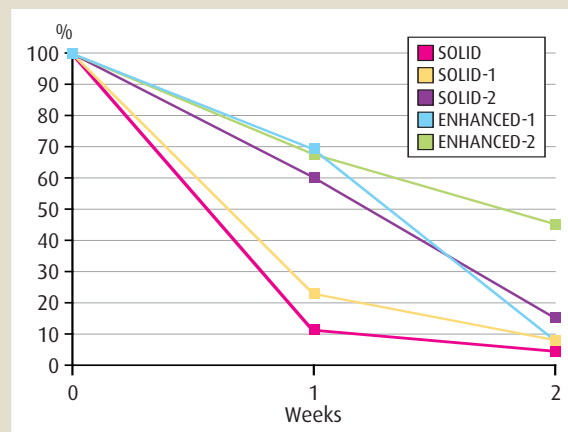
VORALAST GT enhanced polyester-polyurethanes are based on a new family of polyester polyols, containing unusual building blocks that protect against water ageing as a result of their steric hindrance and increased hydrophobicity compared with the raw materials more generally used. In simple terms, it involves creating a protective layer around critical groups of polyester molecules. It is also a well-documented fact that this will increase the hydrolytic stability of polyesters.

Several systems have been developed in order to find the best balance between properties before hydrolysis and their retention after humid ageing. Typical properties of one system (ENHANCED-1) are shown in *Panel 7*. Properties before hydrolysis are very similar to those of the control system (SOLID), while the performance after hydrolysis is definitively better than additive PU (SOLID-1 and SOLID-2). It also shows that the hydrolysis stability that can be obtained with VORALAST GT (ENHANCED-1) is very similar to that achieved using high additive systems. The ENHANCED-2 version has been designed for superior tensile and flex fatigue performance in humid conditions.

Tensile strength and flex fatigue resistance are the properties that typically suffer most through hydrolysis. They are also the ones most relevant to the overall durability of the shoe sole. Flex fatigue resistance tests on VORALAST GT using De Mattia equipment have shown up to 200 kcycles versus the five of a normal polyester-PU and between 10-30 of a system containing polycarbodiimide.

The advantages offered by these new systems are even more evident when ageing is extended to two weeks. ENHANCED-1 has the same behaviour as high additive content PU (SOLID-2),

Panel 6: Retention of tensile strength vs. humid ageing time



while ENHANCED-2 is much more effective, maintaining 50% of tensile strength. In general, the new systems have similar tensile strength and flex fatigue resistance to standard polyester-PUs before hydrolysis, and their retention of these properties after hydrolysis is similar or better than with systems containing additives.

To complete the picture, the new materials have been tested for abrasion and solvent resistance, with the latter carried out to UNI EN 344 (a swelling test in iso-octane with volume increase required to be less than 12%). Abrasion resistance is similar to normal polyester-polyurethane. They can also be used to produce microcellular elastomers with equally good retention of properties after hydrolysis.

Panel 7: Solvent Resistance (iso-octane)

	Volume increase - %
SOLID	< 1
ENHANCED-1	< 1
ENHANCED-2	< 1

Panel 8: Abrasion Resistance (enhanced vs. reference PU)

	Density kg/m ³	Hardness ShA	Resistance mg
SOLID	1100	67	40
ENHANCED-1	1100	64	36
ENHANCED-2	1100	64	60

SUMMARY

These new VORALAST GT enhanced polyester systems do appear to combine the normal properties of an ester-based polyurethane system with the resistance to humid environments over an extended period that many shoemakers are looking for. In particular, the flex fatigue after ageing performance coupled with the good overall performance is a real advance. The fact that this has been achieved for both solid and microcellular PU is also a bonus (*Editor*). 