



Novel technology for polyester PU shoe soling

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Polyurethane was introduced as a shoe soling material in the 1970s. The main advantages are that it is tough, flexible, hardwearing and elastomeric over a wide density range. Hence PU finds applications in a number of different areas, from outsoles to inner soles, and has a 7% market share of all soling materials. Early systems were based on adipate polyesters and, although some polyether-based PU is still used, the majority (83%) of shoe soling is still ester-based. This is because the physical properties of polyester PU are superior (tougher, more wear-resistant, etc.) because of its inter-chain hydrogen bonding. It is also resistant to oils and solvents, which makes it eminently suitable for safety footwear.

However, a major issue for ester PU shoe soling is its susceptibility to hydrolytic and microbial attack, resulting in a significant reduction in physical properties and quality that often appears in the form of cracks (*Figure 1*) and greatly reduces the life of the shoe. Both of these factors are accelerated by heat and humidity, so this is especially important in hot, humid countries. In certain segments, shoes can be stored (or transported via ship container—a particularly aggressive environment) for a significant period of time before they reach the end user, leading to 'new' shoes with vastly inferior properties. Another problem with ester PU is poor low

temperature flexibility. This occurs due to crystallisation of the adipate soft segments. This clearly limits the use of such materials in cold climates. As a result of its special chemical structure, dimer technology avoids these problems.

What are dimer fatty acids?

Dimerised fatty acids are obtained through the reaction of unsaturated fatty acids from sources such as soya bean oil or tall oil under a combination of pressure, temperature and heterogeneous catalysis. Dimer fatty acid is a di-functional molecule, which allows it to be readily built into condensation polymers such as polyamides and polyesters. It has an irregular structure consisting of a large number of isomers, which makes it completely non-crystalline. It also contains 36 carbon atoms and it is this hydrocarbon nature that makes dimer acid and any polymers in which it is included extremely hydrophobic. The combination of hydrocarbon character and non-crystallinity also provides good flexibility even at very low temperatures.

Dimerised fatty acids are used in formulating PU-based products such as elastomers, flexible foams, microcellular foams, coatings, adhesives and sealants. In all these applications, the value of the dimerised fatty acid technology is related to the following features:

- A unique combination of hydrolysis / thermo oxidative / UV resistance
- Flexibility at low temperatures
- Universal adhesion
- Water repellency
- Impact resistance

In footwear, dimerised fatty acid technology is employed to cope with the notorious instability of ester-based soling systems and its susceptibility to hydrolytic microbial attack (hydrolysis). 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 life for the sole.

Uniqema has developed a special polyester polyol based on dimer acid technology. Part of the Priplast range, it addresses



Figure 1: Typical example of sole cracking

FOOTWEAR TECHNOLOGY

this problem without the use of additives. Tests under humid aging conditions (*Figures 2 and 3*) with water vapour at 70°C and 100% relative humidity have shown that, despite starting from slightly lower initial properties, this new form of PU outperforms the adipate industry standard after only a short period of humid aging. It also shows an excellent retention of mechanical properties compared with the standard, suggesting that the life of the sole should be considerably increased and possibly more than doubled.

Figure 2: Retention of elongation at break on humid aging

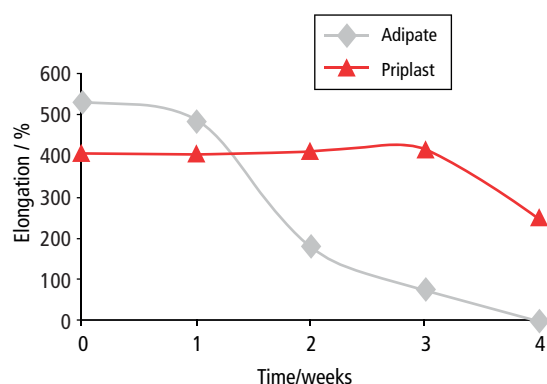
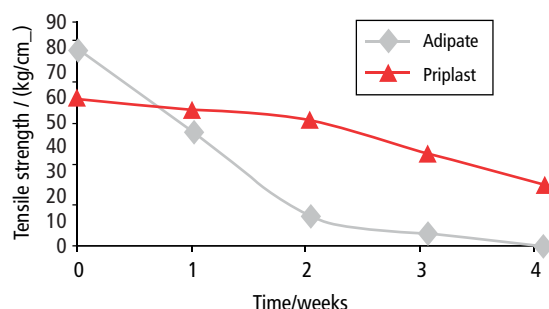


Figure 3: Retention of tensile strength on humid aging



Natural plant oils

A significant difference compared with stabilisation using conventional additives is that Priplast technology actually modifies the structure of the material and it is this that provides the more reliable performance. In addition, as the product is typically derived from natural plant oils, the technology is both safe and sustainable, which is not always the case with normal additives. Furthermore, its plant-derived nature means that it is not directly influenced by ever-increasing oil prices.

The material has also been found to have a number of other excellent properties for footwear soling. These include exceptional low temperature flexibility, satisfactory compression set and resilience performance, which makes it suitable for a broad range of footwear applications. It is already being used in a number of non-footwear applications, such as coatings, adhesives and technical foams. Safety footwear is seen as a key market and the footwear product has been evaluated by several PU system houses with excellent results. 


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