

Millable polyurethane rubber (MPR) is being increasingly used in industrial applications. Since it is made from a number of polyester or polyether polyols along with chain extenders and a variety of diisocyanates, its properties can be made to vary widely. Some of these are ideal for athletic shoe outsoles.

MPR outsoles for athletic shoes

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Millable polyurethane rubber (MPR) can be processed on standard rubber processing equipment and used in applications requiring excellent mechanical strength and abrasion resistance. As with all polyurethane elastomers, it is based on three main ingredients: polyols, diisocyanates and chain extenders. Polyols are either polytetramethylenetherglycols or polyester adipates. Isocyanates can come from a wide variety of aromatic or aliphatic sources, while chain extenders can be ethyleneglycol, butanediol, glycerolmonoallylether, trimethylolpropane-monoallylether or even water.

In contrast to castable polyurethane prepolymer systems, which are produced with an excess of diisocyanate, polyurethane rubbers (PUR) are made with a stoichiometric deficiency of diisocyanate. They, therefore, need to be further cross-linked or vulcanised in order to be useful. This vulcanising can be via sulphur, peroxide or blocked isocyanates. This all sounds very complicated, so let's just see how PUR has been developed for athletic shoes and why.

MPR vs. other PU elastomers

Cast polyurethane pre-polymer systems are made by reacting polyol with a surplus of isocyanate to ensure that they are liquid during processing. They are then mixed with chain extenders to reach stoichiometric equivalence. Thermoplastic polyurethanes are usually produced in one step with a slight excess of isocyanate (NCO) versus the combined OH number of polyol and chain extender. MPR is produced with a final stoichiometric deficiency of isocyanates in order to make it millable. This is why it needs further cross-linking or vulcanisation, so agents like sulphur or peroxide are introduced on a two-roll mill to provide a strong chemical bond between the polymer chains.

Properties of PURs

Although all polyurethane rubbers provide outstanding mechanical strength and high chemical resistance, the appropriate grade must be carefully chosen to match the final application and processing equipment. As a general rule, ether-based materials provide excellent hydrolysis resistance but poorer heat resistance, while ester-based materials show a high degree of oil and fuel resistance.



Two-roll rubber mill

Vulcanisation causes cross-linking between molecular chains resulting in a network structure similar to other vulcanised rubbers. However, compared with other polyurethane elastomers, millable polyurethane rubber contains a smaller number of urethane groups (i.e. a smaller percentage of hard segments). These form hydrogen bonds and contribute substantially to improving the mechanical strength. For this reason, most MPRs require the addition of active fillers like carbon black or silica to reinforce them in the same way as other rubbers. Some grades can be cured with sulphur or peroxide. Sulphur provides higher tensile and tear strength than peroxide. It also offers better flexing and lower heat build-up. However, peroxide-cured compounds have better compression set, heat ageing and resistance to reversion. Abrasion properties and resistance to hydrocarbons are the same for both cure systems.

Most athletic shoes need wear resistant outsoles and one way of achieving this is to incorporate MPR in the outsole to



Typical MPR outsoles

improve abrasion, cut and tear resistance. It can be used in selected areas where abrasion is most severe or blended with synthetic or natural rubber and moulded into complete outsoles. Clear MPR can be used to produce brightly coloured or transparent outsoles with excellent UV resistance which, as well as providing good slip resistance, also offers greater scope for styling.

MPR types & applications

Polyol	Name	Cure	Application
Polyether-1	Millathane CM	Sulphur	High abrasion outsoles
Polyether-2	Millathane 88	Peroxide	Clear outsoles
Polyether-3	Millathane 97	Peroxide	Clear outsoles
Polyether-4	Millathane E34	Sulphur	Coloured outsoles
Polyester-1	Millathane 66	Peroxide	Low cost transparent sole

Polyethers-1 & -4

Polyether sulphur-cured MPR was first used in footwear in the 1960s blended with polybutadiene to make hard, abrasion resistant top pieces for women's shoes. In the 1980s, Polyether-4 was used to make brightly coloured outsoles for running shoes, its advantage being the light weight that was achieved through a very thin but highly abrasion resistant sole.

A few years later Polyether-4 was tried in tennis shoes for abrasion resistance in the toe section. Its success here tennis carried over to walking and running shoes, where it again demonstrated outstanding performance for durability.

Polyether-2

The various types of MPR are important for footwear because the physical properties of each type have advantages and disadvantages depending on the chemical structure. Polyether-2 was marketed in 1989. It was very successful in transparent basketball outsoles and then moved on to men's running shoes.

Achieving good transparency was not easy and a number of new materials and techniques proved necessary. Fumed silica—which although more expensive than normal, precipitated silica—was used to enhance reinforcement and a higher degree of transparency. A di-functional coagent was added to improve hot tear strength and prevent a high reject rate when extracting parts from the mould. Glass-like transparency also demanded a highly polished, chrome-plated mould or one coated with PTFE. Standard tooling gave a dull appearance due to the myriad of tiny surface scratches.

The next hurdle was adhesion to sulphur-cured natural rubber blends. Many chemical additives and bridge compounds were evaluated and, in the end, only peroxide cured natural rubber blended with polybutadiene rubber proved effective. ➤



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WORLD FOOTWEAR

Despite the increased raw material cost and changes in compounding, transparent Polyether-2 was highly successful in basketball and running. Indeed, some runners were able to cover over 500 miles by which time the mid-sole had failed. However, wet traction due to internal crystallisation proved poor compared with standard rubber soles and this limited further expansion in its use.

Polyether-3

What the footwear industry really needs is a MPR with excellent transparency, easy adhesion and good wet traction. Polyether-3 may have these problems solved. It is made from PTMEG but uses a lower molecular weight to eliminate the crystallisation problem. Its overall structure is better because a more stabile aliphatic diisocyanate and a different degree of chain extension are employed. Changing the structure not only improves low temperature performance but also improves the coefficient of wet traction to such a degree as to overtake standard rubber as shown.

Polyester-1

The need to reduce raw material costs resulted in the development of Polyester-1 for running shoes. This PUR was based on a low cost ethylene-butylene adipate especially selected for its colour and low temperature performance, combined with chain extender and reacted with pure MDI. Low

Sample Type	Dry Traction	Wet Traction
Standard Rubber	200	120
Polyether-2	675	100
Polyether-3	553	265
Polyester-1	555	350

temperature properties were very good, no crystallisation occurred at normal temperatures and coefficients of friction in both dry and wet conditions were excellent. With the addition of a UV stabiliser and a tint of blue colour the light stability was also very good. The only problem found was hydrolysis. Polyester-1 was tested for seven days in boiling water and failed, so despite all its other advantages it may not be possible to use a pure polyester-based polyurethane in footwear outsoles.

Cost of MPR

It is not possible to compete directly with natural rubber or EPDM on a cost basis. At present, its use in footwear is made effective by using it only in high wear areas, thus reducing the cost impact. The upside is that around 20% additional raw material costs (processing is no different) can yield an over 40% increase in wear life. In actual wear tests, runners have

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History of MPR

1937	Prof. Dr. Otto Bayer	First PU elastomer based on NDI
1950s	US Rubber	ITVE Vibrathane (Ester/Peroxide)
	Bayer	Desmophen A (Ester/Isocyanate)
	DuPont	Urepan E (Ester/Peroxide)
1960s		Adiprene C (Ether/Sulfur)
	General	TireGenethane (Ester/Peroxide)
	Goodyear	Chemigum (Ester/Sulfur)
		Michelin Gurane (Ester/Sulfur)
	Cyanamid	Cyanaprene VG (Ester/Sulfur)
	Thiokol	Elastothane (Ester/Sulfur and Caprolactone/Sulfur)
	Witco	Fomrez (Ester/Sulfur)
1970s	Michelin, General Tire, American Cyanamid & Thiokol cease PU production	
	TSE Industries starts production of Millathane PUR	
1983	Du Pont sells Adiprene range to Uniroyal	
Today	Only three PUR producers in the Western world - TSE, Bayer & Uniroyal	

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Mould for MPR outsoles

experienced a wear life that was eight times longer compared with a standard rubber outsole.

In many extremely demanding applications polyurethane rubber has outperformed even more expensive synthetic rubbers. Indeed, because the properties of MPR are determined by its chemical structure, there is every indication that solutions can be found to satisfy the demand for polyurethane in the athletic footwear industry at an affordable price. 🌐

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