

Polyolefins could set new standards

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The footwear industry is an interesting environment as it is a great market for the introduction and testing of new ideas, products and manufacturing processes. This is because all footwear presents very demanding structural requirements due to the high stress levels experienced in the everyday wear of shoes. They may look innocuous and low-tech but are in fact high performance products.

Initially they were constructed, by skilled craftsmen, from natural products, mainly leather, wood, natural rubber, reeds, grasses, etc., who utilised the innate properties of these materials along with nails and cotton laces to produce viable footwear in all parts of the world. However, as the population of the world increased and living conditions changed, the demand for greater production and increased performance led to the introduction of

more synthetic materials.

This can be seen most clearly through the way soling materials have changed over the last nine decades as shown in *Table 1*.

From this table it is clear that ever since the 1930s, a new soling material has been introduced every decade with two exceptions. In the 1970s there was intense activity with three new materials appearing—PU, TPR and TPU, whilst the other exception is the 2000s with no new material appearing at all. I would imagine that, by now, most people in the footwear industry are familiar with the first ten materials listed for 2010, from leather down to latex rubber; but what does one make of POE or polyolefin elastomers? Just another Poly-whatsit that no one knows about. Well, it is about time we all did know more about these exciting materials. They are part of the same family of polymers—polythene and

polypropylene—that we use every day, merely produced in a different way to offer new and remarkable properties.

WHAT EXACTLY ARE POEs?

Most industry people are very familiar with the established polyolefin family of materials from their ubiquitous use in packaging films, containers, stackable chairs, automotive, rope and a huge range of other applications. The polymerisation of ethylene into polyethylene has a long history but it was not until the work of Ziegler and Natta during the 1950s and 1960s that efficient catalyst systems based on transition metals (normally titanium with aluminium-based co-catalysts) were developed and the process became fully commercial. Chromium-based catalysts for the production of broad molecular weight products were developed at about the same time by Phillips. Since those early days great progress has been made in both catalyst and process technology.

However, these conventional processes always produce heterogeneous polymers and the grades of polyethylene produced can be made to differ in a range of parameters. For example, variations in molecular weight, chain length, amount of short chain branching (SCB), level of alpha olefin comonomer, density, linearity can all be controlled but, even so, all more or less result in a random polymer that varies in both molecular weight and SCB distribution.

About 40 years ago, a new range of catalysts was discovered; called metallocenes, they revolutionised the production of polyolefins. It is not too dramatic to say that the

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Table 1 – Introduction of soling materials.

1930	1940	1950	1960	1970	1980	1990	2000	2010
L	L	L	L	L	L	L	L	L
NR	NR	NR	NR	NR	NR	NR	NR	NR
	VR	VR	VR	VR	VR	VR	VR	VR
		RR	RR	RR	RR	RR	RR	RR
			PVC	PVC	PVC	PVC	PVC	PVC
				PU	PU	PU	PU	PU
				TPR	TPR	TPR	TPR	TPR
				TPU	TPU	TPU	TPU	TPU
					EVA	EVA	EVA	EVA
						LR	LR	LR
							POE	POE

Key:

L Leather
 NR Natural Rubber
 VR Vulcanised Rubber
 RR Resin Rubber
 PVC Polyvinyl Chloride
 PU Polyurethane
 TPR Thermoplastic Rubber
 TPU Thermoplastic Polyurethane
 EVA Ethylene Vinyl Acetate
 LR Latex Rubber
 POE Polyolefin Elastomer

phrase 'Metallocene Revolution' truly describes the enormous changes brought about in the design and production of polyolefins. Like the Ziegler-Natta catalysts, metallocenes are based on transition metals such as zirconium but are significantly different in structure in that they have several ligands (neutral molecules that bond to a central atom), usually cyclopentadienyl compounds, attached to the metal.

These ligands are also usually bridged by other species. It is the specific nature of these ligands and bridges plus the overall orientation of the molecule that determines the precise catalytic activity of a particular metallocene catalyst. As with the Ziegler-Natta catalysts' metallocenes need co-catalysts to activate the system and are again based on aluminium, usually MAO (methyl aluminoxane). Other cheaper alternatives are under investigation in order to extend the performance and efficiency of the metallocene catalyst package.

The major difference of metallocene catalysts, when compared with Ziegler-Natta or chromium catalysts, is that their structure, often referred to as single site, produces precisely the same polymer species each time. This results in a much more homogeneous product with a narrow molecular weight distribution or MWD and a specific, predictable composition of the short chain branching due to

the co-monomer. So far so interesting—certainly as far as chemists are concerned—but plastics are no of use to the footwear soling industry that requires elastomeric materials.

Whilst these new metallocene polyethylenes were extremely versatile materials, they were still typically 'plastic' in nature, i.e. they do not recover when stretched beyond a certain point but permanently deform. So they are not 'elastic' and therefore not much use in the footwear market. However, in the early 1990s, ethylene-based copolymers were manufactured using metallocene catalysts and were commercialised by Exxon Chemical Company and the Dow Chemical Company that were plastomeric (POPs - polyolefin plastomers) or, more importantly, could be made elastomeric (POEs - polyolefin elastomers) in nature. This was the key breakthrough as far as the footwear industry was concerned.

The 1990s served as a technical and marketing testing ground for a whole range of metallocene products: plastomers and elastomers introduced by Exxon and Dow; the metallocene-based LLDPEs developed by Exxon, Dow and several other producers such as Borealis, Elenac, Evolve, Japan Polychem Corporation, Japan Polyolefins, Mitsui Chemicals, Phillips and Ube Industries Ltd., plus metallocene-based polypropylene introduced by Exxon, Targor and Fina. During this period, DuPont Dow Elastomers also introduced metallocene-based EP elastomers. Over the course of two decades, Dow and ExxonMobil have established themselves as the global market leaders in the metallocene plastomers/elastomers and polyolefins industry.

In the late 90s, the polyolefins industry witnessed the maturing of metallocene-based polyolefins, especially ethylene-based products. At the bottom of the density range, elastomers have been mainly competing against EPDM, LDPE, EVA and flexible-PVC amongst other materials. Plastomers have particularly established themselves in film markets, especially in food packaging applications, where they compete against ionomers, EVA and LLDPE. The use as a sealant layer represents the major application for POPs in food packaging.

HOW DO POEs FIT INTO THE FOOTWEAR MARKET?

Different polymer materials can be used in a wide variety of applications in shoe construction including the following

Infuse could create a new generation of midsoles.



Table 2 – Soling market 2014 (Ktonnes – estimate).

L	NR	VR	RR	PVC	PU	TPR	TPU	EVA	LR	POE	OTH	TOTAL
690	475	2,585	440	2,995	690	1,625	200	970	405	20	150	11,245

Table 3 – Midsole market 2014 (Ktonnes – estimate).

EVA	PU	POE	OTHER	TOTAL
218	128	40	50	436

ten areas (alphabetically): adhesives, coated uppers, counters, foam linings, sockliners, sole inserts, soling, upper components, upper materials and water-proof barriers. To tease out how the polyolefins fit into shoe construction it will be easiest to focus on the products from the current market leader in this area, The Dow Chemical Company Ltd (DOW).

This is especially relevant as the earliest POE introduced to the footwear market, first seen in a trial form at Simac in the late 1990s, was the ENGAGE elastomer then produced by DuPont Dow Elastomers (DPDE) and now by DOW. It made a strong impact but did not immediately find acceptance by sole moulders. There were problems, as is often the case with new materials, regarding the bonding of unit soles to uppers, pigmentation, release agents, lacquers, etc. Even though DPDE offered solutions there were perceived to be too many problems. It was also easier to fulfil the demands of the other application areas being investigated, so they took the limited amount of ENGAGE available at the time, rather than the footwear market. What elastomeric and plastomeric products are now available from DOW that are of interest to the shoemaker and where do they fit into the market? There are four:

ENGAGE – ethylene-octene (or butene) elastomeric homogeneous copolymer. These grades offer a combination of flexibility and toughness, making them very suitable for footwear and have found use in such applications as wellington boots, overshoes and simple unit soles but their greatest presence has been in the production of midsoles for athletic footwear. Here they are used on their own or more usually as a blend with EVA and formulations based on ENGAGE provide numerous improvements compared to EVA on its own, including, as claimed by DOW:

- Lightweight foams at equivalent hardness
- Excellent low temperature flexibility
- Enhanced resiliency
- Lower shrinkage
- Improved abrasion resistance
- Enhanced filler capacity

Taken overall, these qualities can bring real benefits to the performance of athletic shoe midsoles and many of the major OEMs are now using them in their designs.

INFUSE – ethylene-octene elastomeric block copolymer. These are olefin block copolymers (OBCs) that consist of alternating blocks of hard (highly rigid) and soft (highly elastomeric) segments, where the block structure offers a performance balance of flexibility and heat resistance compared to random polyolefin copolymers or other materials. One of the major advantages of these OBCs is their increased dimensional stability. This offers footwear OEMs the potential to reduce production costs while delivering a longer lasting performance midsole and several of today's largest footwear brand owners are launching or are currently in development of new shoe models with INFUSE-based midsoles.

VERSIFY – ethylene-propylene plastomeric and elastomeric copolymers. These plastomers and elastomers are at the early development stage for use in shoe components. Some of the areas being looked at are as diverse as coated fabrics for uppers, toe puffs and heel counters. They provide a good combination of excellent sealing and hot tack performance, plus elasticity, flexibility, softness and compatibility in blends.

NORDEL – ethylene-propylene-diene monomer rubbers. Hydrocarbon rubbers can be used for both outsoles and midsoles, and these next generation EPDMs are clean and consistent. They also deliver improved performance, processing and efficiencies that benefit both

compounders and processors alike in the footwear industry.

The other key player in the metallocene polyolefin market is Exxon and for the footwear industry it has focused on the use of its Exact plastomers. Blending these plastomers with EVA results in midsoles with improved low foam density and durability with similar performance claims to those made by DOW:

- Increased stability, comfort and durability
- Advanced new 'super light' athletic shoes
- Less midsole compacting or breakdown for longer shoe life
- More comfortable cushion and bounce to return energy
- Increased shoe flexibility

The claim is that brand owners can rely on Exact plastomers in shoe design and manufacture to help them achieve optimal cushioning and weight goals without sacrificing performance. Exxon claims that OEMs and EVA compounders use these plastomers for their outstanding toughness and low-temperature flexibility.

It is therefore quite clear that there is now a range of practical polyolefin elastomers and plastomers available to the footwear industry.

HOW SUCCESSFUL HAVE POES BEEN SO FAR?

It is estimated that around 23.4 billion pairs of shoes will have been produced globally in 2014 consuming about 11.3 million tonnes of soling materials. *Table 2* shows the split of this volume across the eleven key different soling materials whilst *Table 3* provides the values for the midsole market. POEs, 15-20 years after their introduction, only account for around 0.2% of the total outsole market and even taking into account the amount of POE used in midsoles this only increases to about 0.6%.

Polyolefin elastomers have therefore still not made a dramatic impact on the footwear market and the question has to be why, as they are excellent products. Is it still down to the original reason they experienced difficulty such as problems with the bonding of unit soles to uppers, pigmentation, release agents, lacquers, etc., or is it more critically down to the focus of the producers of these materials who appear to be focusing more on other applications than footwear?

WHAT IS THE FUTURE FOR POES?

Key points in favour of POEs and POPs are:

- Natural low density
- Can be made in a wide hardness range
- Can be blown to very low density without rapid loss of properties (cf to PVC and TPR)
- Blend easily with EVA
- Improved softness and comfort
- Easy to recycle

Despite all these apparent advantages, both POEs and POPs are struggling to establish a position in the footwear market. Why is this? One reason is that they are still seen as very novel materials; another is that they are competing against a broad range of traditional materials that currently continue to meet the demands of shoe manufacturers.

Finally, there is the question of price. Polyolefins are currently some 15-20% more expensive than EVA which,

while clearly not as good, is well established, reliable and, in terms of performance, still considered satisfactory by a majority of sports shoe producers operating in a competitive market. Perhaps polyolefins are destined to be like polyurethane: excellent materials with much to offer but restricted to a niche in the footwear market due to price, so often the final arbiter as far as the industry is concerned. Time will tell. 🕒



POEs can improve all-round soling performance.

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