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Innovations at Atlanta

The Polyurethanes 2012 Technical Conference sponsored by the Center for the Polyurethanes Industry (CPI) at Atlanta, Georgia in September did not feature as many presentations on footwear applications as in some other years. Nevertheless, two companies that regularly contribute papers, Huntsman and Desma, revealed some interesting new developments.

Huntsman has been a leader in footwear soling systems for over 30 years during which time it has introduced soft thermoplastic polyurethanes (TPUs) and dual density PU/TPU systems to the industry. A recent development programme has been evaluating the practicalities of producing polyols from sources other than oil.

A joint paper presented at Atlanta by Rafael Camargo and Daniel Rosenvasser of Huntsman and Jason M Anderson and Scott Allen of Novomer Inc., raises some interesting possibilities in regard to the creation of polyols using waste CO₂.

Increasing pressure for sustainably produced chemicals and a corresponding reduction of oil consumption in recent years has driven a large number of companies to investigate the possibility of producing raw materials from sources that are not based on fossil feedstock. Consumers and leading finished product companies in many markets are actively seeking raw material options that rely on sources such as recycled goods or products derived from renewable resources.

An alternative approach is to develop products that are based on waste stream or materials that are themselves not derived from oil. The chemical industry in general, and the polyurethane industry in particular, have increased R&D resources dedicated to the development of intermediates and

final products based on such resources.

Huntsman's previous work has involved the use of bio-based 1,3-propane diol (PDO) as a co-monomer in polyesters or as a chain extender and how it was possible to formulate elastomers with similar performance and properties to equivalent ones using existing oil-based products.

This showed that it was possible to introduce new bio-based intermediates in the formulation of footwear elastomers with similar performance and properties to equivalent formulations derived from conventional oil-based intermediates and already in commercial use. The typical bio-renewable carbon content in this instance was as high as 65 percent, as measured by ASTM D-6866 if, in addition to the bio-based glycol, a bio-based dicarboxylic acid such as succinic acid is used to make the polyester.

To further investigate non traditional feedstock alternatives to footwear elastomers, Huntsman teamed up with Novomer Inc. to develop new alternatives. Novomer has pioneered the approach to alternative sources by developing novel catalyst technologies that can convert gases such as carbon dioxide or carbon monoxide into value-added chemicals for a number of applications. This proprietary catalyst technology allows the insertion of carbon dioxide into a propylene or ethylene oxide molecule in order to

produce a number of hydroxyl terminated polycarbonates that can be tailored in molecular weight and composition as polyols for the formulation of PU products.

Over the past few years, a number of companies have explored possible renewable alternatives to petroleum-based polyols for various PU applications. Huntsman and Novomer, however, have taken a novel approach by developing flexible footwear foams using an entirely new class of CO₂-based polyols. These new polyols appear to offer a real chance to increase the possibilities of developing sustainable foam alternatives for the footwear industry.

Novomer's technology offers the potential to deliver renewable polyols that are up to 50% CO₂ by weight and have a 3-9x carbon footprint advantage versus existing petroleum-based materials and are at the same time cost effective. The flexible platform technology involved enables polymer structure and molecular weight to be tailored for specific applications.

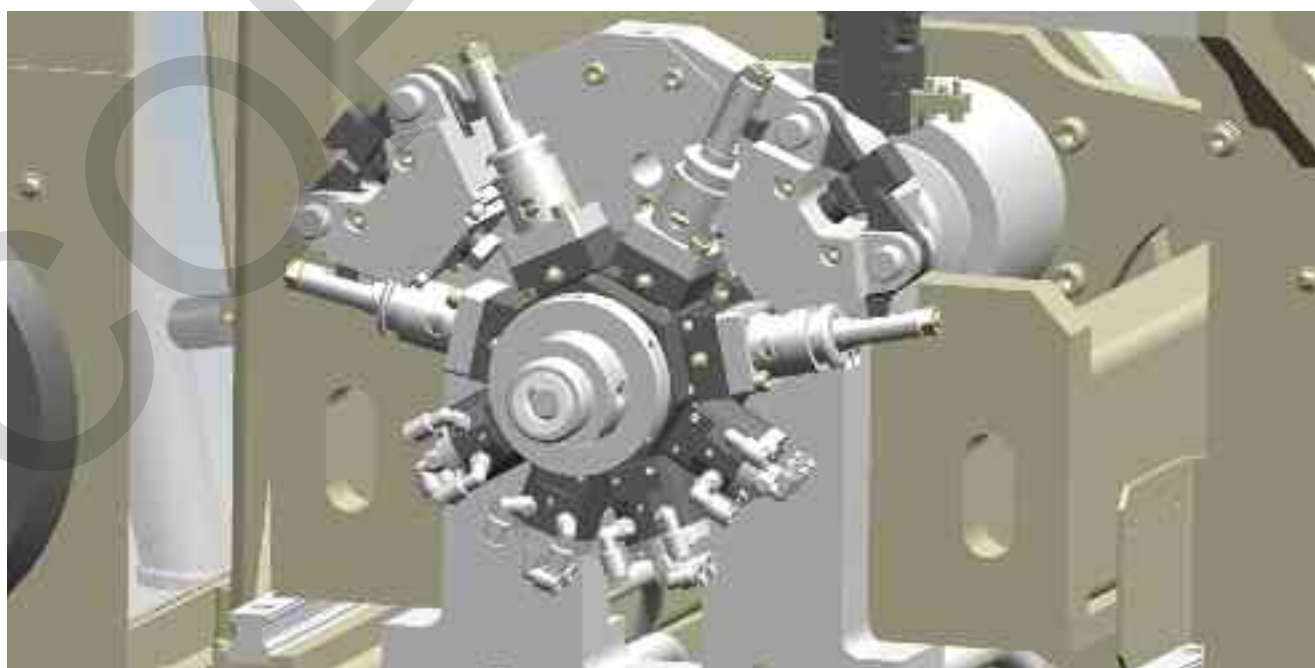
This highly flexible polyol technology can be applied to a wide range of thermoplastic or thermoset applications including coatings, foams, adhesives, elastomers and TPUs. Huntsman has worked closely with Novomer in order to combine this technology together with its expertise in formulating PU systems and product development capabilities, to explore

the use of these materials in conventional footwear foams. The resulting materials possess some interesting performance characteristics which it is best to sum up rather than to explore in depth as the chemistry involved is extremely advanced and complex.

This new family of polycarbonate diols obtained by the polymerization of carbon dioxide and propylene oxide creates urethane systems with unique properties when compared with conventional footwear elastomers. For the most part, straight use of these polyols without other polyols in the formulation leads to high strength microcellular foams that can be both soft and high dampening or rigid and very tough. This would not make them suitable for use as drop-in substitutes in traditional midsole applications.

However, the increased hardness, tensile strength, and tear strength of PPC-based foams suggest that these polyols have interesting potential as a performance enhancing component of a polyol formulation in foams requiring these characteristics, including certain footwear foams and elastomers. Given the high dampening behaviour of some formulations, these materials are also worth exploring in energy absorbing applications including vibration dampening and viscoelastic foams.

So, while it is clear that these new polyols cannot be used as drop-in replacements for existing polyol



Desma self-cleaning mixing head.



The mixing screw is designed in several different shapes to match the materials to be processed. CREDIT: DESMA

systems, they do nevertheless offer a unique set of properties that are not easily achievable with existing raw materials and thus warrant additional exploration in formulated foam systems. It is innovation such as this that continues to make PU such an exciting and valuable solving system for footwear.

REACTION INJECTION

As usual, PU moulding machine manufacturer Desma of Germany has been busy. Christian Decker, Managing Director and Bjoern Dormann, Manager Technical Department, presented two papers, the first described the company's new Reaction Injection System where liquid additives are injected directly into liquid PU via the mixing head. Using this technique Desma says that the weight of a shoe can be reduced by at least 20% with positive benefits in terms of walking and running. The reduction in density also makes it increasingly practical to replace EVA as a midsole material in sports shoes.

Low pressure mixing technology for PU is already well established and this type of machine is working reliably and cost-effectively in the industry. Based on the fact that PU machines have to be flexible and serviceable in a wide range of applications, Desma has developed a new one where it is possible to use a further four on top of the existing four

valves in the mixing head. These extra valves can be used for dosing a huge variety of different liquids such as colours, stabilisers and cross-linkers.

ACCURATE CONTROLS

An extremely accurate control system allows mixing parameters in the most sensitive of PU material systems to be varied and offers a wide range of benefits:

- No solvents due to a self-cleaning mixing screw system
- Up to eight components on the mixing head with changes from shot to shot without an intermediate dump shot
- Up to six additives or colours on the mixing head with additive or colour change from shot to shot without an intermediate cleaning dump shot
- Dosing of physical foaming additives and up to 25% in static inhibitors direct into the mixing chamber
- Wide material range of ether or ester PU systems and the ability to multi-layer PU/PU, TPU/PU and Rubber/PU in one process

Desma says that a big advantage of its mixing technology is consistency as this means that the manufacturer does not have to think about the mixing ratio. The machine is equipped with patented controlled component valves which ensure their simultaneous

opening and therefore guarantees the same mixing ratio all the time. This in turn leads to better quality and more satisfied customers.

FLEXIBILITY

The new machine is designed like a toolbox kit where many different valve configurations are possible. The standard version starts at two component valves and can be expanded to four component valves plus four additive valves. Three component valves plus four additive valves is also perfectly practicable. Where the four component mixing head can handle two PUs with totally different chemical configurations, the three component head can cope with two different polyols plus one isocyanate. Furthermore, the new system is able to change the entire mixing ratio as well as total article parameters and PU components from shot to shot without any interruption to the production cycle.

The control system uses a DEScan control database where details on every final product are stored. It covers shot weight and formulation to be used as well as additives or colours and any other parameter-defining machine data. This intelligent control makes it possible for all the properties involved to be varied by changing the percentage formulation of components and additives over thousands of different system formulations.

The new machine uses Desma's low pressure mixing technology where the screw is used as an auger to mix the polyol with the isocyanate. This makes it possible to react to every kind of different material independently whether ether or ester is used. It is therefore able to handle a huge variety of different PU components. The new twelve-capacity screw changer operates in just a few seconds with dirty screws cleaned by an environmentally friendly process before being returned to the changer.

AGENT FOR CHANGE?

Gas or additives are used with PU to increase certain properties or reduce overall weight. Now, a liquid gas or additive can be introduced at the same time as the actual PU components. The specially designed mixing screw ensures everything is thoroughly and

homogenously distributed into the mould with the chemical reaction starting immediately after. Furthermore, the precise gear pumps used make it possible to inject every shot into the mould with absolute precision every single time.

As remarked earlier, the resulting lightweight PU system is now a viable substitute for EVA as a midsole material. This also means that a number of predominantly manual operations such as roughing, cementing and pressing can be avoided so that by using this form of direct injection, production can become fully automated. Desma also believes that this could in turn bring back more shoe production to high labour cost countries and closer to major consumer markets.

DIRECT INJECTION AND FOOTWEAR DESIGN

The second paper from Desma in many ways followed on from where the first left off. It dealt with the use of direct injected PU not only for the outsole but also the midsole, shank and to add other ergonomic or visual properties to the shoe while also cutting production time and costs. For instance, most shoes are still produced using the cemented processes due to the soling materials involved. Rubber outsoles for example have to be produced as a shell and filled with a lightweight midsole to save weight. While the result is a light, comfortable and hard wearing shoe, this can only be achieved using the cemented process.

This has been perfectly adequate while labour costs in developing countries have remained low. It is changing and costs there are rising rapidly while, at the same time, there is increasing interest in bringing manufacturing back to consumer markets to cut lead times and transport costs. This however requires a high degree of automation and, as far as soling is concerned, this means direct injection.

EVA is still used for the midsole of almost every athletic sport shoe. The disadvantage is that almost no automated production steps are possible plus the inconsistent dimensions associated with the material are often unacceptable. In addition, technical properties such as life cycle and compression set are much lower than those of PU.

The simple ballerina style shown in the photo is a single density PU-soled shoe where the sole functions both as the outsole as well as a comfortable midsole. All the technical performance has to be contained within the soling material which results in compromise. By using this simple method of direct injection, no further functions can be performed. The shoe designer needs to add additional components to the shoe in order to provide the shoe with necessary functions such as stability and comfort.

Adding these, however, requires additional manufacturing steps which, in turn, mean higher labour and production costs. Direct injecting of a combined outsole and midsole is an obvious solution but one that also calls for more advanced moulds. A few manufacturers are already using them and have also taken the opportunity to explore visual and ergonomic factors at the same time. Today's PU systems are highly effective and the material can be used not only as a sole material but, in some cases, as a stabiliser or shank in the heel and waist area. The material can also be used visually by creating 'windows' to add further design highlights to the shoe.

ERGONOMIC SHOES

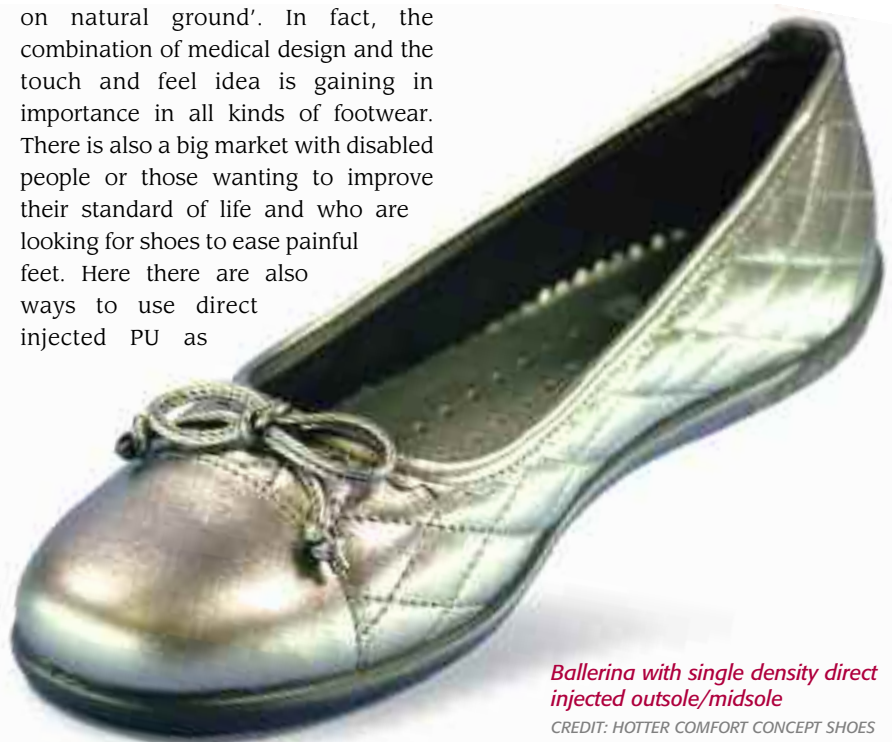
Some brands concentrate on ergonomic walking and there are designs around that follow the barefoot concept that promotes 'natural walking on natural ground'. In fact, the combination of medical design and the touch and feel idea is gaining in importance in all kinds of footwear. There is also a big market with disabled people or those wanting to improve their standard of life and who are looking for shoes to ease painful feet. Here there are also ways to use direct injected PU as

different parts of the midsole with different densities that can be adjusted to target the shoe's performance to the needs of this type of consumer.

LESS ADHESIVE

The other big advantage of direct injected PU is of course the elimination of adhesives. This is a relatively new trend but has already become a basic strategy for many companies. The aim is to improve the conditions for the people involved in the production process. The shoes produced nevertheless feature excellent design, performance and variety, the latter growing from season to season. Designers do not like to be limited and PU offers them complete design freedom.

Two other gains are cost and flexibility. The costs of adhesive-based production are higher than direct injection and continuously rising as wages in previously low labour cost countries are increasing, such that they are influencing total product cost to an ever greater extent. Automation has therefore become a keyword in the equation of containing costs while still pursuing the highest possible quality. PU direct injection has the potential to eliminate more than 50% of adhesives used in the cemented process while at the same time offering high performance bonding between the various layers of the sole and better compression-set properties compared with EVA. 



Ballerina with single density direct injected outsole/midsole

CREDIT: HOTTER COMFORT CONCEPT SHOES