



TPU GOES GREEN

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Since its inception in the 19th century, the chemical industry has been using 'old' carbon taken from fossil resources, especially oil. It has used it to produce products such as polymers which, after use, are either converted into CO₂ by burning or remain unchanged for centuries in landfill sites. While this CO₂ will gradually photosynthesize back to an organic form, it will be millions of years before it can once more become a useful resource to make chemicals. This time lag between consumption and replenishment means that fossil fuels will become exhausted sometime in the not too distant future.

On the other hand, if we transform the 'new' carbon from bio resources such as oil plants or sugars to make chemicals, it can be burnt to produce CO₂ or landfilled and will only take one year—the time the plant takes to grow—before it can be used again (Figure 1).

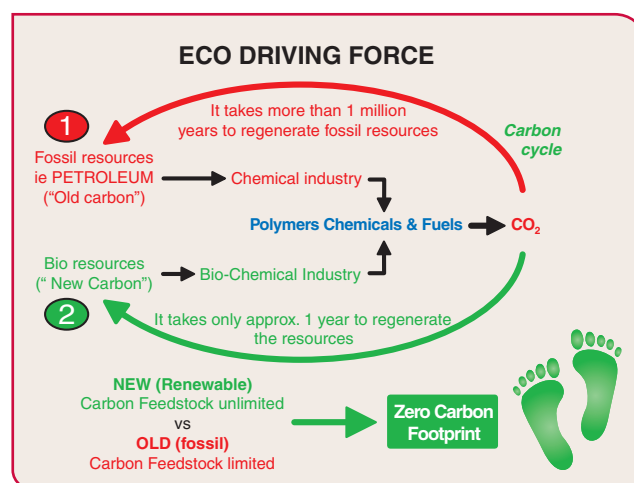


Figure 1 - carbon cycles 'old' and 'new' carbons

CREDIT RAMANI NARAYAN, MICHIGAN STATE UNIVERSITY

“...to answer the question...”

What constitutes sustainability?

Sustainability is considered to comprise three basic concepts.

- **Biodegradability** where a polymer is decomposed into its primary components (ideally CO₂ for the carbon content) under certain temperature and humidity conditions. ECO TPUs are not biodegradable.
- **Recyclability** where a polymer can be re-used several times, maintaining most of its defining properties above a certain performance limit. ECO TPUs are thermoplastic materials and therefore inherently recyclable.
- **Renewability (or bio-based)** where the polymer is produced from raw materials not derived from fossil sources such as petroleum. ECO TPUs fulfil this concept in certain proportions.

Consumer pressure in regard to health and safety aspects of potentially hazardous chemical additives in plastics has encouraged manufacturers to seek alternative plant-based plastics. In 2001, Mattel, the world's largest toy manufacturer switched to plant-based plastics for all new products. Others such as LEGO, IKEA and Nike are moving in the same direction.

NEW TECHNOLOGY

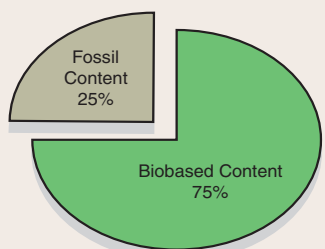
These 'green' plastics are derived from a variety of plant sources such as hemp oil, palm oil, soya bean oil and corn starch. They are therefore more sustainable as there is less reliance on fossil fuels such as petroleum as a carbon source. At Merquinsa, we thought it would make sense to develop a range of polymers based on renewable sources that would match as far as possible the properties of the established high performance polymers being used in industry.

A thermoplastic elastomer is a high performance product, whose macroscopic properties reflect a three-dimensional microscopic organism. The first step, therefore, was to design the right chemical structure. Based on our proprietary technology we have been able to develop thermoplastic polyurethanes that can be used to create adhesives and elastomers with bio-based content of between 30% and 90% (Figure 2). Moreover, these are made using renewable raw materials from non-food or feed competing sources.

A PU-based polymer is formed by the chemical reaction of one or several polyols and one or several isocyanates. Because high performance PU elastomers have excellent mechanical and elastomeric properties, plant-based bi-functional polyols derived from renewable sources must have the same. The breakthrough came when we managed to develop a new family of plant-based TPUs (thermoplastic polyurethanes) which have these characteristics and can be used in adhesive, extrusion and injection moulding applications. Furthermore, they show better hydrolytic resistance compared to current top grade petrochemical-based TPUs and are able to maintain equal mechanical properties.

The new plant-based polyols are made using either oily fraction via chemical transformation or from carbon hydrate fraction via fermentation. They are then processed using standard procedures and their properties varied by means of different molecular weights and monomer combinations. When used in standard reaction conditions with isocyanates, they create thermoplastic polyurethanes

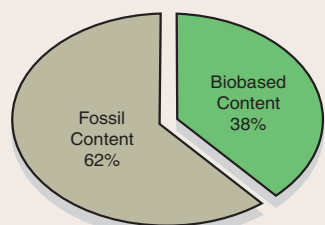
Report of Biobased Content Analysis using ASTM-D6866



Submitter: Merquinsa Mercados Quimicos, S.L.
 Submitter Label: D900
 Laboratory Number: Beta-241482
 Material Analyzed: PEARLBOND
 Date Received: February 21, 2008
 Date Reported: February 27, 2008

Mean Biobased Result: 75% *

Proportions Biobased vs. Fossil Based indicated by ¹⁴C content



Submitter: Merquinsa Mercados Quimicos, S.L.
 Submitter Label: 12T95
 Laboratory Number: Beta-241483
 Material Analyzed: PEARLTHANE
 Date Received: February 21, 2008
 Date Reported: February 27, 2008

Mean Biobased Result: 38% *

Proportions Biobased vs. Fossil Based indicated by ¹⁴C content

Figure 2 - Bio-based content certification according to ASTM D 6866. CREDIT BETA

with mechanical properties closer to polyester or polyether TPU, depending on the particular raw material used in preparing the base.

While this new patented ECO family of TPUs is being launched in all the traditional markets, the footwear industry is seen as a major potential consumer. A range of products has been specifically designed for both injection moulding and adhesive applications in the production of both components and finished shoes that will allow the industry to improve its carbon footprint without any sacrifice of quality or performance.

PROPERTIES

Tensile strength – Merquinsa's Pearlthane ECO TPU grades have mechanical properties which are very close to those of standard TPU products in terms of tensile strength and modulus (Figure 3). The same diagram shows the result after ageing for 168 hours at 85°C. If the right ECO TPU grade is chosen, the equivalent mechanical properties can be achieved.

Abrasion resistance – this is one of the key properties of polyurethane compared to other elastomers and which makes it the soling material of choice for applications where good abrasion resistance is essential (Figure 4). The ECO products show abrasion resistance equivalent to that of petrochemical TPUs and are able to demonstrate the same

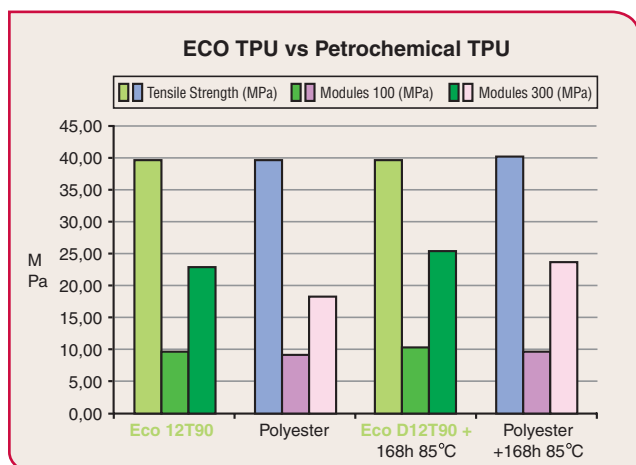


Figure 3 - Pearlthane ECO D12T90 tensile strength and modulus (ASTM D 638). CREDIT BETA

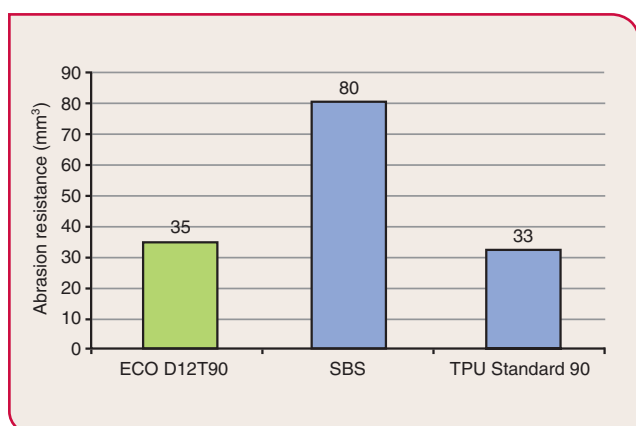


Figure 4 - Pearlthane ECO D12T90 abrasion resistance (DIN 53516). CREDIT BETA

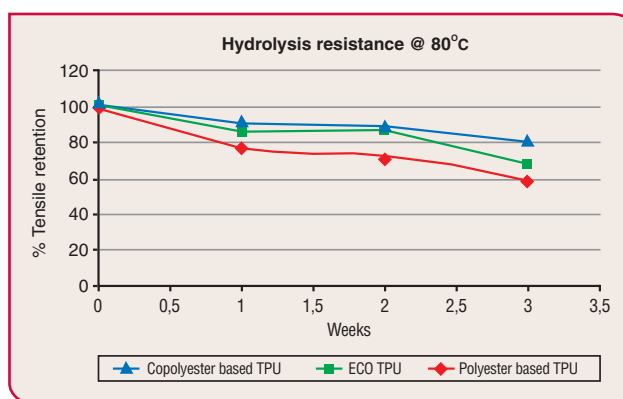


Figure 5 - Pearlthane ECO D12T90 hydrolysis resistance at 80°C.

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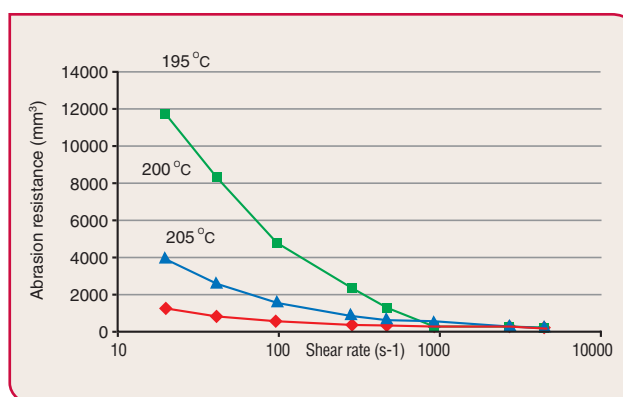


Figure 6 - Pearlthane ECO D12T90 melt vs. shear rate.

CREDIT BETA

outstanding mechanical properties and abrasion resistance inherent to polyurethane with polymers that have a plant-based content of around 40%.

Low density – this is always a plus in applications where weight is a factor and most of the new ECO TPU grades show a useful injected density reduction of between 2% and 5% compared to conventional petrochemical TPUs. In addition, the new polymers can be used to produce dual-density soles either as pre-moulded units or by direct injection bottoming. ECO TPUs can therefore be used with confidence by those wishing to pursue a greener path with their products.

Colouring – raw materials from natural sources tend to have more colour than those derived from petrochemicals due to the more difficult purification procedures. Natural products are complex mixtures some of which are prone to discoloration through oxidation. Purification of these mixtures is therefore difficult and expensive if a high degree of purity is required. Those used to produce ECO TPUs are based on commercially available products with standard but careful purification. Consequently, some yellowish colouration does remain in the final TPU compound which might limit usage in transparent soles or components. There are no problems where pigments are added to produce dense colours.

Hydrolysis resistance – this is also very good (Figure 5), as are thermal and resistance to oils and chemicals, reaching levels normally associated with the best polyester TPUs.

“...and it should be noted...”

Bioplastics market set to grow rapidly

A number of different driving forces lie behind the growing effort to develop bioplastics:

- Their non-toxicity
- Cost of oil leading to price hikes of petrol-derived raw materials creating an up-down pressure on the traditional chemical industry
- Growing sense of ecological and social responsibility among consumers which in turn passes up the value chain
- Carbon footprint reduction, sustainability and environmental balance are on the political agenda and creating a bottom-up pressure on the traditional chemical industry

The global market for bioplastics is predicted to grow by 8-10% annually, increasing its value from \$1billion in 2007 to \$10bn by 2020. New applications in the automotive and

electronics sectors will drive the growth although packaging will remain the dominant market despite forecasts of its share falling from 65% in 2007 to 40% in 2025.

Key findings in a recent report into the bioplastics market by the Helmut Kaiser Consultancy (02/06/2008) suggest that by 2025 Asia will be market leader with a 32% stake, followed by Europe with 31% and the USA with 28%. Asia is forecast to gain a lead in the market because genetically modified plants are easier to grow there and new outlets for agriculture are quicker to establish and expand.

Bioplastics currently cover an estimated 10-15% of the total plastics market but this will increase to 25-30% by 2020. This expansion will increase further as the technical properties of bioplastic materials are improved and their innovation creates new applications in the automotive, medical and electronics industries.

Flow and crystallinity – here is where the ECO TPUs show some important advantages. They have a lower melt viscosity and a better flow at high shear rate at the same molecular weight as that of standard TPUs (Figure 6). Flow is therefore reduced at the same temperature and the injection process greatly improved together with the injection cycle time and productivity in general. Factory trials have shown their injection behavior to be outstanding and very close to other thermoplastic compounds. The high flow properties also have a direct bearing on the high crystallinity parameters shown by ECO TPU.

As with any change in moulding compound, adjustments to some machine settings may be found necessary and trials are essential before bulk production begins. A good starting point is between 10° and 15°C below standard TPUs.

ECO TPU FOR HOT MELT ADHESIVES

TPU hot melt adhesives are extensively used in the footwear industry for coating toe-puffs and counters where they add extra stiffness to the component as well as providing a strong bond to the upper and lining. Merquinsa uses a continuous process fed by a mixture of polyol, isocyanate and chain extender (low molecular weight diol) to produce a range of plant-based ECO TPUs that can be used as an alternative to petroleum-based TPUs in this application.

Figure 7 compares Pearlbond ECO D900 against two standard TPUs used to produce hot-melt adhesives. It is immediately apparent just how high the rate of crystallisation is with these plant-based polyols with ECO 900's rate being practically half that of the petrochemical-based products.

Hardness has a direct effect on the rate of crystallisation but, in this comparison, Shore D hardness for all three products is in the same range of 50 to 54. The reason for that is the extremely ordered microstructure of the new

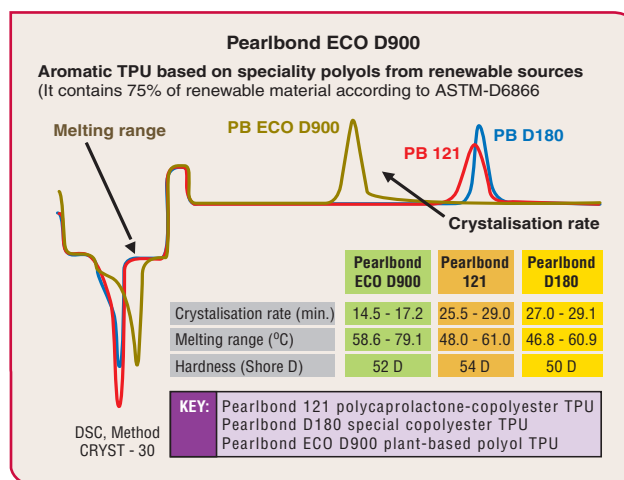


Figure 7 - comparative crystallisation rates. CREDIT BETA

TPU and a very regular distribution in the soft segment. In simple terms, the inherent chemical composition is having a positive effect on the crystallisation properties of the plant-based TPU. Although the melting point for ECO TPU is from 10° to 20°C higher than that of a regular TPU, it does not pose any major problems in the extrusion process involved in producing these adhesives. Furthermore, despite the fact that the softening and melting range of the new ECO product is clearly higher than those of its petrochemical partners, hot-tack at 80°C is very good. The ECO TPU will therefore offer very good initial peel strength coupled to higher productivity. An extra bonus for shoemakers is that it shows excellent adhesion to leather substrates. 🌱

Dr. Jesús Santamaría is New Business Development Manager for Merquinsa, Barcelona, Spain. The company is a leading producer of speciality TPUs for injection moulding, calendaring, melt coating and adhesive applications.