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TECHNOLOGICAL ADVANTAGES OF POLYETHER COPOLYMER BASED TPUs (FOR EXTRUSION AND INJECTION MOULDING END-USES)

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1. INTRODUCTION

This paper describes a unique family of TPUs (*PEARLTHANE®*) developed and optimized over the past 2 years by MERQUINSA. This special type of TPU is based on a soft segment composed of well defined alternating blocks of polyester and polyether chains. After a general description of TPUs, the advantageous properties as well as the main application areas of this family will be described.

1.1 General description of TPUs

Thermoplastic polyurethanes (TPUs) are thermoplastic elastomers consisting of linear segmented block copolymers composed of hard and soft segments. It is well known that TPUs are formed by the reaction of: (1) diisocyanates with short-chain diols (so-called chain extenders) and (2) diisocyanates with long-chain difunctional diols (known as polyols). The practically unlimited amount of possible combinations varying the structure and/or molecular weight of the three reaction compounds makes it easy to understand why the variety of different TPUs is enormous. This allows urethane chemists to fine-tune the polymer´s structure to the desired final properties of the material.

1.2 Morphology

The final resin consists of linear polymeric chains in block-structures. Such chains contain low polarity segments which are rather long (called soft segments), alternating with shorter, high polarity segments (called hard segments). Both types of segments are linked together by covalent links, so that they actually form block-copolymers.

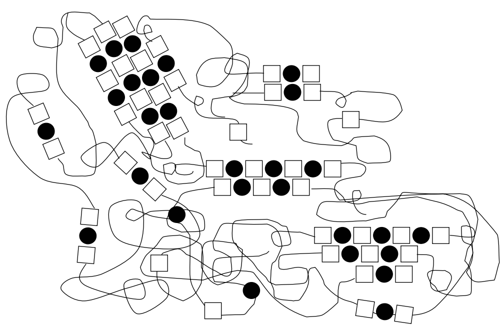

Fig. 1: Segmented structure of a TPU (● chain extender; □ isocyanate; — polyol).

The polarity of the hard segments originates a strong attraction between them, which causes a high degree of aggregation and order in this phase, forming crystalline or pseudo crystalline areas located in a soft and flexible matrix. This so-called phase separation between both blocks will be more or less important, depending on the polarity and the molecular weight of the flexible chain, the production conditions, etc. The crystalline or pseudo crystalline areas act as physical crosslinks, which account for the high elasticity level of TPUs, whereas the flexible chains will impart the elongation characteristics to the polymer.
These "pseudo crosslinks", however, disappear under the effect of heat, and thus the classical extrusion, injection moulding and calendering processing methods are applicable to these materials. Consequently –and not less important- TPU scrap can be reprocessed.

For TPUs up to 98 Shore A, the dimensions of the crystalline areas are smaller than the wavelength of visual light, which makes these TPUs transparent — a unique property of TPUs within the family of TPEs.

1.3 Overview of TPUs on the market

Among the features of commercially available TPUs are:

- excellent abrasion resistance
- outstanding low-temperature performance.
- excellent mechanical properties, combined with a rubber-like elasticity
- very good tear strength
- high elasticity
- high transparency
- good oil and grease resistance

The currently available TPUs can be divided mainly in two groups, based on soft segment chemistry : (1) polyester based TPUs (mainly derived from adipic acid esters) and (2) polyether based TPUs (mainly based on tetrahydrofuran (THF) ethers). The differences between these two groups are outlined in the table below:

Table 1: Main differences between polyester and polyether based TPUs.
(+ + excellent; + good; o acceptable; - poor; - - very poor)

Property	Polyester based TPU	Polyether based TPU
Abrasion resistance	+ +	o
Mechanical properties	+ +	+
Low temperature flexibility	o	+ +
Heat ageing	+	-
Hydrolysis resistance	- -	+ +
Chemical resistance	+ +	-
Resistance to microbes, fungi etc.	- -	+
Adhesion strength	+	-
Injectability (cycle time)	+ +	o

In short, one can say that polyether based TPUs are used only in cases where excellent hydrolysis and microbial resistance is required as well as in cases where extreme low temperature flexibility is important.

2 . ADVANTAGES OF COPOLYMER BASED TPUS

MERQUINSA has recently developed a range of polyether copolymer based TPUs called *PEARLTHANE®* D15NXX[*], *PEARLTHANE®* D14NXX (patent pending). These polymers combine the most relevant properties of polyether and polyester based TPUs.

Thanks to new polymerisation processes, polyether copolymers in alternate blocks have been obtained, which give rise to polyurethanes with specific properties. Following, the advantages of these copolymer based TPUs will be presented in comparison with the most wide-spread TPUs on the market, i.e. TPUs based on adipic polyesters and TPUs based on (THF-) polyether.

2.1 Hydrolysis resistance

This is the main feature that favourably differentiates polyether-based from polyester-based TPUs. As a result of the much higher hydrolytic resistance of the ether group, in comparison with the ester group, polyether based TPUs are indicated for end-uses which require a more or less prolonged contact with water, although at a higher cost.

Figure 2 shows the hydrolytic resistance, which is measured by the loss of mechanical properties shown by a polyurethane immersed in water at 80ºC. Measurements have been made with three TPUs that had the same hardness (85º Shore A) and molecular weight, differing only in the nature of their soft segments, which were respectively: polyester, polyether and polyether copolymer (*PEARLTHANE®* D15N85). A considerable difference can be observed between the polyether and polyester-based TPUs whereas the polyether copolymer shows a noticeably higher hydrolysis resistance, in comparison with the conventional polyester-based TPUs. This enables its use for a variety of applications which usually require a polyether-based TPU such as cable sheathing, garden hoses or geophysical cables for the oil industry.

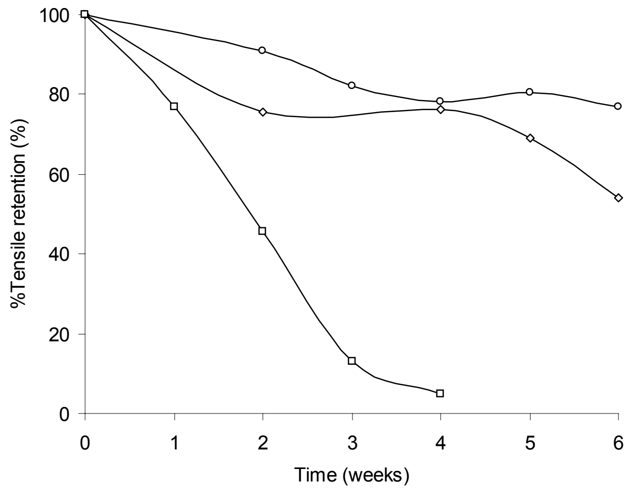

Fig. 2: Hydrolysis resistance *PEARLTHANE®* D15N85 versus polyester and polyether types (o Polyether based; ◊ = *PEARLTHANE®* D15N85; □ polyester-based TPU)

[*] XX stands for shore A or Shore D hardness, e.g Pearlthane D15N85 is an 85 Shore A grade.

PEARLTHANE® D14N85 shows a hydrolysis resistance curve similar to *PEARLTHANE®* D15N85.

Strongly related to hydrolysis resistance and important for the cable industry is the saponification index which is shown comparatively in Table 2:

Table 2: Saponification index according to DIN VDE 282-10.

Product	Value (mg KOH/g TPU)
PEARLTHANE® D11T85	260
PEARLTHANE® D15N85	155
PEARLTHANE® D16N85	110

According to the German cable standard DIN VDE 0282-10, a maximum value of 200 mg KOH/g is specified for TPU cable jackets. As shown in the table above, *PEARLTHANE®* D15N85 meets this standard.

2.2 Heat resistance

One of the major drawbacks of polyether based TPUs is their poor heat resistance. The heat resistance of the copolymer based TPU is significantly better as shown in the so-called half-life graph of Figure 3.

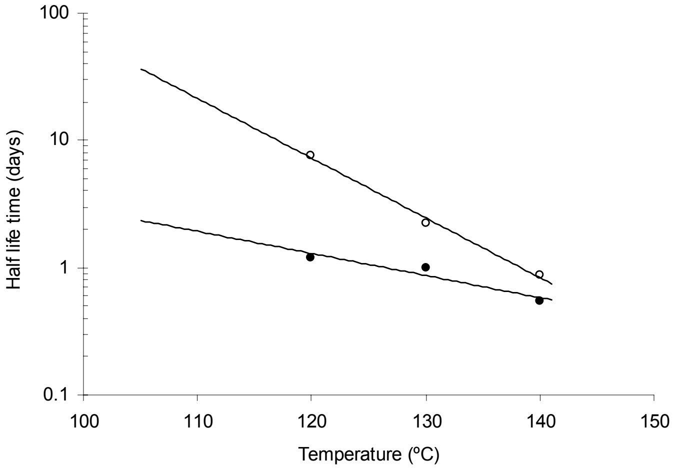

Fig. 3: Heat resistance of *PEARLTHANE®* D15N85 (○) versus a standard polyether (●).

2.3 Elasticity

Hysteresis

A synergy was found in the elastic properties of extruded Pearlthane D15NXX TPUs. As seen in the figure below, the elasticity on 100% elongation of the copolymer based TPU is as high as a polyether based grade. This makes the polymer perfectly suitable for applications such as transparent brassiere straps.

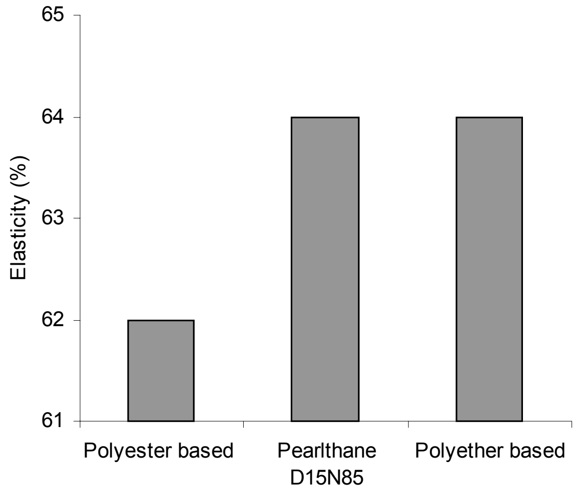

Fig. 4: Elasticity of extruded films (0.2 mm thickness) compared.

It is well known that the elasticity increases with decreasing hardness. The Figure below shows the elasticity as a function of hardness for the copolymer based TPU can reach values of over 80% at a hardness of 70 Shore A.

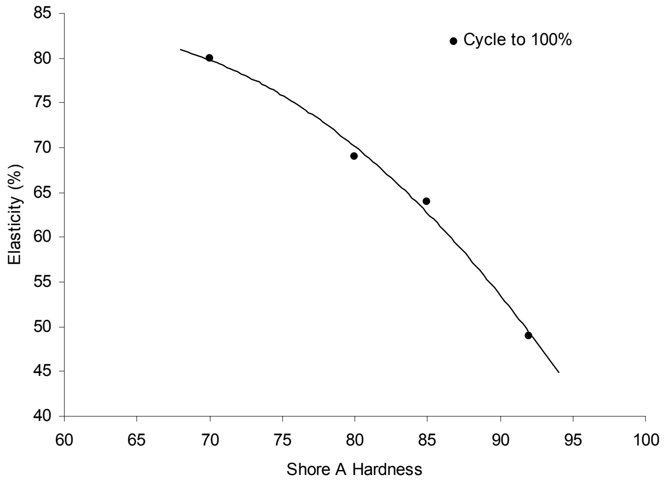

Fig. 5: Elasticity as a function of hardness for *PEARLTHANE® D15NXX.*

Compression set behaviour

The compression set characteristics of Pearlthane D15N85 and D14N85 compared to standard polyether based TPUs are slightly better over a wide range of temperatures. This is shown in Figure 6.

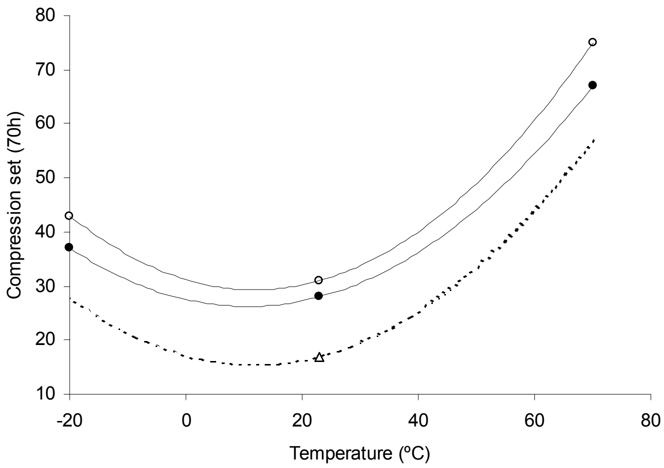

Fig. 6: Compression set (70h) at several temperatures. (• *PEARLTHANE®* D15N85; ○ polyether-based TPU; △ *PEARLTHANE®* D14N85).

Pearlthane D14N85 has very low compression set values, e.g. 16% at 23 ºC (70h).

2.4 Flexibility at low temperatures

Considering the dynamic mechanical properties in the Tg area, of the three TPUs which have already been mentioned, the polyether-based polyurethane has its peak tan δ value (and thus its Tg) lower than the polyester-based one. This is due mainly to a lower polarity, which causes a lower interaction with the polar hard segments of the polyurethane and, as a result, a higher separation between the phases.

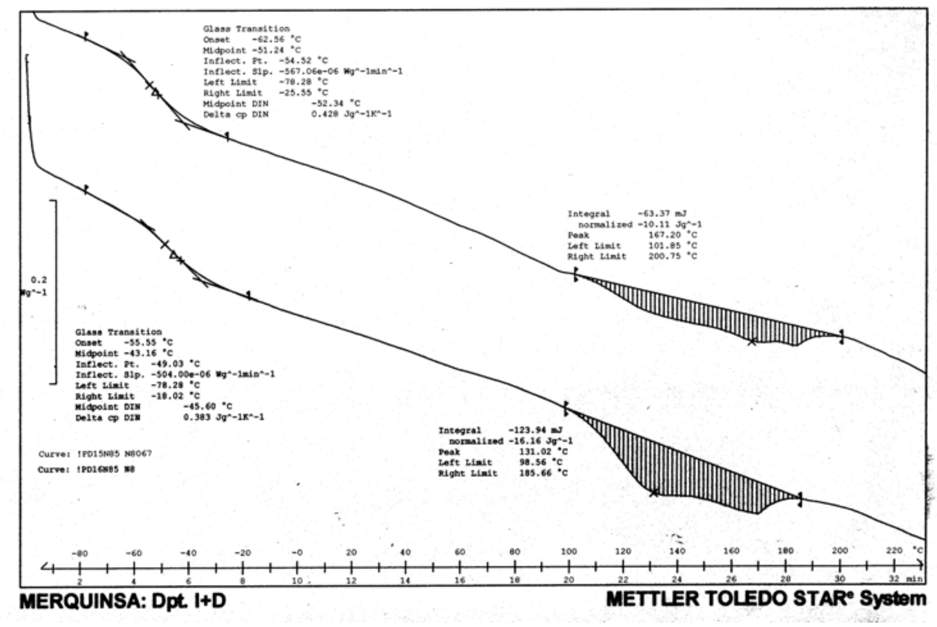

Fig. 7: DSC diagram for *PEARLTHANE®* D15N85 (upper curve) and polyether-based TPU.

The measurements obtained with the polyether copolymer are very similar to those obtained with the pure polyether, as already shown with the previously described test of hydrolysis resistance: the Tg is slightly lower, which is an advantage from the point of view of low temperature flexibility.

In addition, the lower Tg is confirmed by DSC analyses giving a Tg of –52ºC for *PEARLTHANE®* D15N85 and –46ºC for a pure polyether of the same hardness and molecular weight (See Figure 7).

2.5 Processing window

PEARLTHANE® D15NXX has a very wide processing window which is especially important in extrusion applications. This allows the resin to be extruded over a wide range of temperatures thus fine-tuning the process to the extrudate´s quality requirements. For example, it is possible to obtain a constant matt surface finish by simply lowering the die temperature.

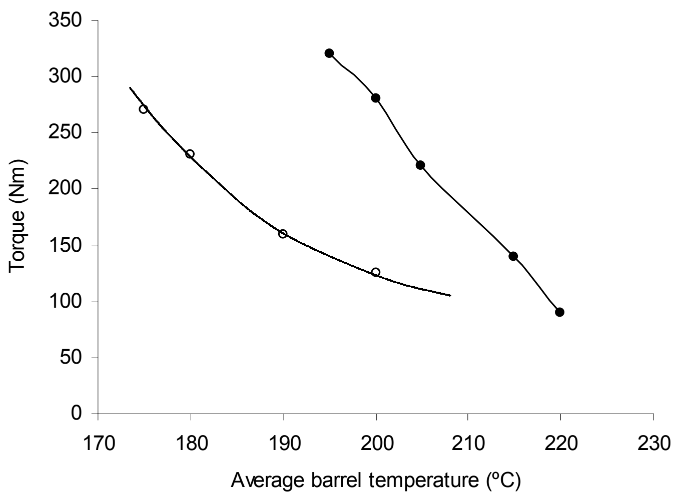

Fig. 8: Torque values as a function of the average extruder barrel temperatures. (○ Pearlthane D15N85 ; ● Polyester based extrusion grade).

The wide processing window in terms of temperatures can be easily seen in the graph of Figure 8. This plot shows the torque (amperage) as a function of the average extruder barrel temperatures. The decrease of torque with increasing temperature is much more pronounced in the case of the polyester grade than in the case of Pearlthane D15N85. This implies both a wider processing window in terms of temperatures and a more stable extrusion in the case of the copolyether TPU.

2.6 Water vapour transmission

The copolyether based products show a high water vapor transmission in comparison with polyester based TPUs as shown in the figure below. The data presented in this graph were measured according to DIN 53122 at RH=85%.

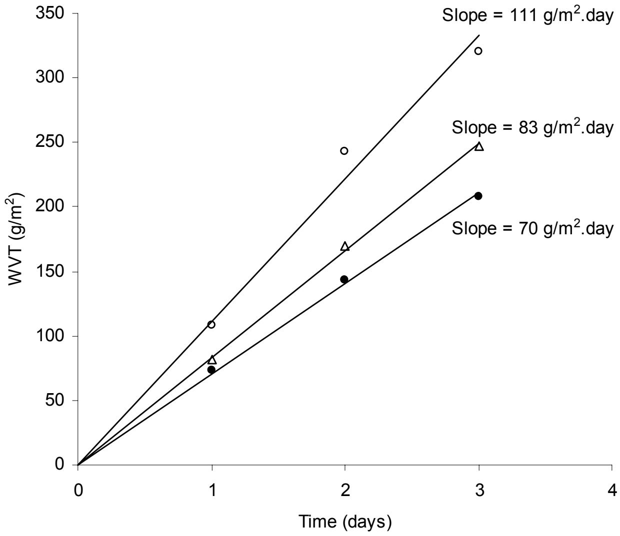

Fig. 9: Water vapour transmission as a function of time.(○ *PEARTHANE®* D15N85; △ Polyether based TPU; ● Polyester based TPU).

The high water vapor transmission is advantageous in film applications where breathability is important, for example in textile coating and brassiere straps.

2.7 Other advantages of the copolymer based TPUs

Other advantages observed in the market include:

- Excellent puncture resistance of blown films
- Good sound transmission properties (echo-mapping application)
- Very good hot-stamping behavior (high performance ear-tags)
- Extremely low gel content
- High transparency

To sum up, the copolyether copolymer based TPU *PEARLTHANE®* D15N85 shows general properties very similar to those of a polyether based TPU, with excellent mechanical properties as well as elasticity, which make it most attractive to the user.

3. POLYCAPROLACTONE COPOLYESTER BASED TPUs

MERQUINSA has been producing low molecular weight polycaprolactone for captive use (polyurethane production) for over 15 years. This has allowed our company to take advantage of this considerable experience for the development of speciality copolymers based on polycaprolactone, on which the new-developed TPUs are based.

In comparison with conventional polyester-based TPUs, the presence of polycaprolactone in its chain enhances two well-known properties of polyurethanes, which are hydrolysis resistance and low temperature flexibility.

If we jointly consider a polycaprolactone and a conventional polyester (such as 1,4 Butanediol polyadipate), the global chain ratio between the methylene non-polar groups (-CH_2-) and the ester polar groups (-COO-) is of 5:1 in the case of a polycaprolactone, and of 4:1 in the case of 1,4 Butanediol. This means that polycaprolactones are more non-polar than conventional polyesters, which involves a higher hydrolysis resistance and more phase-separation. The latter causes a lower Tg and consequently, an increase in the flexibility at low temperatures.

4. CONCLUSION

The mentioned macrodiol characteristics, originated by the soft segments in polyurethanes, clearly influence the inner structure and thus the final properties of TPUs based on them. The speciality copolymers developed by MERQUINSA have enabled the development of a new range of high performance TPUs, with most peculiar characteristics which make them different from traditional TPUs.
It was shown in this paper that *PEARLTHANE®* TPUs based on copolymers of polyesters and polyethers take away many of the disadvantages of the individual polyester and polyether based grades. This is shown in the table below, an updated version of table 1.

Table 3: Main differences between polyester and polyether based TPUs.
(++ excellent; + good; o acceptable; - poor; - - very poor)

Property	Polyester based TPU	Copolymer based TPU	Polyether based TPU
Abrasion resistance	+ +	+	o
Mechanical properties	+ +	+	+
Low temperature flexibility	o	++	+ +
Heat ageing	+	+	-
Hydrolysis resistance	- -	+	+ +
Chemical resistance	+ +	+	-
Resistance to microbes, fungi etc.	- -	-	+
Adhesion strength	+	o	-
Injectability (cycle time)	+ +	+	o

This positions *PEARLTHANE®* copolymer based TPUs as a unique product in the market, suitable for a wide range of extrusion and injection moulding applications.

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