New aspects on thermoplastic elastomers

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Thermoplastic elastomers (TPE) are elastomeric materials based on a co-polymer with a crystalline or amorphous solid phase and a flexible soft phase or an olefinic polymer compound of a rigid and an elastomeric polymer. When characterizing TPE the elasticity seems to be a self-evident aspect. In this study we present a basic approach to learn more about the elastomeric behaviour of TPE. Furthermore we look at the current ISO nomenclature of TPE and identify optimization potential.

1 Nomenclature

Thermoplastic elastomers (TPE) are elastomeric materials based on a co-polymer with a crystalline or amorphous solid phase and a flexible soft phase or an olefinic polymer compound of a rigid and an elastomeric polymer. The TPE family is a very diverse one. All grades have the same profile, they are elastomeric and meltable for the thermoplastic processing. The classification is defined by the ISO 18064 **(tab. 1).** A continuous education is advisable that everybody who dives into the TPE materials has a basic understanding about the materials included.

2 Markets

The growing market of these products make it more valuable to promulgate these polymers and learn what is behind the term TPE. More than two years ago in Germany an open network ("TPE Forum", www.tpe-forum.com) was founded to promote the understanding of that material group and to establish it as one material family. Apart from the activities of the TPE Forum there are initiatives to found a DIN group to bring TPE issues together as good and reasonable as possible. One activity started to work on the ISO Norm 18064 with the goal to harmonize the nomenclature of TPE with the available product families in the market at the time being. Additionally dedicated norms for particular TPE groups are ongoing, especially for TPV and TPS which are still not described in own documents.

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A recent market study from Freedonia Group gives an indication about the global TPE consumption. An exact number cannot be given because outside the technical application are some different ones, like melt adhesives or TPE for coating use out of a dissolution to create a very thin film on fabrics. Even the differentiation between a TPO blend and an impact-modified thermoplastic polyolefin is not clearly to analyze on the market view. There is no defined line when to name it a thermoplastic or elastomeric material. That will never be obvious, because all formulations should have been disclosed and nobody wants to do that. Nevertheless, since many years there is an annual growth slightly above 5 % expected which had been verified the last 20 years **(fig. 1).**

In the current version of ISO 18064 it is not taken into account that olefinic co-polymers are well established in the market since approximately 20 years. This family is called as POE or OBC (polymeric olefinic elastomer or olefinic based co-polymer). Very helpful in the Freedonia study is, that the TPO part is separated into compounds and olefinic co-polymers (POE). These olefinic-based thermoplastic elastomers are made in a reactor with crystalline and amorphous sequences. With a global market share of 16 % the POE are an important group of materials.

3 What does elastomeric mean?

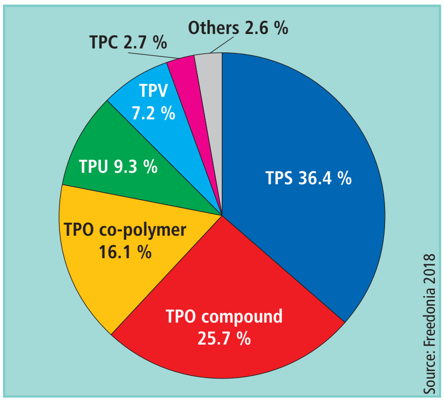
One of the crucial questions on elastomeric products is: What does elastomeric mean? Obviously, there is a big difference between an elastomeric behavior and the stretchability. An ideal elastomer is supposed to agitate like a spiral spring. Usually TPE are characterized by mechanical properties, stability, durability, and processability. The elasticity seems to be a self-evident aspect.

Every elastomer has a viscous and an elastic part, means they are visco-elastic ma-

Tab. 1: TPE nomenclature according to ISO 18064

TPE	Characterisation
TPO	Pure olefinic compound of rigid and flexible polymer (e.g. PP-EPDM)
TPV	Pure compound of rigid and flexible vulcanized polymer (e.g. PP-EPDM-vulcanized)
TPS	Styrene-based co-polymer with an olefinc soft phase
TPU	Urethane-based co-polymer
TPC	Co-polyester or ester-ether co-polymer
TPA	Amide-based co-polymer

Fig. 1: Market share of the different TPE groups (total world market estimated 5.56 million t)



terials. The first part transforms the energy in case of an impact, the elastic one gives the energy back mechanically. When a TPE is stretched, some areas start to flow and change the morphology that the test bar does not move back to the original shape completely.

That effect is described as a stress softening one, too, and known as Mullins Effect [1]. The reason of softening or remaining change in morphology can have different reasons, like breaking of filler-matrix adhesion, shear in crystalline structures or cleaving of bonds.

3.1 Intermitted stress strain measurement

The weakest structure element is touched first and the more the material will be pulled, the more changes in morphology happen. The cylinder in **figure 2** represents the viscous part and the spring the elastomeric one. After stretching and relaxing the smallest ("weakest") cylinder has changed the morphology which does not recover. There is a reliable test method to visualize that behaviour called intermitted stress strain measurement [2]. A test bar is pulled by 20 %, relaxed until the initial tensile, subsequently pulled by additional 20 %, relaxed and so on. The extension is given, and the residual elongation will be detected. The typical behaviour is illustrated in **figure 3**, where the residual extension is increasing more than in a linear increase besides the forced extension. That means the flatter such a curve is the more an elastomer keeps his elasticity and the less changes in morphology take place. An ideal elastomer with no viscous elements does not exist in the real life, because every material flows. But a non-filled rubber with a low cross-linking rate is close to such a pure elastomer. Fitness belts for therapy for example show this elastic behaviour pretty much. Even the constant modulus over the extension rate represents that as well and that is very important for the use in physiotherapy.

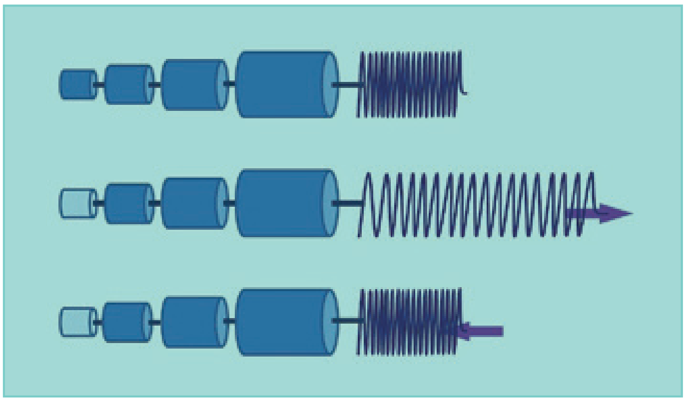


Fig. 2:
Every elastomer has a viscous and an elastic part, means they are visco-elastic materials.

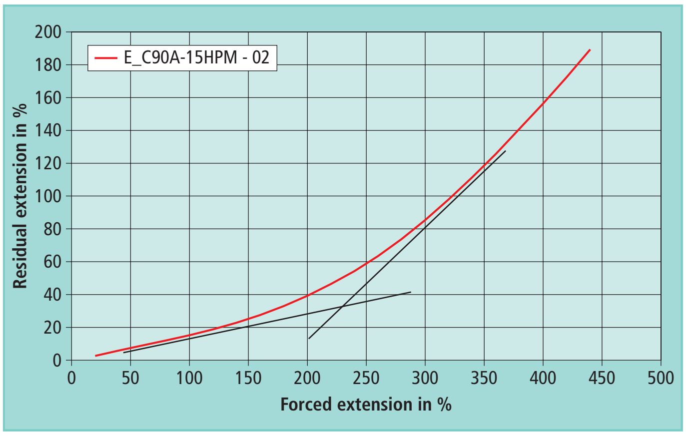


Fig. 3:
Intermitted stress strain measurement

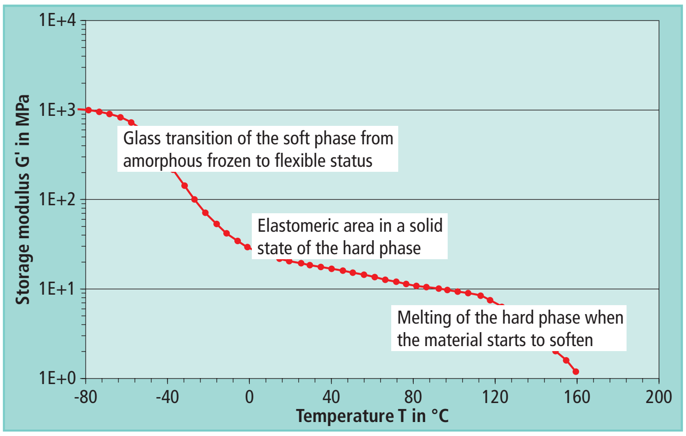


Fig. 4:
DMA of an ether-based TPU (Shore hardness 90A), torsion 1 Hz

In most cases TPE are not used for such applications where a high recovery is requested after extension of several 100 % and this is one of the reasons that TPE has a good chance to jump into many applications where rubber is established. In these fields TPE show advantages, that is the thermoplastic processing with short cycle time compared to the vulcanization process with rubber and the opportunity to recycle the material by thermoplastic processing again.

3.2 Dynamic mechanical analysis (DMA)

Another measurement gives a good picture about the property profile of a TPE, it is the dynamic mechanical analysis (DMA). Well known in the plastics community, it is in the TPE world mainly used internally and often not so crucial for selecting the right material for a specific technical solution. Mechanical properties are the first and most important data to evaluate the opportunity where to use a TPE, but in every case it is recommended to talk about different conditions and property requests with the vendor.

Nevertheless, the DMA gives a decent impression on the behaviour of a TPE in a wide range of temperature from minus Celsius degrees close to the melting area. How does it work? A test bar is forced by a dynamic torsion between two clamps. One side is setting the force the other side is detecting the answer of the material, in a specific phase displacement. The frequency is usually set by 1 Hz and the deflection is very small, because the measurement is only reasonable when the material supposed to be in a linear visco-elastic status. In best case it should stay in the ideal elastic one where no flow happens. The residual modulus curve shows the different status of the material and the transfer of aggregate phase. The example in **figure 4** is a DMA of an ether-based TPU (Shore hardness 90A). The transition from the rigid glassy status, the frozen one, to the temperature area where the material is used until the softening range, is clearly depicted.

What is the main difference between a TPE and a rubber mixture, shown by a DMA curve? Since TPE are disclosed and presented in the market, the comparison to rubber materials had been started [3] and is still ongoing. One crucial point is the melting area. Cross-linked rubber does not melt and the curve ends-up somewhere. It can be burned or decomposed by temperature. High elastic rubber has a very clear and deep glass transition and a wide range of horizontal plateau of modulus over temperature. In many applications it is important to have that behavior, e.g. in tire applications. To some extent, TPE materials can be developed to bring them close to a vulcanized rubber. For sure, that does not mean a complete profile can be covered by a special designed TPE. Only in certain cases a TPE can replace a rubber, depending on the full property request.

The DMA curve in **figure 5** shows the comparison of a soft TPU (Shore hardness 61A) which is designed to be close to a rubber mixture (natural and butadiene rubber, Shore hardness 65A) which is used for car tire profiles. Nevertheless, TPU never can be used for that application because of the heat build-up and the non-sufficient wet slip resistance. The DMA presents a section of a property profile only, but more than a single mechanical testing.

Usually most of the grades do not have such a flat modulus curve as depicted in **figure 5.** But in usual technical applications not a wide range of temperature impact happens. Another example of comparison is presented in the DMA in **figure 6,** where a cross-linked EPDM rubber (Shore hardness 63A) is plotted with a TPS compound (Shore hardness 65A). That TPS is a standard SEBS compound with polypropylene and white oil. Like the modulus of rubber compounds is achieved by cross-linking rate and inorganic filler content, the quite similar technology is done in TPE technology, especially with TPS and TPO. The well-known advantages of such a TPE compound is still there, faster processing and the easy way of recycling. One of the nicest applications of soft TPE grades is the overmolding of rigid devices to give the surface a pleasant touch. In case of the rubber use it has to be molded separately and applied to the hard component by gluing. The two-component process in injection molding or co-extrusion is much easier and faster and does not need any treatment in most cases.

4 Conclusion

The conclusion of the reflections above is to consider about the property profile which is needed for the application. Beside the mechanical properties the described methods are helpful to focus on a certain TPE family. At the end it has to be taken into account that every TPE portfolio opens a wide range of products including special mixtures for certain requests which can be designed by a compounding vendor. In every case it is recommended to come into contact with the TPE supplier.

5 Acknowlegdment

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6 References

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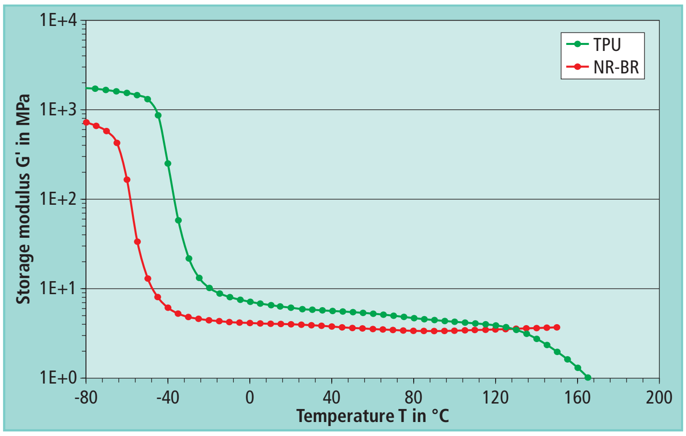

Fig. 5:
DMA of a TPU (Shore hardness 60A) compared to NR-BR rubber (Shore hardness 65A), torsion 1 Hz

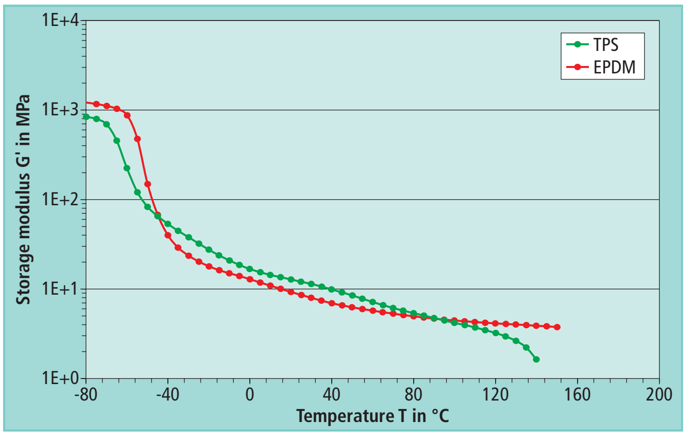

Fig. 6:
DMA of a TPS compound (Shore hardness 65A) compared to EPDM rubber (Shore hardness 63A)