Solving scratch problems and achieving low friction demands in TPE compounds

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Thermoplastic elastomers are present in many industrial and consumer applications nowadays (automotive, electrical and electronics appliances, consumer goods, etc.) and they are gaining each day market share in new ones by replacing other materials. All of them demand better properties in TPEs and producers need to fine-tune their products to give an answer to these requirements. One of the most demanding improvements in these areas is the surface contact properties optimization, such as scratch resistance and coefficient of friction (COF). This paper will focus on how to modify these properties in TPE compounds by the combination of Dynasol SEBS copolymers and Evonik Industries AG organomodified siloxanes.

1. Introduction

Polyolefins such as polypropylene (PP), rubber-modified PP thermoplastic olefins (TPOs) and thermoplastic elastomers (TPEs) are increasingly used in automotive and other applications because they have advantages in recyclability, light weight, and low cost compared to engineering resins [1].

Portions of the TPE market are maturing and exhibit the characteristics of commodities. At the high end, TPE suppliers are stretching toward high performance rubber markets and expanding performance (softness, transparency, etc.). Because of its large share of the TPE market (40 – 50 %) automotive remains a major driver for TPE growth based on systems cost savings via flexible/rigid combinations and continued replacement of high volume rubbers, especially EPDM [2].

Thermoplastic elastomers based on hydrogenated styrene block copolymers (TPE-S) are already widely used in the automotive industry. Compared to other materials such as soft paint films, TPO, PVC-P, TPU and TPE-S is not very scratch-resistant. Therefore it is not particularly suitable for car interior components. Materials for such applications have to meet stringent requirements as regards processability, durability, and resistance to a great number of substances and forces throughout the service life of the part **(fig. 1)**. By developing TPE-S with better scratch resistance, this material would become a viable option for a much wider range of products [1].

A cooperation between Dynasol and Evonik Industries AG focuses on the development of TPE-S compounds with improved scratch performance and optimization of low coefficient of friction for several applications. Evonik as producer of multifunctional additives, like organomodified siloxanes (OMS), brings the technical expertise in the performance and combination of their tailor made Tegomer and Tegopren products to this development. Dynasol as SEBS producer provides its experience in TPE-S compounding for combining the performance of Evonik additives with its Calprene H thermoplastic rubbers to achieve performing properties for applications such as: automotive parts, mobile phones, cables, glass run channels, etc.

2. Surface contact properties of materials

The surface contact properties of polymers can be divided into two categories: those in which the surface remains intact when it comes into contact with another surface, and the polymer surface's resistance to damage. Friction and cling fall in the first category. Surface damage can be caused by erosion, abrasion or cavitation. Scratch resistance is also included in this last category of surface damage.

2.1 Friction

Friction is the resistive force that we experience when we try to slide one object over the surface of another. The coefficient of friction is the ratio of the lateral force required to slide the surfaces past one another relative to the force holding them in contact. Polymers exhibit:

- static coefficient (measure of the force required to initiate the movement)

Fig. 1:
Materials for car interiors have to meet stringent requirements.

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- dynamic coefficient (measure of the force required to sustain movement at a constant rate).

In general, the force required to initiate sliding is somewhat greater than that required to maintain a constant rate of movement.

The coefficients of friction of a polymer depend on many variables, including the chemical composition of the material against which it is sliding, surface roughness, sliding speed, temperature and frictional heating. The relationships controlling friction are complex and varied, so it is difficult to generalize with regard to how most of the factors affect the coefficients of friction. Friction generally increases as a polymer's temperature rises, because it becomes softer and the viscous component of its nature plays a greater role. We see the effect most clearly when we compare the coefficient of friction of a polymer measured below and above its glass transition temperature.

Details of static and dynamic coefficients of friction can be found in **table 1.** In this study the dynamic coefficient of friction μ_d is measured; **figure 2** shows the equipment and method.

2.2 Wear resistance

Wear is the removal of surface material by erosion, abrasion, or cavitation.

Tab. 1: Static and dynamic COF

Static COF $\mu_s = F_g/M$	Dynamic COF $\mu_d = F_d/M$
μ_s: static coefficient	μ_d: dynamic coefficient
F_g: lateral force required to initiate movement	F_d: lateral force required to sustain movement
M: normal force of the sled	M: normal force of the sled

- Erosion is the removal of a polymer's surface by abrasive materials carried in a fluid medium. We see this type of wear in plastic pipes used to transport waterborne slurries of mineral in mining operations and in vacuum transfer pipes used to convey powders in a stream of air.
- Abrasion is the result of two surfaces sliding against each other. We commonly observe abrasion of polymers in the fabrics of clothes and upholstery.
- Cavitative wear is caused by voids in a liquid medium collapsing against a surface. It is essentially an impact process. Cavitation is a relatively uncommon cause of wear in polymers. Pump impellers are one of the few applications where polymers must resist this type of wear.

Abrasive wear of polymers has two components: material can be removed by the rasping action of a counter surface or it can be sheared off viscoelastically by a counter surface to which it adheres. The precise balance of mechanisms depends on the characteristics of the counter face and the conditions under which the abrasion takes place. Many polymers exhibit excellent wear resistance, which in combination with their low coefficients of friction suit them for applications where the use of lubricants is either impossible or undesirable [3]. The wear method evaluated in this study is abrasion.

2.3 Scratch resistance

Scratch resistance is the ability of a material to withstand abrasive interaction with another body. It is not the same as abrasion resistance and wear commonly addressed in the literature. A scratch is created when the material yields under an indentation force. In a scratch, the uneven surface results in non-uniform light scattering and "scratch whitening" especially for filled materials [4, 5].

Overall scratch resistance can be expressed as a function of hardness, coefficient of friction and toughness. Several factors, such as polypropylene type, impact modifier, filler type and amount, surface hardness, additives, colour and pigments and gloss level, are crucial to the increase of the scratch resistance of TPEs or at least to the visual change along the scratch [5].

TPE-S surfaces are soft and warm to the touch. In contrast to hard thermoplastic compounds, they tend to look more attractive and have a mat finish with minimum reflection. Scratch and mar resistance are two clear indicators for the mechanical strength of the surface finish. Solutions for improving scratch performance include minimizing roughness of the polymer ground and lowering the shoulder of the scratch, resulting in less light scattering and lower scratch visibility.

The scratch resistance can be measured with different devices:

- Erichsen Scratch tester 430P (common and reliable equipment to measure scratch especially in the automotive industry.
- Crockmaster Model 670 (soft materials such as TPE, TPU and TPO can be evaluated with this type of equipment.)

Fig. 3: Chemical structure of OMS

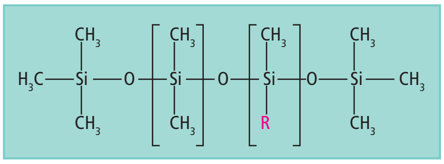
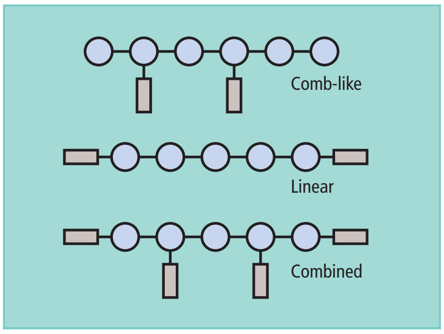


Fig. 4: Different forms of OMS



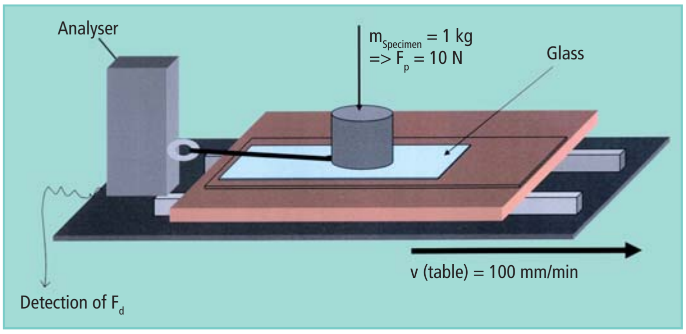


Fig. 2: Measuring the dynamic coefficient of friction

3. Effect of OMS in the surface properties modification

The organomodified siloxanes (OMS) used in this study are chemical compounds containing various organic functional groups as well as dimethylsiloxy units. Examples of such groups are alkyl, polyester, polyether, acrylate, epoxy, hydroxyalkyl and aminoalkyl groups **(fig. 3)**.

Organically modified siloxanes may be linear (with the organic groups at the two ends); comb-like (with the organic groups at right angles to the siloxane chain); or a mixture of the two variants **(fig. 4)**.

The organic group architecture can be fine-tuned and it can be controlled whether the siloxanes are distributed within a polymer or confined to the surface **(fig. 5)**.

The desired effect for scratch reduction improvement is that the siloxane is confined to internal and external surfaces of the polymer bulk phase. It will improve the distribution of fillers and pigments and to fix them into the polymer matrix. In the case of the reduction of coefficient of friction this effect would be also desirable, as the anchorage groups ensure a durable and permanent set with no migration effect nor fogging effect [6].

An example of the effect in the surface modification performed by these additives in SEBS compounds is shown in **figure 6.**

4. Scratch improvement in TPE-S hard compounds for automotive and electronic applications

Scratch resistance is one of the most demanded requirements for automotive interior parts as aesthetics for instrument panels, consoles and door panel skins is highly appreciated. TPE-S are competing in this area with other materials such as TPO, TPU, or even PP grades. In applications such as electronics or tools, scratch properties are also a plus for high end quality materials **(fig. 7)**.

Standard TPE-S grades offer better scratch resistance than TPOs or PP grades, but there is still room for improvement. This study shows how the use of additives from Evonik combined with Dynasol SEBS formulation suitable for these applications gives advantages in scratch properties and also can offer improvements in other properties like flowability and abrasion resistance.

The formulation consists of SEBS, polyolefin (PP homopolymer), oil, mineral filler, black masterbatch, antioxidants and additive for scratch resistance. The hardness of the compound is 75 Shore A (ASTM D2240).

Three different types of scratch additives have been used (dosing 2.5 %).

- Tegomer A type
- Competitor slipping additive
- Special mineral filler

Results of the evaluation with test specimens (plates 20 x 100 x 50 mm) are shown in **figures 8 – 10.** There is an optimization in the scratch performance under 5 N of testing force when using Tegomer A additive compared to the other alternatives. When applying a force of 10 N heavy defects on the surface where created. Trials in Crockmaster tests did not reveal significant differences between the evaluated compounds. The tests were done under force of 9 N and applying 5, 10 and 20 strokes **(fig. 8)**.

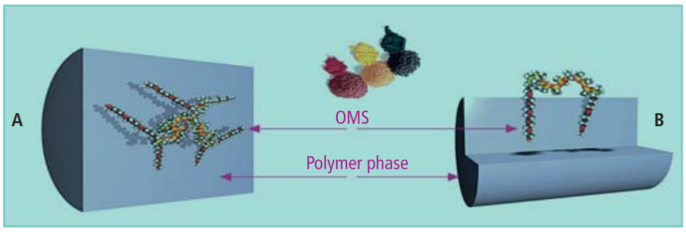


Fig. 5: Functionalization of a polymer matrix with OMS (A = bulk modification, B = surface modification)

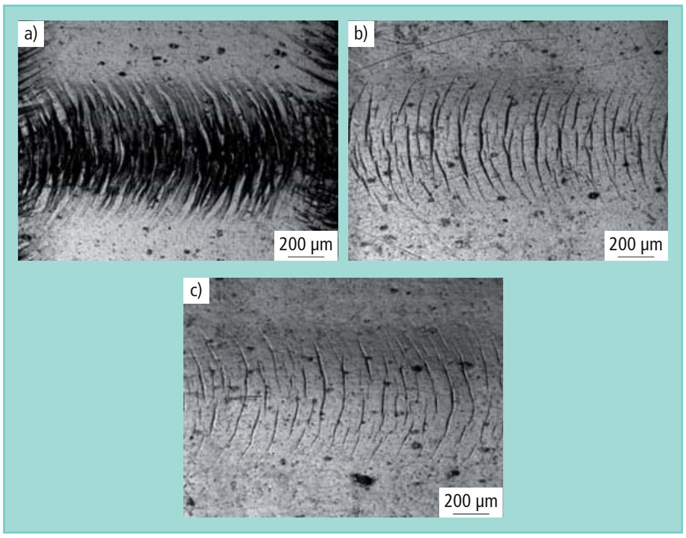


Fig. 6: Effect of siloxanes in a SEBS compound
a) without any additive,
b) with 2 % Tegomer A,
c) with 2 % Tegomer B

Fig. 7: Scratch resistance is key in applications such as electronic devices or power tools.

Directly linked to the scratch performance, abrasion resistance also shows a significant improvement in the compound developed with Tegomer A additive that offers 50 % reduction in this value **(fig. 9).**

As a side effect the use of Tegomer A enhances of the flowability and as a consequence increases productivity **(fig. 10).** Production cycles can be shortened and this could be beneficial for the injection of complicated geometries with long channels or paths.

5. Scratch improvement and low COF in TPE-S compounds for glass-run channels and soft applications

Compared to other materials such as soft TPU, PVC or TPO, TPE-S is not very scratch resistant and needs to be modified to achieve better scratch resistance. This modification would make soft TPE-S a viable option for applications such as cables, skin protective layers, sealing profiles, etc. **(fig. 11).**

The formulation consists in SEBS, polyolefin (PP homopolymer), oil, mineral filler, black masterbatch, antioxidants and additive for scratch resistance. The hardness of the compound is 60 Shore A (ASTM D2240).

Five different types of scratch additives have been used at two dosing levels (0.5 %, 2 %):

- Tegomer A
- Tegomer B
- Tegomer C
- Tegomer D
- Tegopren A

Results of the evaluation in comparison to a formulation without additive (test specimen plates 20 x 100 x 50 mm) are shown in **figures 12 – 15.**

At a dosing level of 0.5 % already, scratch resistance is improved when using Tegomer B **(fig. 12).** However, better results are obtained when adding 2 % Tegomer B to the formulation. In this case, a good scratch performance under the applied forces is obtained. From all samples in the test this combination performed best. It can also be seen that there are combinations negatively affecting the scratch resistance; this could indicate a bad dispersion of the additive or a lack of compatibility of the ingredients. The trials performed with Crockmaster scratching equipment do not evidence any difference between the specimens. The test conditions are applying a force of 9 N and passing 5, 10 and 20 strokes.

Aligned with the scratch resistance results, best results for abrasion values are achieved with 2 % of Tegomer A **(fig. 13).** Tegomer A is a liquid and therefore can probably better dispersed in the polymer matrix.

For sealing gasket applications, it is beneficial to obtain low COF values. **Figure 14** shows that the addition of 2 % Tegomer D has a strong effect as COF is reduced by 50 % of its original value.

As general result, the addition of 2 % of additives to the reference compound enhances the flowability of the blends **(fig. 15).** There is a significant improvement with Tegopren A (100 % of increment) whereas Tegomer C does not modify the flowability of the compound at all. Considering all results obtained with Tegomer C we assume that there is a lack of compatibility of this additive with the SEBS used in the formulation.

6. Conclusion

Formulations with Dynasol SEBS copolymers and Evonik Industries additives offer alternatives for optimizing scratch resistance in compounds used for automotive interi-

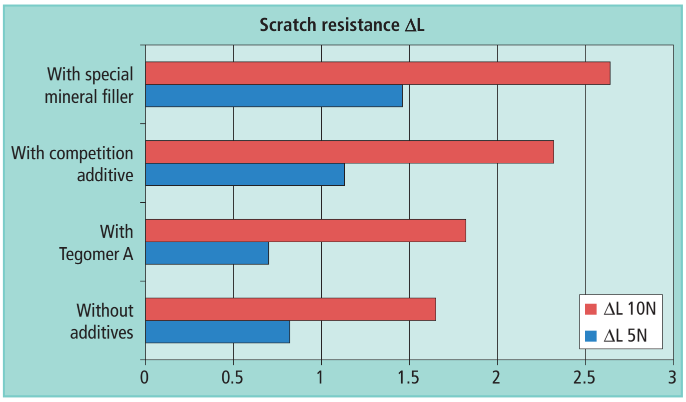


Fig. 8: Scratch resistance (tested with Erichsen Scratch tester 430P)

Fig. 9: Results of the abrasion resistance test (ASTM D5963)

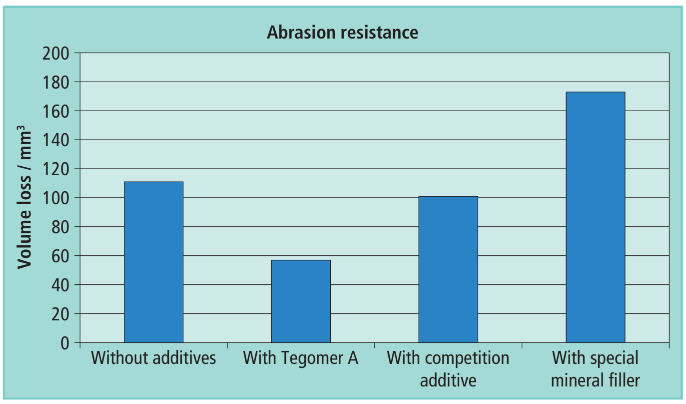
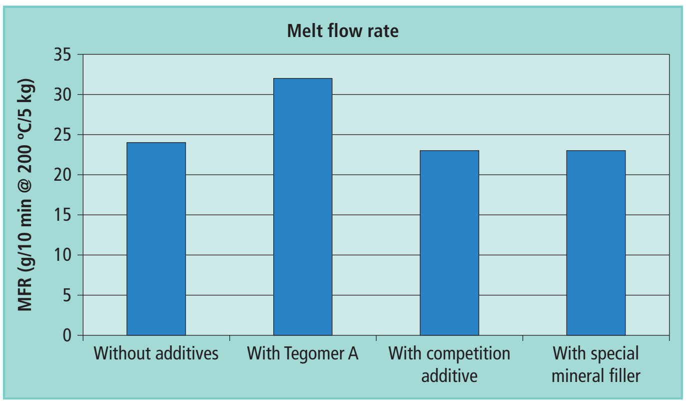


Fig. 10: Melt flow rate (ASTM D1238)



or parts, enhancing the flowability of the compound as well as the abrasion resistance. There is no modification in other principal mechanical properties, such as tensile properties or elastic retain.

Soft compounds formulated with Dynasol SEBS copolymers and Evonik Industries additives offer a wide range of possibilities in performance, especially for scratch resistance improvement and COF reduction. Results obtained indicate a significant improvement in both properties with the addition of 2 % of additive. Other properties such as melt flow rate can also be optimized and increased by formulating the compound with 2 % of additive without any loss in the main mechanical properties of the compound.

7. References

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Fig. 11: Scratch-resistant TPE-S are an option for glass-run channels, cables, etc.

Fig. 12: Scratch resistance (tested with Erichsen Scratch tester 430P)

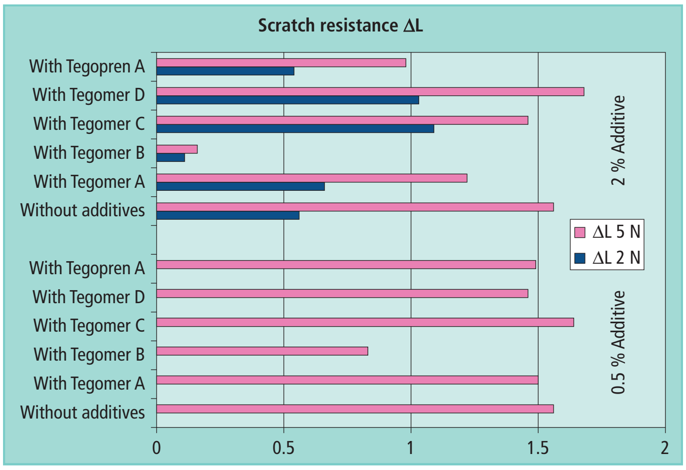


Fig. 13: Results of the abrasion resistance test (ASTM D5963)

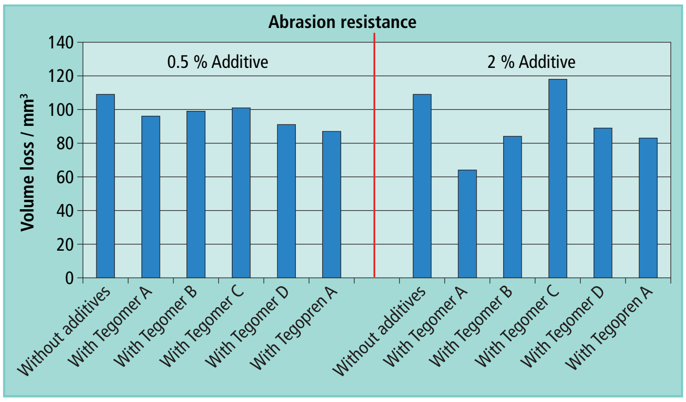


Fig. 14: COF improvement (applied force 10 N)

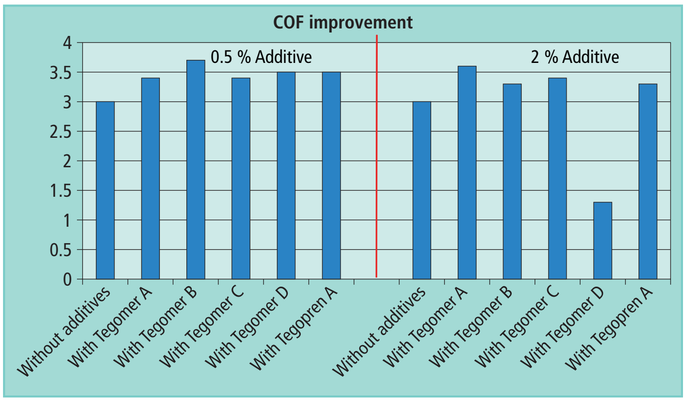
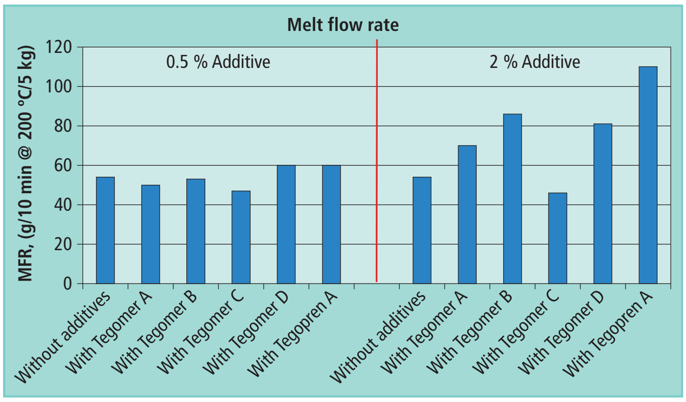


Fig. 15: Melt flow rate (ASTM D1238)



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