



# THERMOPLASTIC ELASTOMER HYBRIDS

WHITE PAPER | OCTOBER 2018

## A NEW TECHNOLOGY PLATFORM IS SHIFTING THE PERFORMANCE LIMITS OF THERMOPLASTIC ELASTOMERS

**FOR MANY YEARS, TPE MANUFACTURERS AND PROCESSORS HAVE BEEN STRIVING TO SHIFT THE PERFORMANCE LIMITS OF THERMOPLASTIC ELASTOMERS (TPES) TOWARD THOSE OF RUBBER MATERIALS. THE DESIRE FOR IMPROVED CHEMICAL RESISTANCE AND HIGHER TEMPERATURE RESISTANCE PLAYS A MAJOR ROLE HERE. THE NEW THERMOPLASTIC ELASTOMER HYBRIDS (TEH) HAVE ENABLED KRAIBURG TPE TO FURTHER REDUCE THE DIFFERENCES IN PERFORMANCE BETWEEN THE WORLD OF TPE MATERIALS AND RUBBER MATERIALS. THE DEVELOPMENT OF AN INNOVATIVE PRODUCTION TECHNOLOGY HAS MADE ACCESS TO TEHS POSSIBLE.**

Shortly after the launch of TPE materials in the mid-1980s, it was the industry's declared intention to combine the excellent properties of rubber with the advantages of thermoplastic elastomers. TPE processors appreciated the newly gained advantages of thermoplastic processing with reduced cycle times, as well as the considerably enhanced flexibility with regards to component design and the options provided by two-component injection molding. However, applications that required technically sophisticated materials were still out of reach. There was a strong need for a universal material solution based on TPEs that has even grown over the years.

Developments soon focused on thermoplastic copolyester elastomers (TPCs) and thermoplastic polyamide elastomers (TPAs) due to their chemical composition. They were intended to meet the high requirements with regard to resistance against oil, grease and fuel while providing high thermal stability. In recent decades, numerous approaches have been taken in the field of Shore D reactor-made TPEs such as TPC and TPA. Looking back, these products represented considerable progress, but they were not able to compete with the elasticity and softness of rubber.

Soft TPEs that belong to the Shore A hardness range such as TPS, TPO or EPDM/PP (TPV), however, showed a maximum permanent working temperature of 125 °C (257 °F) with moderate to no resistance against oils, greases and fuels. This situation hasn't changed until today.

The continuing need for a universal TPE solution capable of replacing rubber remained. This led to a veritable boom in developments more than ten years ago in this technologically open field, with high demands for the temperature resistance and chemical resistance of Shore A materials. Many different approaches were taken in the effort to reduce or eliminate the performance deficits of TPEs. Numerous so-called super-TPEs or super-TPVs entered the market and then gradually disappeared again.

Successful representatives of these TPE classes are super-TPVs based on acrylate rubber, for example. KRAIBURG TPE has also been able to establish soft TPE compounds known as HIPEX® which are characterized by good oil resistance and are already used in transmissions and lubrication circuits for automobiles since a couple of years.

There are many reasons why these developments were not able to really establish themselves on the market. It is noticeable, however, that these thermoplastic elastomers are each based on only one specific raw material, which means the main ingredient choice is rather rigid. Attempts were repeatedly made to satisfy the needs of as many applications as possible with one TPE class and its special raw-material base. The desired "universal solution" failed to materialize.

When one looks at rubber and vulcanized rubber compounds, it is noticeable that there is a broad raw-material base that allows for different applications with various requirements in relation to temperature and chemical resistance. These include NBR, H-NBR, EVM, AEM, ACM, ECO, CR, SBR, IIR, BR, EPDM, VMQ. **Figure 1** shows the technical classification of a wide variety of rubber types according to temperature and chemical resistance. The elastomers listed are related to the corresponding rubber compounds made from them. The applications and their material requirements with different temperature and chemical resistances in the specified areas vary so widely that rigid materials solutions would be only suitable for a very small percentage of them. The reason for the success of rubber compounds is that they can be individually compounded based on a variety of elastomers. The same, therefore obviously also applies to new types of TPE materials. The approach involving replacing versatile technical applications with a single universal TPE solution was thus bound to fail.

		Max. Permanent Working Temperature		
		100 °C	120 °C	150 °C
Chemical Environments	Hot air and polar chemicals (aqueous solutions)	SBR	IIR	VMQ
		NR	EPDM	
	Paraffinic greases and oils (IRM 901)	CR	CSM (CI-Sulfon)	EVM
			CM (CI-PE)	ACM
				AEM
	Aromatic greases, oils and fuels (IRM 903)	NBR	UA (PU-Kau.)	HNBR
			ECO	F-Rubber
				F-Silicon

**Figure 1:** Classification of rubber types based on different elastomers relative to temperature and media resistance

As in the past, there are still impediments that prevent TPE materials from being used for a wide range of applications. Rubber materials have had an established position for sophisticated applications for decades now. Their resistance in terms of temperature and chemicals plays an important role here. In addition, the machinery used for rubber processing is fundamentally different from that used for thermoplastic processing. Even if the technical performance of thermoplastic elastomers was sufficient, it will be hesitant to replace rubber compounds with TPEs.

#### **The starting point for developing a new technology platform and thermoplastic elastomer hybrids**

It already became apparent at KRAIBURG TPE a few years ago that the previous approach of an “universal solution” needed to be reconsidered. The unique structure of the KRAIBURG Group proved to be a great help in this situation. With the Gummiwerk KRAIBURG the company KRAIBURG TPE has a competent partner at its side when it comes to rubber technology and its fields of application.

The world of rubber and the diversity of its elastomers is opening up new horizons for possible TPE materials. It is interesting to note that nearly all of the different rubber compounds are manufactured with the same technology. Despite chemical differences and the cross-linking chemistry of the elastomers used, the flexibility of the manufacturing process is the key element for success.

KRAIBURG TPE's objective was to combine different thermoplastics and different elastomers using only a single manufacturing technology and thus to achieve the maximum possible number of combinations with a low level of complexity in production technology. In short: to combine flexible manufacturing technology with a wide variety of raw materials. This approach is in line with the concept of application-engineered solutions from KRAIBURG TPE, which has already been successfully implemented with THERMOLAST® products.

### **Application-engineered TEHs**

After intensive research and process development, KRAIBURG TPE has succeeded in implementing a technology platform that allows a large number of thermoplastic elastomers to be tested within a short period of time. Whereas the initial developments took months to complete, conclusions about the suitability of a new raw-material combination can now be reached within a few test cycles and only few weeks of material testing. This enables a TEH material for a specific application to be promptly developed, so that the overall development times for new products can be significantly shortened. Each application with its individual technical specifications determines which raw-materials combination of a matching thermoplastic and elastomer is chosen.

During the past years, KRAIBURG TPE has tested different thermoplastics such as PP, PE, EVA, PA, PBT and modified thermoplastics, as well as thermoplastic elastomers such as TPE, TPC, TPA and TPU as a thermoplastic phase. The elastomers that were used include NBR, H-NBR, EVM, AEM, ACM, SBR, IIR, BR, NR, EPDM and VMQ.

In handling of raw materials and handling of the many different types of elastomers available on the market, KRAIBURG TPE again benefited from an intensive exchange of ideas and know-how with the experts from Gummiwerk KRAIBURG. The availability of the raw materials used was an essential factor in choosing the elastomers. The scale-up to production has also been successfully completed for selected TEH compounds and patents for thermoplastic elastomer hybrids and their production technology were published.

The innovative, flexible technology platform enabled KRAIBURG TPE to considerably extend the property profile of soft TPE compounds with a hardness below 80 Shore A. Customers benefit from

completely new, application-specific material solutions provided by this manufacturing process. Thermoplastic elastomer hybrids can now be used for applications in which classic TPEs reach their limits and in which rubber materials have been preferred so far. At the same time, thermoplastic processing offers design flexibility, short cycle times and wide-ranging options with two-component injection molding. This is complemented by an inherent advantage over rubber that thermoplastically processable materials have – TEHs are recyclable in the same way as traditional TPEs. **Figure 2** shows a comparison of major product properties between TEHs, standard TPS/TPV and rubber.

	TEH	TPS/TPV	Rubber	Remarks
Chemical resistance	+	--	++	Depending on material formulation, used raw materials and applied conditions
Max. permanent working temperature	+	--	++	Depending on material formulation, used raw materials and applied conditions
Compression set	+	+	++	Depending on material formulation and used raw materials
Mechanical properties	+	+	++	Depending on material formulation and used raw materials
Processing method	++	++	O	Processing of TEH is highly advantageous to mass production (cycle time)
Two-component injection molding	++	++	-	TPE allows for increased freedom of design
Post processing	None	None	Mandatory	Rubber calls for labor intensive post processing. (chamfering and/or annealing, etc...)
Raw material storage	++	++	-	Rubber come with limited shelf life

With the TEH manufacturing technology, KRAIBURG TPE is shifting the boundaries between the materials groups, with the resulting compounds extending the range of possible applications. The advantages of thermoplastic elastomer hybrids lie in the way they are processed. Thermoplastic processing considerably reduces cycle times and thus substantially increases efficiency. In contact with various chemicals, TEHs are on a par with rubber compounds. Another advantage of TEHs is their suitability for two-component injection molding. This opens up new options in the construction and design of components that have so far been out of range using rubbers. TEH compounds with optimized adhesion that are processed using two-component injection molding make the costly installation of separately produced rubber parts unnecessary and avoid related causes of defects.

### Selective comparisons between rubber and TEHs

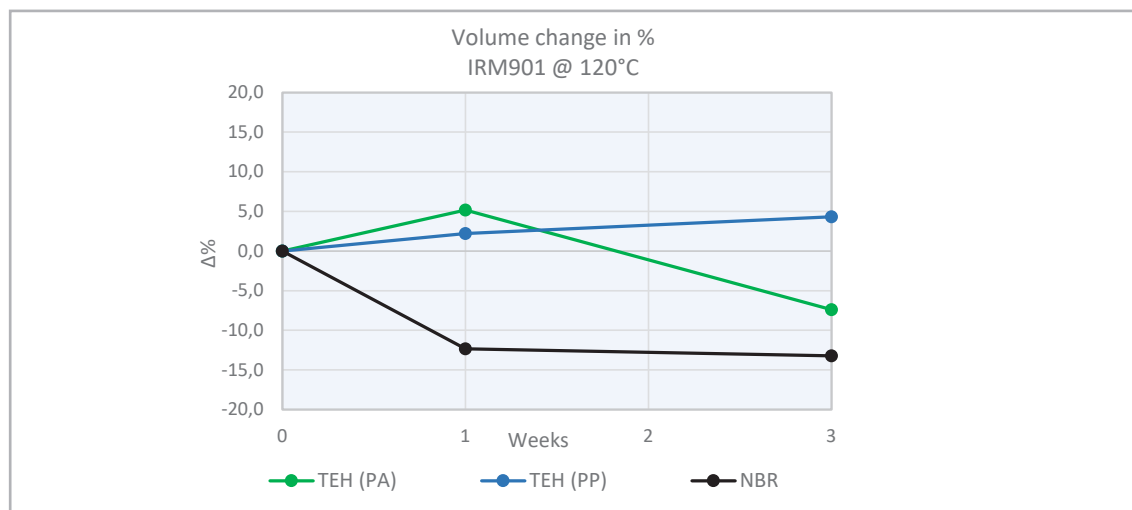
The following examples are intended to demonstrate the technical potential of the new TEHs. For this purpose, TEHs are directly compared with typical representatives of the world of rubber.

**Figures 3 to 8** display examples of test results for two TEH compounds in comparison with an NBR-based rubber. One TEH compound was developed for adhesion to polypropylene (TEH (PP)) and the other one for adhesion to polyamide (TEH (PA)). The tests were designed for permanent stress at up to 120 °C (248 °F), as needed in transmission systems in automobiles, for example.

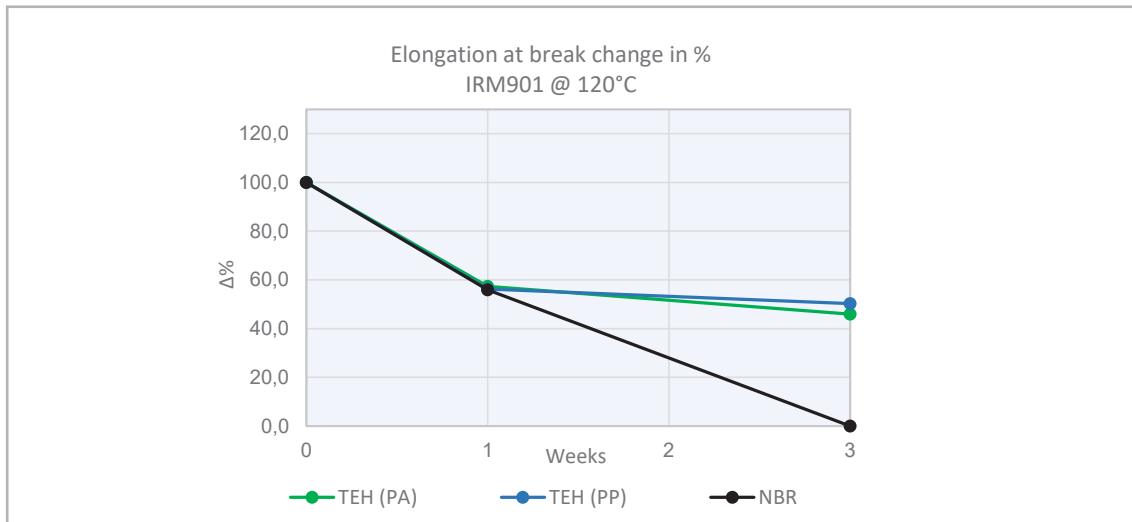
**Figure 3** shows the mechanical values for the two TEHs. An important aspect worth mentioning is the extremely low compression sets of TPEs.

	TEH (PA)	TEH (PP)
Hardness Sh A	73	67
Tensile strength N / mm <sup>2</sup>	6.3	6.5
Elongation of break %	300	330
Tear resistance N / mm	18	19
Compression set 70°C / 22 h	31	40
Compression set 100°C / 22 h	35	37
Compression set 120°C / 22 h	38	47
Adhesion N / mm	2.7	6.0

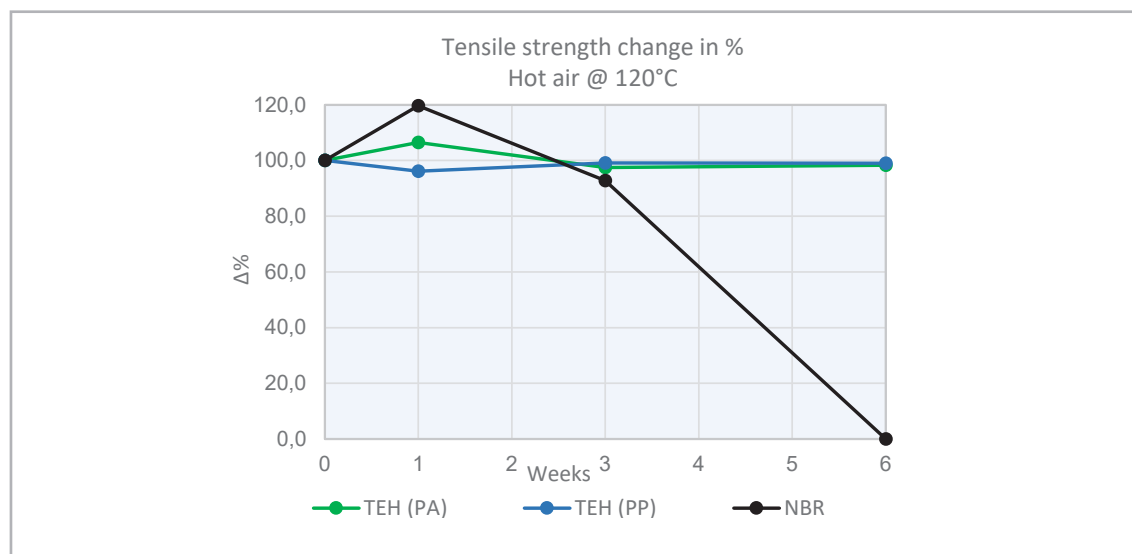
A significant decrease in volume for the NBR-based rubber compound can be observed in **figure 4**. This may present a problem for sealing applications. By contrast, both TEHs show a very low volume change, even in extreme conditions with three weeks' exposure to IRM901 oil at 120 °C (248 °F).



The NBR-based rubber compound also becomes extremely brittle during storage in IRM901 at 120 °C (248 °F). This can be clearly identified by a reduction of the elongation at break to 0 at the end of the measurement period. Both TEHs stabilize at an elongation at break value of 50% compared to the output value, as shown in **figure 5**.



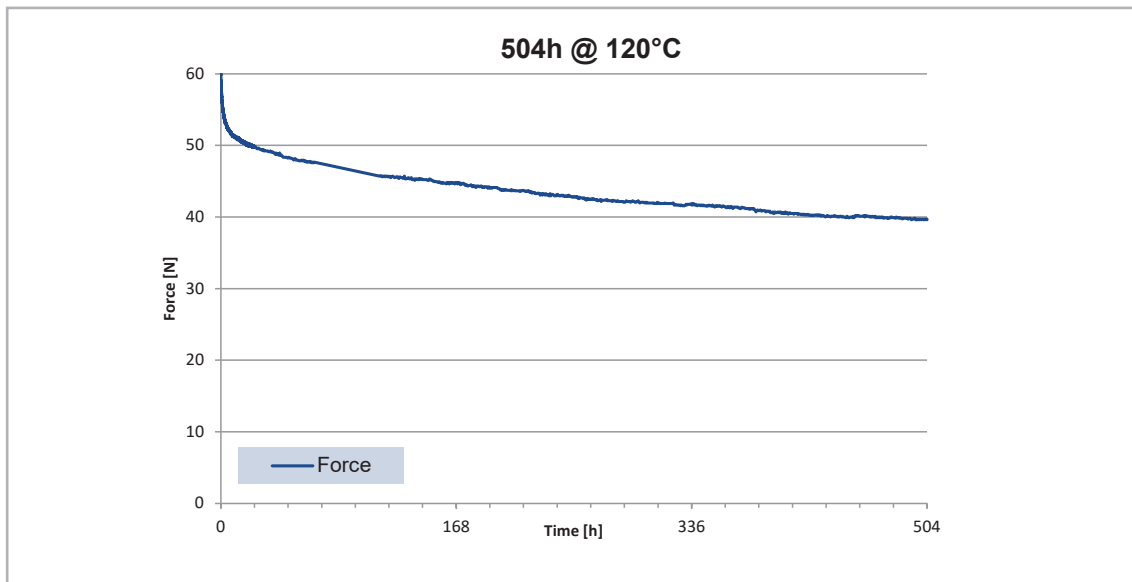
A similar trend can be seen in **figure 6**, which displays the materials' tensile behavior when stored in elevated air temperature for six weeks at 120 °C (248 °F). The products' behavior in an oxidative environment at 120 °C (248 °F) shows significant differences between the performance of TEHs and NBR-based rubber. The durability of NBR-based rubber compounds is already exceeded after three weeks, while the TEHs' tensile strengths remain almost constant over a measuring period of six weeks.



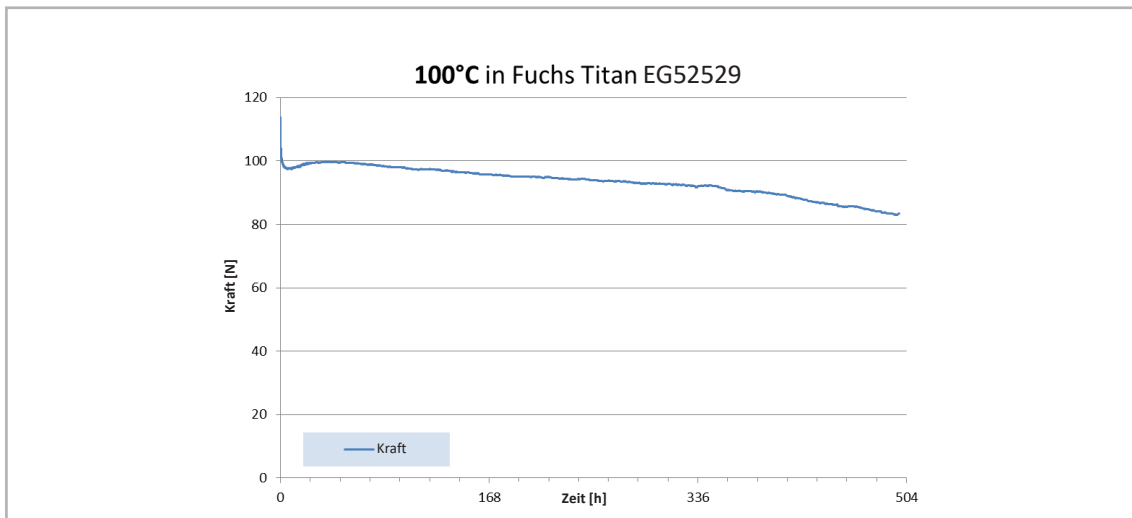


Measuring the compression stress relaxation is a practical test method for selecting sealing materials and it is more conclusive than compression set results. The results for the two TEHs, TEH (PP) and TEH (PA) are graphically displayed in **figures 7 and 8**.

A compression stress relaxation test of TEH (PP) exposed to elevated air temperature at 120 °C (248 °F) over three weeks results in a tension drop of only 39%. The compression set is only 58% after this test time and temperature, which is an outstanding performance for a TPE material.

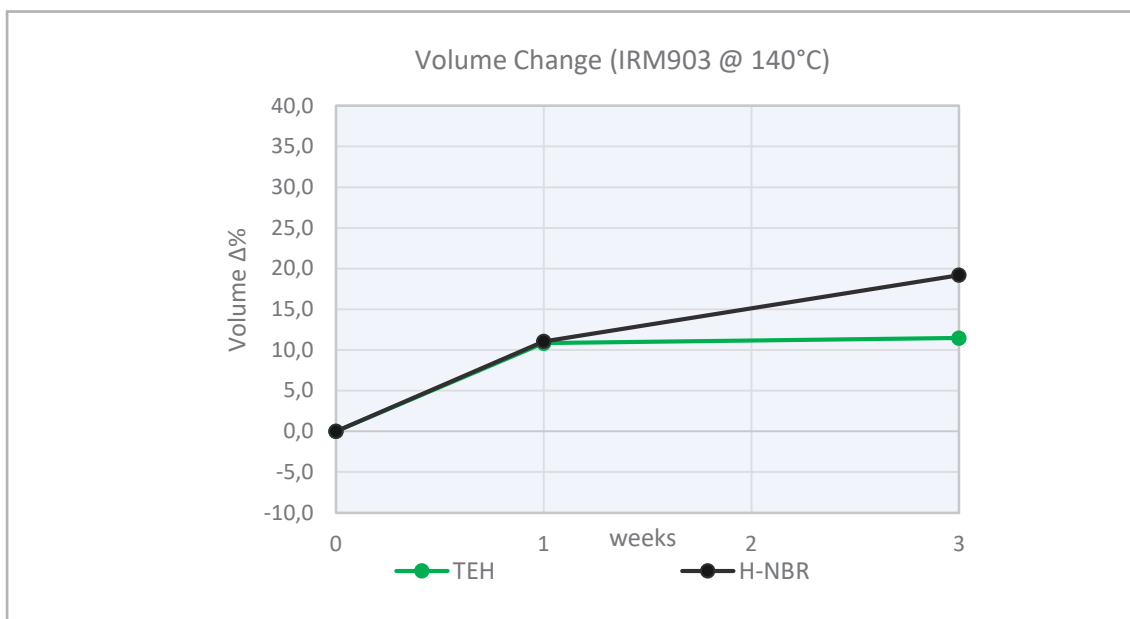


After a three-week compression stress relaxation test of TEH (PA) in gear oil (Fuchs TITAN EG52529) at 100 °C (212 °F), the material illustrates the high-performance level of TEHs. An interesting observation is a slight increase in tension at the start of the measurement when two factors overlap: swelling of material in gear oil and a decrease in tension that is most pronounced at the start of the measurement.



As can be seen from the measurements, the materials are best suited for use in permanent contact with paraffinic oils. Especially at peak temperatures of 120 °C (248 °F), they show better resistance than a comparable NBR-based rubber compound.

Comparison of a TEH with a H-NBR-based rubber for high-temperature ranges provides another representative example. **Figure 9** displays the swelling behavior of material in aromatic IRM903 oil at 140 °C (284 °F) over three weeks. The swelling behavior of the TEH is once again superior to that of rubber.



### **Conclusion:**

The new thermoplastic elastomer hybrids (TEHs) enable KRAIBURG TPE to further reduce the differences in performance between TPEs and rubber. The new technology platform makes it possible to supply a variety of “application-engineered” materials solutions, which provide a diversity of potential modifications comparable to that of TPE or rubber compounds.

The TEH materials are characterized by more efficient processing than rubber compounds, while at the same time they are able to match the rubber compounds’ range of performance. In contrast to rubber, TEH materials can be recycled due to their thermoplastic processability. They open up completely new options in component design for designers and new fields of application for molders, which have not been previously been available with TPEs.

### **Patents:**

- 1.: DE102015007200A1; WO2016188517A1; EP3303471A1;
- 2.: DE102016103822A1; EP3214119A1; US2017253732A1; JP2017155235A; CN107151356A
- 3.: DE102016103823A1; EP3214120A1; US2017253731A1; JP2017155234A; CN107151354A

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