Pushing boundaries! - VESTENAMER® in Recycling Rubber Applications

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ABSTRACT

Recycling rubber is globally gaining traction in efforts towards a circular economy. Beside sustainability aspects, it is also increasingly recognized as a cost-efficient raw material in applications like modified asphalt, virgin rubber blends, and molded goods from ground tire rubber. However, its applicability is limited by performance gaps or processing challenges whenever it is compared to virgin rubber products or polymer materials. The rubber additive VESTENAMER® has proofed to be a valuable tool in overcoming these gaps. We will show latest examples of how trans-polyoctenamer transforms recycling rubber into a valuable resource by improving performance and processing of rubberized asphalt, rubber blends, and molded goods.

INTRODUCTION

Trans-polyoctenamer (TOR) was firstly described by Natta et al. in the nineteen-sixties,1 but it took until the nineteen-eighties to recognize its value as a rubber material.2 Commercialized under the trade name VESTENAMER®, trans-polyoctenamer has first been made available to the rubber industry by Hüls AG, Germany, later part of Degussa, and is today provided by the specialty chemical company Evonik.

TOR provides an unusual set of properties (Table 1) like having partially macrocyclic polymer structure,3 high crystallinity,4,5 a low melting point and glass transition temperature,6,7 high thermal stability,8 as well as the ability to be vulcanized like common rubber polymers. This unique combination of properties makes it a valuable tool in rubber product manufacturing. TOR is typically applied as a component in rubber formulations, and not as a base polymer, due to its very low Mooney viscosity. Typically, 5-15phr of base polymer are replaced by TOR to achieve the desired effects. Many benefits have been described in processing:2,9–11

- Plasticizing in mixing and processing
- Better dispersion
- Improved green strength and dimensional stability
- Compatibility improvements in rubber blends
- Better surface finish and higher extrusion speeds

Some combinations of effects are counter-intuitive and can exclusively achieved by TOR, like plasticizing effect and improving green strength at the same time.12 This “magic behavior“ in rubber applications becomes also visible by many formulation examples where TOR acts as a processing aid (lower Mooney viscosity, improved finish), without compromising and often improving mechanical and dynamical properties of the vulcanizate. Some typical effects by TOR, when introduced into formulations are:

- Hardness is maintained in hard mixtures
- Elasticity is improved
- Less heat build-up under dynamic stress
- Reduced abrasion
- No migration

Property		Method (norm)	Unit	Value
Molecular weight	Mw	GPC (acc. DIN 55672-1)	g/mol	140.000
Glass transition temperature	Tg	DMA (ISO 6721-5)	°C	-67
Crystallinity @23°C		DSC (ISO 11357)	%	~ 30
Melting point (2nd heating)	Tm	DSC (ISO 11357)	°C	54-56
Thermal decomposition		TGA (ISO 11357)	°C	> 400
Double bonds cis/trans ratio		IR (SOP 0188)	%	20/80
Mooney viscosity @100°C	ML (1+4)	DIN 53523, ASTM D 1646	MU	<10
MVR (190 °C, 2.16 kg load)		ISO 1133	cm3/10min	20

Table 1 - Specification and properties of trans-polyoctenamer (VESTENAMER® 8012)

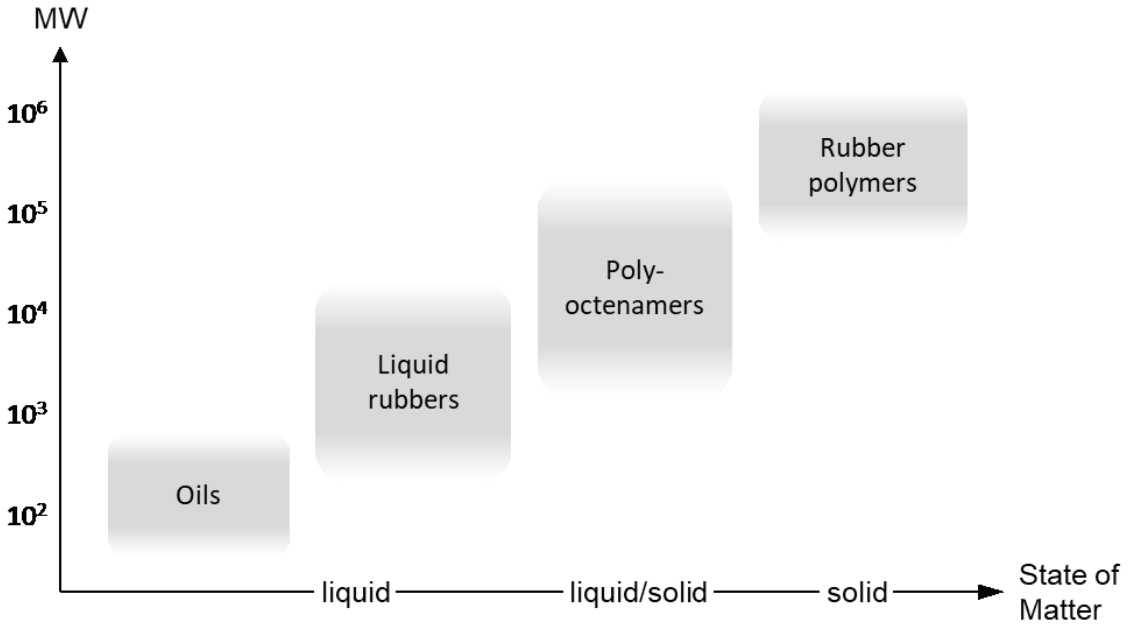

Figure 1 – Categorizing poly-octenamers by molecular weight (MW)

Due to its versatile nature in rubber processing, it is difficult to categorize TOR in the sense of additive by function: it shares features of a plasticizer, green strength enhancer, anti-tack agent, compatibilitizer, and others. Therefore, trans-polyoctenamers should be considered as a class of its own.

By looking at the molecular weight, trans-polyoctenamer is in the range of 140.000 g/mol and can be understood as a material between liquid rubbers and "real" rubbers (**Figure 1**). In fact, TOR shares the best of two worlds by providing processing benefits like liquid rubbers and giving performance like a specialty rubber. The thermoplastic properties of TOR provide additional advantages, like being an easy to dose pellet at room temperature or showing a fast recrystallization what helps to keep green compounds stable in shape, reducing tack, and improving the storage stability of rubber blends.

This full package of properties is valued today in almost all application fields of rubber like tires, hoses, profiles, belts, molded products, linings, calandered articles, sports goods, medical products, foams, and many others. The widespread use is underlined by the growing number of scientific and patent publications about trans-polyoctenamer (**Figure 2**), indicating that this material continuously undergoes a global application innovation process - even beyond rubber applications.

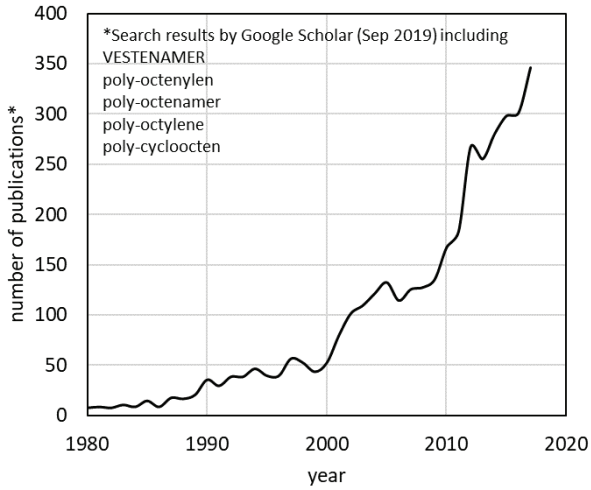

Figure 2 – Bibliometry of poly-octenamers in scientific and patent literature

CHALLENGES IN RECYCLING RUBBER

An appealing application on the rise is the combination of TOR with recycling rubber powders. Although first publication on this use have been published by Diedrich and Burns already 20 years ago,[13] the meaning of recycling rubber has nowadays gained much more importance.

One reason is that end-of-life tires are more and more recognized as a serious global waste problem, but also as raw material of ubiquitous availability – today the global amount of recovered tires is estimated 17.2 million metric tons.[14] The trend of how to use tire derived materials points clearly in the direction of material recovery (e.g. ground tire rubber) instead of energy recovery (e.g. burning in cement kilns). In Europe, the material recovery has grown from a one-digit minority share towards the dominating valorization route over the last 25 years.[15] In 2016, the amount of end-of-life tires that undergoes material recycling to ground tire rubber (GTR) has reached 1.424 metric kilotons, what states more than one third of the used tire arising in the European Union.[16]

Some typical applications of GTR and recycling rubber powders are rubber mats, molded goods, polymer component in virgin rubber compounds, infill for sports fields, rubber-modified asphalt, fillers for paints or coatings, and various other applications. Since recycling rubber is offered at much lower prices compared to virgin polymer materials, it can often significantly improve raw material costs of manufactured products.

Nevertheless, there are some common problems in the use of recycling rubber materials that limit its extended use in many cases. Recycling rubber is often difficult to process – increased viscosity, stickiness, and swelling by hydrocarbons are some examples. Moreover, a serious loss of mechanical properties limits the use of ground tire rubber as component in virgin rubber materials or thermoplastics. Ramarad et al. gives a comprehensive overview about typical challenges in polymer blends.[17] In general, we can summarize three major factors that determine ease of processing and performance of ground tire rubber (GTR) in applications:

1) Source of GTR
2) Particle size & morphology
3) Surface treatment

The source of GTR determines the base polymer content of the recycling material, e.g. whether it is from truck tire tread (high natural rubber content), passenger car tires (higher synthetic rubber content), or production scrap from EPDM products or other rubber types. For example, in rubber-modified asphalt, the choice of rubber has influence on the diffusion kinetics of bitumen – truck tires reach their swelling equilibrium state faster and can absorb more bitumen than car tires do.[18] This might be an advantage in application.

The particle size has also significant influence on product performance. In the above mentioned case of rubber-modified asphalt, smaller particle sizes improve storage stability[19] and reduce equilibrium swelling time even further.[18] When blending GTR into virgin rubber compounds, smaller particles typically result in better mechanical properties.[17] Moreover, the different grinding methods like ambient grinding, cryogenic grinding, or water jetting influence the particle morphology and result in different surface areas.

Finally, the surface modification of ground tire rubber can improve processing and product performance to a large extend. It can help to reduce processing problems like stickiness, raised viscosity, or better compatibility and interfacial bonding to matrix materials - whether it is about bitumen, virgin rubber, or thermoplastic materials. With regards to bonding, chemical cross-linking has been demonstrated to improve mechanical properties.[16] There are many ways to address the different challenges, e.g. using plasticizers to improve processing, or using chemical

treatments to improve compatibility. TOR plays an outstanding role here, since it fulfills all aspects, namely being a processing aid, improving performance, and being cross-linkable.

MODE OF ACTION

In general, TOR forms dispersed phases in rubber polymers, as shown by DSC measurements and microscopic analysis.[20] The fine-dispersed TOR phases provide a wetting effect, resulting in less shear forces, and hence easier mixing and processing of the rubber compound. In binary rubber blends, addition of TOR forms a third phase at the interphase. This intermediate layer compatibilitizes the rubber domains by reducing the interfacial tension between the two rubber components. Furthermore, the recombination of domains (coalescence) is inhibited by the TOR layer. This finally results in better dispersed blends and mechanical properties, even for practical immiscible combinations like EPDM/NBR.[21]

The ability to compatibilitize rubbers is a good pre-condition for application in recycling rubber powders. Materials like ground tire rubber typically comprise a wide spectrum of rubber polymer types and compositions, depending on their source and sorting. For example, passenger car tires dominate in synthetic rubber polymer content, whereas truck tire treads typically have more natural rubber content.

Adding TOR to recycling rubber crumbs or powders results in a similar wetting effect like in virgin rubber compounds. The difference is the "domain" sizes that are limited by the sizes of the already vulcanized recycling rubber particles. At temperatures above the melting point, TOR forms a surface layer on top of the particles. Although the coating process has been described,[13,22] few information on the surface coating itself is available. To close this knowledge gap, we conducted scanning electron microscopic (SEM) and transmission electron microscopy studies (TEM) to prove and investigate the quality and morphology of the assumed TOR coating layer.

Samples were prepared with internal laboratory mixer by mixing cryogenic milled GTR of 200µm size with 4.5 wt% TOR for 7 min. 10 randomly selected particles were taken from the prepared samples and analyzed by SEM, confirming successful coating for 9 of the 10 samples. **Figure 3** shows an uncoated GTR particle with rough surface structure, compared to a TOR-coated particle covered by a smooth surface. This visually confirms the wetting effect of TOR as well as the good compatibility and affinity to the recycling rubber particle surface.

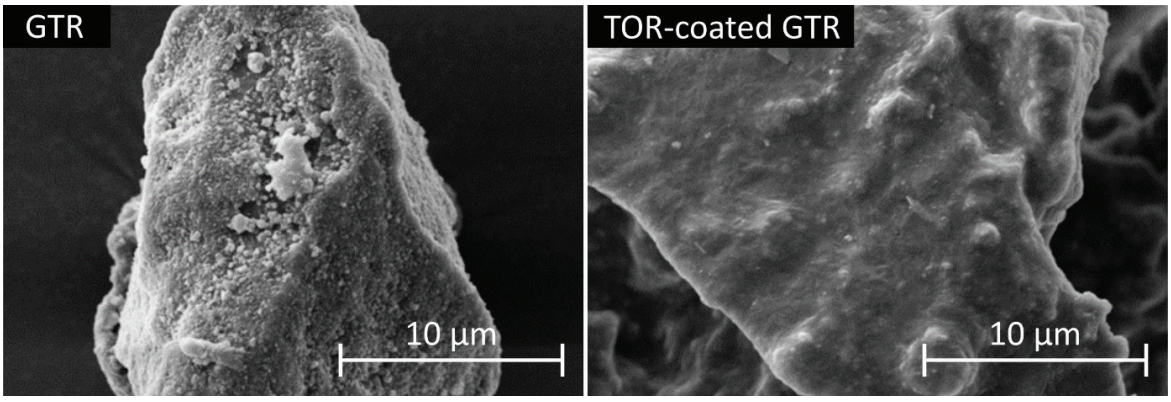

Figure 3 – SEM pictures of GTR particle (left-hand) and coating layer of TOR (right-hand)

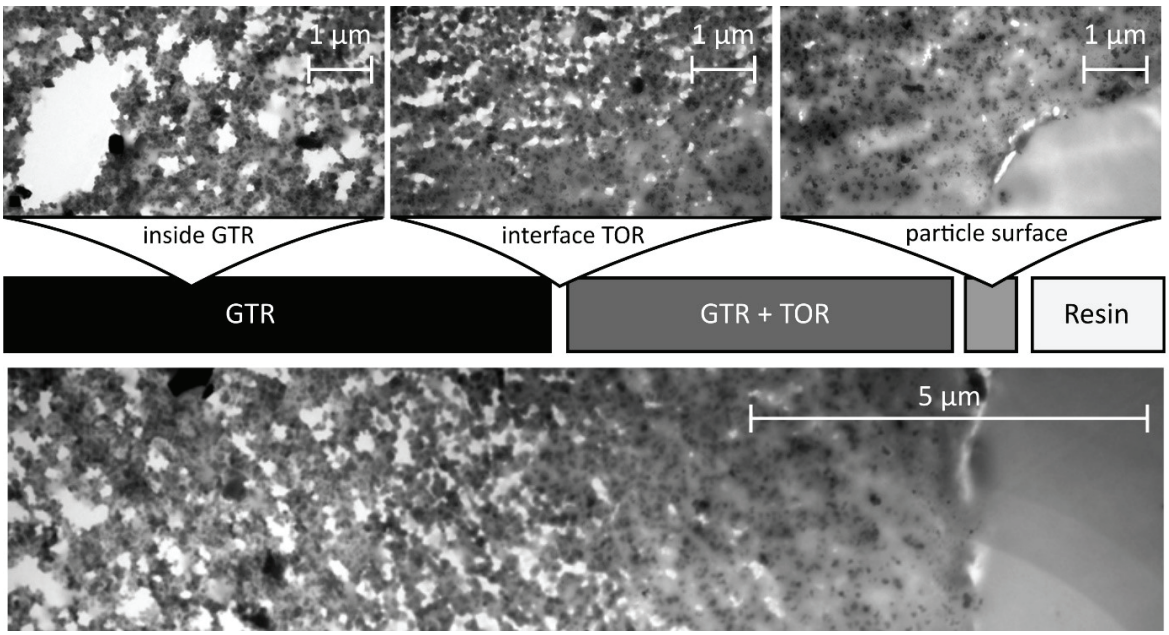

Figure 4 - TEM pictures of thin-film cuts of TOR-coated GTR particle

An even more detailed insight is revealed by the transmission electron microscopy of samples that were prepared by thin-film cuts. **Figure 4** shows the cross-section of a TOR-coated GTR particle, where the different zones of the GTR particle, TOR layer, and sample matrix can be identified. The TOR coating layer thickness can be estimated around 3-5 µm. Whereas the outer boundary of the surface layer is clearly visible, the inside of the particle shows a blurred transition from the TOR layer to the inside of the GTR particle. This indicates a diffusion and interpenetration of TOR into the surface of the GTR particle. This is in line with expectations from the solubility point of view - TOR shares similar chemical characteristics like common rubber polymers, and hence shows good compatibility as expressed by their solubility parameters.[20] Moreover, the concept of interpenetrating layers has already been described by Wenig et al. for blends of TOR with thermoplastics.[23,24]

The evidence for a good surface coating of GTR by TOR explains the well-described benefits in processing. TOR "masks" the GTR surface and thus prevents difficulties like higher stickiness and viscosity. It can also be assumed that the TOR layer influences diffusion kinetics, when it comes to migration processes between GTR and the embedding matrix. Reports about reduced emissions of GTR by TOR in asphalt applications[25] give some indications for that.

The performance improvements observed can also be explained by the TOR-coating layer. Since TOR is unsaturated and can be cross-linked like rubber, it offers a reactive surface towards the outside of the particle for compatibilization and/or cross-linking and can further cross-link inside the GTR particle along the interpenetrating layer. FTIR studies on the surface of TOR-coated GTR in bitumen application have shown that TOR undergoes chemical reaction at processing.[26] Since all curing chemical additives and accelerators are already present in the GTR particle (and furthermore undergo migration processes) this can be expected. Improved performance by adding additional sulfur has been reported.[27,28]

From the gained insights by electron microscopic analysis, as well as the literature review shown above, a mode of action for surface modification of GTR by trans-polyoctenamer can be concluded as depicted in **Figure 5**.

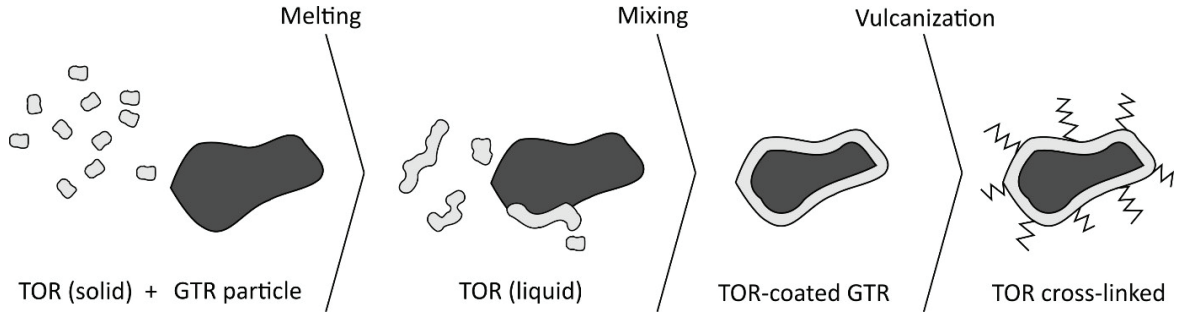

Figure 5 – Mode of action for TOR with ground tire rubber

TOR COATING PROCESS

For a proper function of the "TOR effects", a good coating of the rubber particles is an important pre-requisite. From our experience there are different ways on how to achieve this, depending on the available mixing equipment.

If internal mixer is available, like in rubber compounding facilities, TOR can simply be added together with GTR to get the desired result.[13] In laboratory procedures, a pre-heating of TOR can improve results and lower the mixing time. The samples shown in **Figure 4** and **5** were prepared with a mixing time of 7 min, without addition of oil.

If internal mixer is not available, powder blenders can also be used. This states a less capital-intensive mixing option. Since this option provides less intensive mixing compared to internal or Banbury type mixers, the coating process of the particles can be facilitated by employing an oil solution of TOR. A common formulation is 20 wt% of TOR dissolved at elevated temperatures (100-120°C) in a suitable oil, like paraffinic oil. Rubber process oils like TDAE work as well. Different solubilities of TOR have been observed by us in various oil types (**Table 2**).

A further option is extruding equipment used for continuous mixing of GTR with TOR. If curing-chemicals are added, recycling rubber compounds can be produced that are ready for press- or injection-molding process. This has proved to be an efficient process for large-scale production of rubber mats from recycling rubber powders.

	Naphthenic black oil	**TDAE process oil**	**Paraffinic process oil**	**White oil**
	Nytex 4700	Vivatec 500	Sunpar 2280	Infrasolv LC1
10 wt% TOR	yes	yes	yes	yes
20 wt% TOR	yes	yes	yes	yes
30 wt% TOR	yes	partially	no	yes

Table 2 – Solubility of TOR in different oils at 100°C

TOR AS BINDER SYSTEM FOR MOLDED PRODUCTS FROM GTR

The dominating binder system for molded products from GTR is polyurethane (PU), what is easy to process, and needs no elevated vulcanization temperatures for production of molded goods. TOR is an alternative binder option to make new molded products from GTR but needs vulcanization temperatures in press-curing comparable to production of virgin rubber products. Although the energy consumption might be higher than in PU processing, TOR can be an attractive option due to the good mechanical properties of the vulcanizates and their superior weathering resistance.[29] Considering the lower dosage needed for TOR compared to PU, it can also economically compete by taking the total costs of formulation and processing into account. The effective amount of TOR needed is 3 parts per hundred parts of GTR. A standard formulation for GTR compound with TOR binder, and the range of the respective physical properties for 20-40 mesh size GTRs of various sources is shown in **Table 3**.

It can also be assumed that the chemical resistance of TOR-bound GTR articles is superior in many points compared to PU because it shares characteristics of polyolefinic materials and has a non-branched chemical structure. This is desirable for products that undergo chemical stress like animal bedding mats that are exposed to excrements, and hence must withstand acid environment. Therefore, TOR improves price performance ratio of such products by enhancing their lifetime.

Recyclability becomes more and more important in the long-term transformation of our society that pushes towards a circular economy. In this respect we see some further general advantage of using TOR compared to other binder systems. Since TOR is a rubber-material itself, “rubber stays rubber” and does not become a composite product like PU/GTR. This could simplify a further recycling step of GTR products and might help to give tires not only a second life, but even a third live: in rubber products or up-cycling to other applications like rubber-modified bitumen and asphalt. Nevertheless, studies are needed to show the practical feasibility of such a third life concept.

Material	phr	Properties	Unit	Value
GTR (20-40 mesh, PCR tire)	100	Press curing	min	20
TOR / Oil	3 / 12			
ZnO	0.1	Hardness	Shore A	64-74
Stearic acid	0.5	Tensile strength	MPa	4.5-8.5
Sulfur	0.8	Elongation at break	%	150-300
CBS	0.8	Modulus 100 %	MPa	2.0–3.0
TMTD	0.2	Rebound resilience	%	50-60

Table 3 - Standard recipe for GTR products with TOR and properties of the vulcanizate

TOR-COATED GTR IN VIRGIN RUBBER

The cost of GTR can go down to one order of magnitude lower than virgin rubber materials, depending on grinding method and size. This makes it an attractive raw material - not only from the ecological, but also from the economic point of view. On the other side, serious processing and performance problems arise when production scrap or ground tire rubber materials are introduced into virgin rubber compounds. The reason for this is due to migration processes between GTR and rubber matrix as well as insufficient incorporation and bonding of the embedded GTR particles. The problems typically scale with the percentage of recycling rubber compounded into the virgin formulations.[17] Hence, its applicability is strongly limited, especially in safety critical applications like tires.

Technologies that enable the use of production scrap or ground tire rubber materials are key to extend the use of these recycling materials. TOR can narrow, or even close, many technical gaps that are often prohibitive factors for using GTR in virgin rubber compounds. This has been demonstrated by trials with some test SBR and NR compounds that were filled by 20 and 40 phr GTR. The reviewed formulations[29] are summarized in **Table 4**.

Materials	**SBR**	**SBR-GTR**		**SBR-GTR-TOR**		**NR**	**NR-GTR**		**NR-GTR-TOR**	
SBR 1500	100	100	100	100	100	-	-	-	-	-
NR	-	-	-	-	-	100	100	100	100	100
Carbon black N33	60	60	60	60	60	60	60	60	60	60
GTR	-	20	40	-	-	-	20	40	-	-
GTR coated (TOR)	-	-	-	20 (0.6)	40 (1.2)	-	-	-	20 (0.6)	40 (1.2)
Oil, aromatic	10	10	10	10	10	10	10	10	10	10
Antiageing package	5	5	5	5	5	5	5	5	5	5
ZnO	5	5	5	5	5	5	5	5	5	5
Stearic acid	1	1	1	1	1	1	1	1	1	1
Sulfur	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5
CBS	1	1	1	1	1	1	1	1	1	1
CTP	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5

Table 4 – Test formulations of SBR and NR

A typical challenge is the viscosity increase of the green compound that arises when GTR is added in larger amounts. The use of TOR-coated GTR shows improvements over untreated GTR as summarized in **Figure 6**. This is a result of the TOR/oil solution coating that reduces Mooney viscosity very close to the level of the reference compound. Further data reveals improved tensile strength where TOR improves by around 1 Mpa. The test data on compression set shows an impressive effect that illustrates the cross-linking function of TOR between GTR and virgin polymer matrix quite well. As visible from the data in **Figure 7**, the loss in compression set by GTR incorporation can be completely prevented by applying the TOR-coating. This can be of great advantage for applications in seals, gaskets, or dampers, where compression set is an important property.

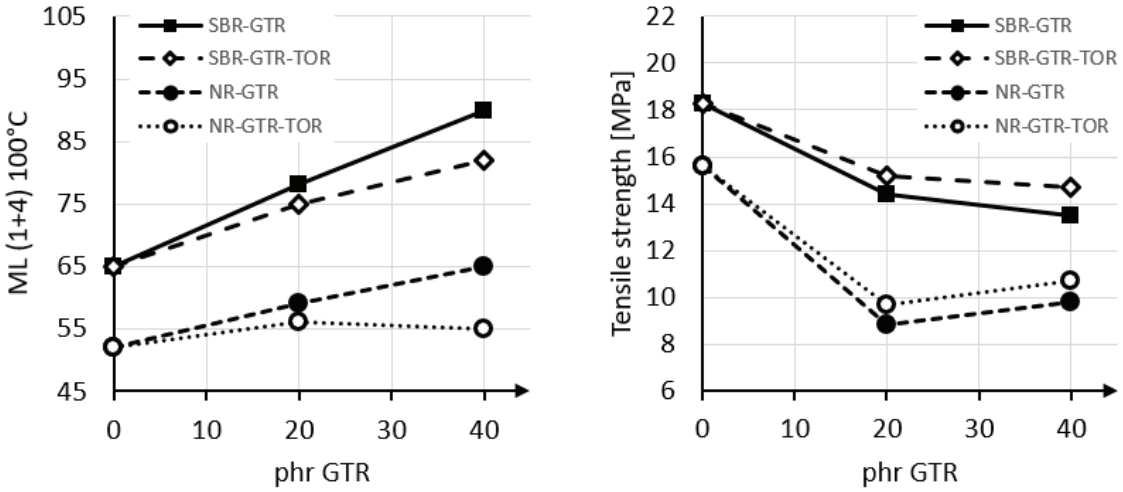

Figure 6 - Influence of TOR-coating on Mooney viscosity (left-hand) and tensile strength (right-hand)

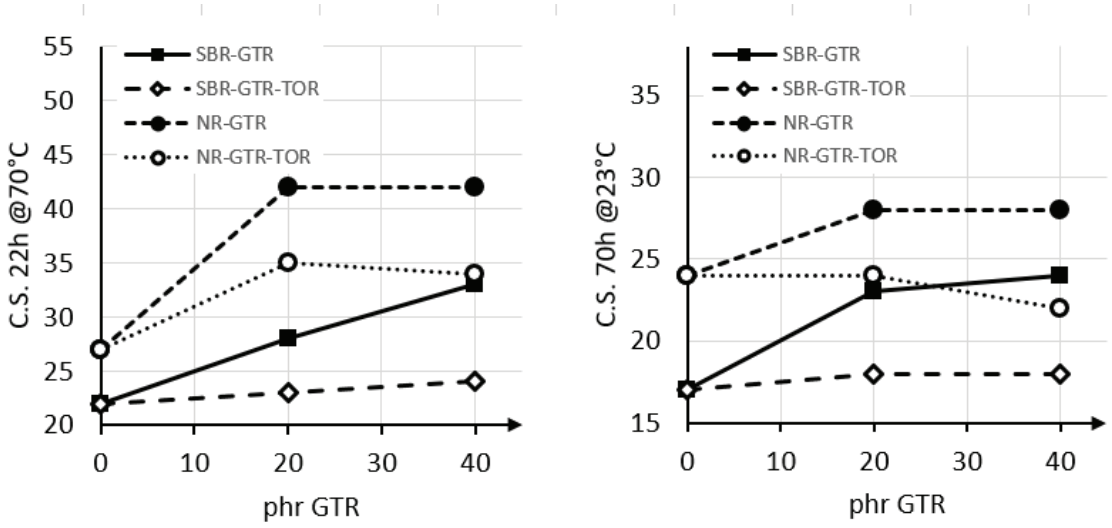

Figure 7 - Influence of TOR-coating on compression set

RUBBER MODIFICATION OF BITUMEN AND ASPHALT

Trans-polyoctenamer has a track-record of more than 25 years as a processing additive in the bitumen and asphalt industry. Recycling rubber acts as a polymer modifier that improves binder properties of bitumen, and hence of the modified asphalt.[30] The environmental benefits of using recycling rubber is an additional argument from the perspective of sustainability and circular economy discussions.[31–33]

Although the benefits of rubber in road construction are known for a long time, it is faced with practical problems in processing like stickiness, storage problems, or emission. Moreover, lack of knowledge about best practices in working with rubber has been a hurdle that inhibited wider adoption of rubber-modification in asphalt in the past. For example, swelling times[18] and working temperatures[34,35] are critical issues to take care of in rubber-modification.

Situation has changed today as rubber-modification moves towards more acceptance and has even found entry into national strategies.[36] TOR is part of this process, since it helps to overcome the critical challenges in the practical application of rubber in road construction. The benefits of reduced stickiness, improved rutting resistance, and reduced cracks have been confirmed by many researchers all over the world.[26,27,37–47] TOR moreover helps to improve storage stability and pumpability of rubberized asphalt,[26,48] what is a key challenge in wet process. Positive effects on thermal stability have also been reported recently.[25,44]

From road construction perspective, rubber is a temperature-sensitive raw material, what means that working at lower temperature is favorable in terms of emission. On the other side, low temperatures lead to higher viscosities, what can be a problem when bitumen is processed at too low temperatures. During paving the TOR-effect brings significant benefit, since it reduces the compaction resistance of rubber-modified asphalt. This opens a wider temperature window for processing and therefore gives more process safety. Influence of TOR on lower compaction resistance is shown in **Figure 8**. The effect can also be explained by the coating mode of action (**Figure 5**), since the swollen and sticky GTR surface is coated by TOR what reduces the effective stickiness of the rubber particles. This is also valued at un-loading of trucks, where asphalt residues on the machinery often makes

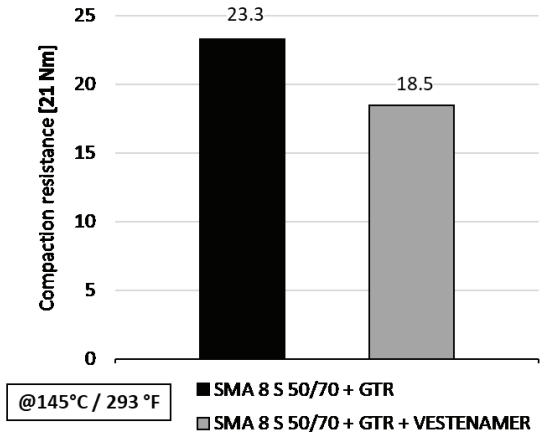

Figure 8 - Compaction resistance reduction of rubber-modified asphalt by TOR

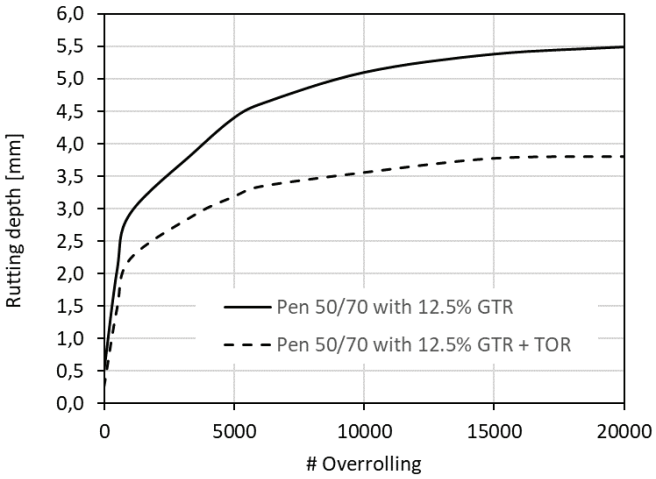

Figure 9 - Rutting depth results by Hamburg-tests of rubber-modified asphalt by GTR and GTR/TOR

tedious cleaning efforts necessary. Beside the easier processing, TOR has also positive impact on the performance of asphalt pavements. One example is the improved rutting resistance. As visible from the Hamburg-tests in **Figure 9**, rutting depth is reduced using TOR compared to the rubberized asphalt mixture without TOR. In this laboratory test method, a test wheel rolls over the prepared asphalt sample for several thousand times.

Together with the other benefits, like improved long-term aging, GTR and TOR can therefore significantly extend the lifetime of pavements. Long-term experiences by well-documented paving projects, e.g. laying for more than 11 years now, prove the laboratory results by showing a road surface in perfect state, without any rutting or cracks (**Figure 10**).

Figure 10 - Rubber-modified industrial area in Germany after 11 years of heavy traffic load

In asphalt application, the use of reclaimed asphalt pavement (RAP) is a further leverage towards more sustainability in road construction. The use of rubber-modification is a perfect fit to improve the aged binders in reclaimed asphalt. From our recent studies that will be published soon, we see that use of 50% RAP in top layer is possible without compromising standards and expectations of modern road construction.

SUMMARY

In summary, TOR is a unique tool to overcome many challenges that arise in the use of GTR, hence pushing boundaries of what is possible with the cost-efficient, sustainable, and ubiquitous available raw material ground tire rubber.

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