

Natural rubber and NR-based polymers: renewable materials with unique properties

A.V. Chapman

Tun Abdul Razak Research Centre, Malaysian Rubber Board
Brickendonbury, Hertford, SG13 8NL UK
achapman@tarrc.co.uk

Abstract

There is increasing pressure for products to be manufactured in part or entirely from renewable materials and for the energy consumption over the life cycle of products to be minimised. In the case of products based on rubber, NR and polymers based on NR can help to meet these challenges.

With its very uniform microstructure, NR has very low hysteresis and undergoes strain crystallisation, leading to very high tensile strength and resistance to tearing and abrasion. The high strength, tear resistance and resilience are suited to many engineering applications. Because of its low heat build-up and good green strength, tack, tear strength and adhesion to brass-steel cord, large amounts of NR are used in tyres, especially in larger tyres where NR dominates. NR latex provides high strength in unfilled thin-walled products, such as condoms and gloves.

Epoxidation of NR raises increases the polarity of the polymer and the glass transition temperature, while the ability to strain crystallise is retained up to about 50% epoxidation. ENR interacts strongly with silica, without the need for coupling agents. Because of these unique properties, ENR-25 in silica-reinforced tyre tread compounds provides low rolling resistance, together with high wet grip. Thus ENR, as well as being a renewable material, can contribute to reducing climate change by lowering vehicle fuel consumption.

Thermoplastic elastomers based on NR and ENR combine the use of renewable rubbers with the convenience and recyclability of thermoplastic processing. NRTPV, a dynamically vulcanised blend of NR and polypropylene, has similar basic properties to other commercially available TPVs, together with enhanced recovery behaviour, making it suitable for automotive sealing applications. TPENR, a dynamically vulcanised blend of NR and polypropylene, provides excellent heat and oil resistance, as well as good general properties, and is thus suitable for automotive applications likely to come in contact with heat, oil or fuel.

Introduction

Environmental impact, sustainability and life cycle analysis are new factors to be considered, alongside cost and technical performance, when developing new materials, products and processes. The increasing desire by societies for products to be environmentally friendly has led to manufacturers exploring means of producing products entirely or mostly from renewable resources. The aspiration is to replace materials from non-renewable feedstocks, in particular petroleum oil, by materials derived from renewable agricultural or biomass feedstocks. Recent examples in tyre manufacturing include the use by Goodyear of starch as a filler¹⁻³ in their BioTRED technology, applied in the Goodyear GT3 tyre, and the

development by SRI Dunlop of an environmentally friendly tyre with only 30% petroleum-based materials^{4,5}. The latter is being sold as the Enasave ES201 tyre in the replacement market. It contains epoxidised natural rubber (ENR) and silica in the tread; mineral oil has been replaced by vegetable oil, and synthetic fibre by vegetable fibre⁶.

This presentation focuses on the polymer used in a rubber product, specifically on the use of natural rubber or of polymers based on natural rubber – ENR and thermoplastic elastomers based on NR and ENR. With the growing concerns about climate change and global warming, the carbon footprint of materials, products and processes and the energy consumption over the life cycle of a product have grown in importance. Use of NR and polymers based on NR helps to address these concerns, as natural rubber plantations efficiently sequester carbon from atmospheric carbon dioxide. By contrast, synthetic rubbers are derived from a fossil fuel, petroleum oil; energy is consumed and carbon dioxide released during their manufacture, and oil resources are depleted. However, the environmental impact of a rubber material cannot be judged in isolation. When the entire life cycle a rubber product is considered, other factors must be taken into account, including the impacts of transportation of materials and products, the manufacture of the product, its use, its lifetime, and its disposal or recycling. Thus, in by the far the most important application of rubber, tyres, most of the impact on energy consumption arises from the rolling resistance during use, which in turn effects the fuel economy of the vehicle. Indeed, Michelin have estimated that 86% of the environmental impact of an average European passenger tyre occurs during use⁷.

Natural rubber

The obvious example of use of a renewable material in rubber products is natural rubber itself, which accounts for about 40% of rubber consumption. As already mentioned, the rubber tree (*Hevea Brasiliensis*) efficiently sequesters carbon. In full sunlight the photosynthetic rate of a mature *Hevea* leaf is about 11 $\mu\text{mol}/\text{m}^2/\text{s}$, as compared with 5-13 $\mu\text{mol}/\text{m}^2/\text{s}$ in other species of trees⁸. As the leaf area produced by a mature rubber tree is also high⁹, biomass production per hectare is high. Over the 30-year life of the *Hevea* tree, the carbon sequestration per hectare has been determined as 272 tonnes, in comparison with 234 tonnes per hectare by rain forest and 150 tonnes by secondary rain forest¹⁰.

The energy inputs for production of natural rubber are given in Table 1¹¹. The total energy input, 15-16 MJ/kg, contrasts with that required for the synthetic rubbers, typically 100 MJ/kg, which equates to an emission of about 3 kg carbon dioxide per kg of rubber. Part of the reason for the low energy input is the low demand on fertilisers, as nutrient removal from the soil by *Hevea* is much less than that of other tropical crops, such as tea, coffee and oil palm¹². As well as not impoverishing the land on which it is grown, biodiversity remains remarkably high in rubber plantations, in contrast to most forms of monoculture¹³.

Table 1. Energy inputs for natural rubber production (MJ/Kg)

Fertilisers and other chemicals	5
Primary processing	3
Transport	5-8
Total	15-16

Hevea is also a valuable source of timber. Indeed, until the recent increase in price of NR, the timber from the *Hevea* tree was becoming more profitable than the rubber latex.

Table 2. Comparative properties of natural and synthetic rubbers

	NR	IR	SBR	BR*	IIR	EPDM	CR	NBR
Glass transition temp., °C	-70	-70	-60	-105	-65	-58	-49	-24
Service temp. range, °C								
lower limit	-55	-55	-45	-70	-50	-40	-35	-20
max. continuous	+70	+70	+70	+70	+100	+125	+100	+100
max. intermittent	+100	+100	+100	+100	+125	+150	+125	+125
Hardness range, IRHD	30-100	35-100	40-100	45-90	35-85	30-90	35-95	40-100
Typical tensile strength (MPa)								
gum	24	21	3	3	10	3	17	4
reinforced	28	24	24	17	17	21	21	21
Tear resistance	E	G-E	G	F	G	F	F	P-F
Abrasion resistance	E	G-E	E	E	F	F	E	F
Compression set	G	G	G	G	F	G	F-G	G
Creep/stress relaxation	E	E	G	G	F	F	F	F
Resilience	E	E	F-G	E	P	F-G	G	P-F
Gas permeation	F	F	F	F	E	G	G	G-E
Electrical/resistivity	E	E	E	E	E	E	G	F
Oxidation resistance	F	F	F	F	G	E	G	G
Ozone resistance	P	P	P	P	G	E	G	P
Flame resistance	P	P	P	P	P	P	F	P
Water resistance	G	G	G	G	E	E	F	F-G
Acid resistance	F-G	F-G	F-G	F-G	F-G	G-E	G	F-G
Alkali resistance	G	G	G	G	G	G	F-G	F-G
Solvent resistance:								
aliphatic hydrocarbons	P	P	P	P	P	P	G	E
aromatic hydrocarbons	P	P	P	P	P	P	P-F	F-G
halogenated solvents	P	P	P	P	P	P	P	P
oxygenated solvents	F-G	F-G	F-G	F-G	G	G	F	P-F
Oil resistance	P	P	P	P	P	P	G	G-E

Key: E = excellent, G = good, F = fair, P = poor

*BR is usually blended with other rubbers

Some properties of NR are compared with those of other commonly used rubbers in Table 2. NR has a very high structural regularity, providing it with unique and valuable characteristics. In particular, NR crystallises under strain, or at low temperatures, and has very low hysteresis and high resilience. The strain-induced crystallisation gives NR its very high tensile strength, even in gum vulcanisates, and resistance to tearing and abrasion. Because of this crystallisation and also high molecular mobility, uncured NR has very high green strength and building tack, which is particularly useful for building tyres. NR has very high elasticity. Coupled with low hysteresis, this leads, in dynamic applications, to low heat build-up and high fatigue resistance.

The potential drawbacks of NR are its limited resistance to heat, oils and some chemicals, and susceptibility to oxidation and ozonation, mainly due to its unsaturated structure. Consequently NR products must be protected by suitable antioxidants/antiozonants, such as p-phenylenediamines, dihydroquinolines, phenols and waxes. Thick NR products can remain in service for very long times. Indeed, there are examples of NR bridge bearings in service and functioning well after about 100 years. In thin articles where only a short lifetime is required, the oxidative degradation may even be an advantage.

Traditionally, NR was considered as a general purpose rubber and was used in the production of virtually all rubber products, because of its well-balanced range of physical properties. However, due to increasing specialisation and improvements in synthetic rubbers, NR use is now more limited to applications for which its technical performance is particularly suited.

The tyre industry consumes about 70% of NR. With the introduction of radial tyres, the proportion of NR used increased, due to its good green strength, tack, tear strength and heat build-up. The low hysteresis of NR minimises heat build-up and provides good rolling resistance. Typically, 40% NR is used in passenger car tyres. Higher levels are used in tyres for commercial and industrial vehicles, the NR content increasing with tyre size. Thus, almost 100% NR is used in the large truck and earthmover tyres, which require maximum cut growth resistance as well as low heat build-up. NR similarly dominates the market for aircraft tyres. Its excellent fatigue resistance together with the low heat build-up is exploited in the sidewalls of radial ply tyres. NR is also used in the carcass of passenger tyres, for its building tack, ply adhesion and good tear resistance, and in belt compounds, for braced-steel cord adhesion and crack growth resistance. In the treads of passenger tyres, NR use is limited mainly to winter tyres. Some NR is used in blends with halobutyl rubbers in inner liners. It is also used in the bead, apex and rim strip compounds.

Applications of NR latex, in which its high strength in thin-walled unfilled products combined with low modulus at low strains is especially valuable, include gloves and condoms. NR is also used in industrial goods such as hoses, conveyor belts, rubberized fabrics and rubber linings. The properties of NR, such as high strength, tear resistance and resilience, are suited to many engineering applications. These include bridge bearings, dock fenders, springs, anti-vibration mountings and vehicle suspension systems.

Epoxidised Natural Rubber (ENR)

Epoxidation of NR latex with hydrogen peroxide and formic acid (Scheme 1) is used to produce 25 and 50 mol% epoxidised natural rubber, which are marketed as ENR-25 and

ENR-50, respectively¹⁴. Despite the modification, ENR is still a strain-crystallising rubber with high strength up to about 50% epoxidation, as shown in Figures 1 and 2. Epoxidation increases the polarity of the polymer, improving compatibility with polar polymers, such as PVC, and substantially reducing oil-swelling. Epoxidation raises the glass transition temperature, thus reducing gas permeability and decreasing the low temperature resilience, leading to increased damping and making ENR-50 a highly damped rubber. However, at higher temperatures the high resilience of NR is maintained.

Scheme 1 Epoxidation of natural rubber

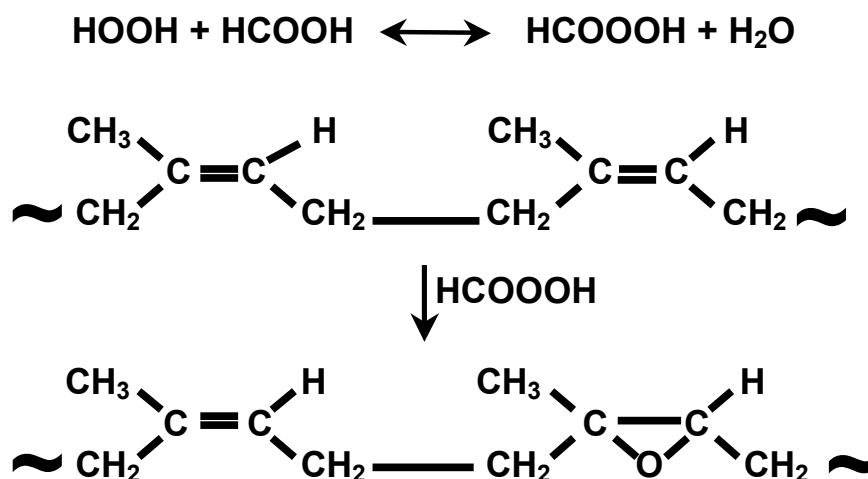


Figure 1 Tearing energies of ENR-25, ENR-50 compared with NR and SBR

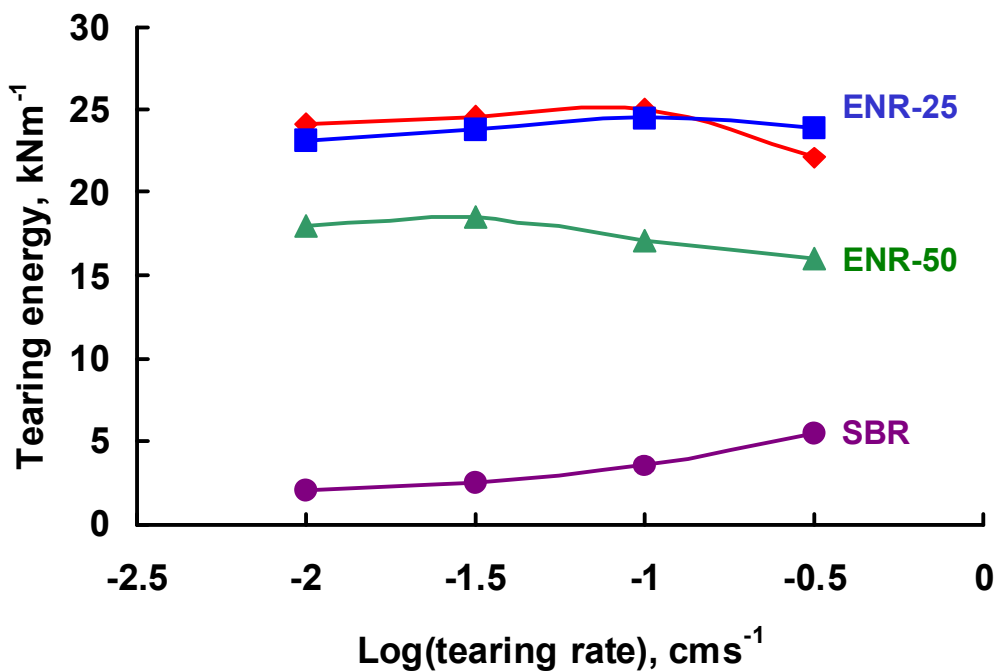
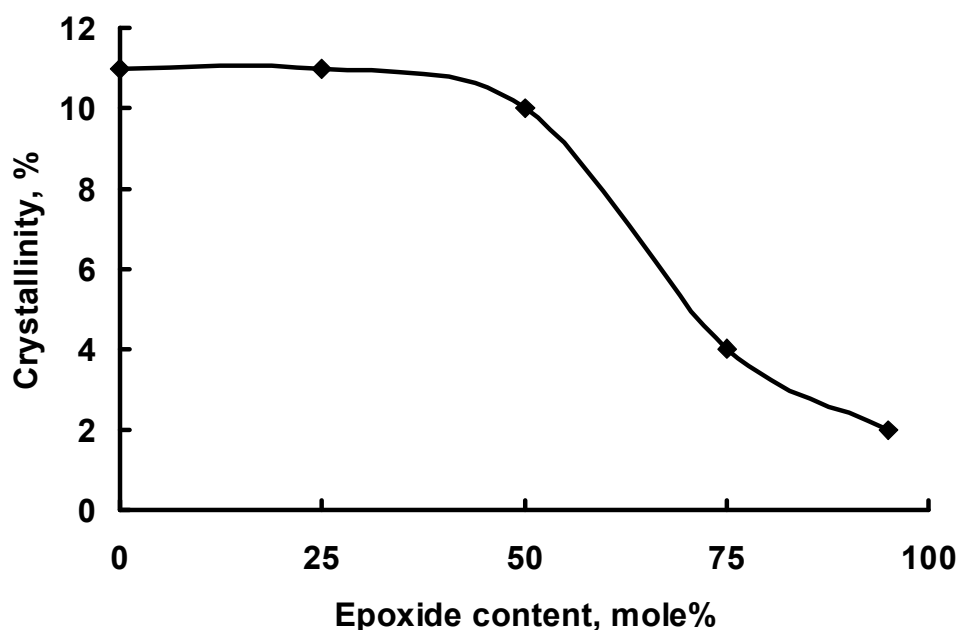


Figure 2 Variation of strain-induced crystallisation with epoxide content



ENR is also reinforced strongly with silica without a coupling agent. Thus, measurements of bound rubber content by swelling uncured compound in toluene show that a high level of ENR-25 is bound to silica (>1 g ENR per g of silica), while in contrast very little BR is bound without coupling agent (Table 3). Interestingly, high levels of NR are also bound to silica. A probable explanation is that hydrophilic proteins and occasional polar functional groups on the NR are hydrogen bonding to the silica.

Table 3 Bound rubber contents of uncured masterbatches¹⁵

Property	ENR-25	NR	BR	70:30 ENR-25/NR	70:30 ENR-25/BR
Bound rubber, g/g silica	1.373	1.407	0.249	1.469	1.444
Bound rubber content, %	27.5	28.2	5.0	29.4	28.9
Volume swelling, V_r	0.022	0.012	0.006	0.020	0.023

While a measurement of bound rubber indicates how much rubber is associated with the filler, a measurement of volume swelling (V_r) of the swollen gel indicates how strongly the bound rubber is interacting with the filler. Despite the similar bound rubber contents found for the ENR-25 and NR compounds, the V_r value determined for the silica filled ENR-25 compound, given in Table 3, is close to double that found for silica filled NR. This indicates that ENR-25 binds much more strongly to silica than does NR. The very low V_r value for the silica filled BR compound indicates that cis-polybutadiene binds very weakly to silica.

A strong association between ENR-25 and silica is not surprising considering the relatively polar nature of ENR-25; in addition to it containing 25 mol % epoxy groups, it also contains a small proportion (about 1 mol % as measured by ¹H NMR) of ring opened species containing

hydroxyl and furan functionality¹⁶. It is proposed that these polar groups associate through hydrogen bonding to the siloxy functionality on the surface of the silica to effectively couple the ENR-25 to the silica.

The interaction between ENR and silica was also investigated by a technique developed at TARRC, referred to as ‘network visualisation’¹⁷. The technique is based on swelling a vulcanised rubber sample in a polymerisable solvent, usually styrene, containing a radical initiator. After swelling to equilibrium, the sample is heated to initiate polymerisation of the styrene. The result is a swollen rubber sample embedded in a polystyrene matrix, which is then sectioned and stained for TEM analysis to enable regions of unsaturated rubber to be identified. When the sample is vulcanised, it is usual to see an image showing a mesh structure consisting of regions of stained rubber network separated by regions of unstained polystyrene matrix. The dimensions of the phase separated mesh structure can be related semi-empirically to the physical crosslink density in the rubber¹⁷.

This technique was used Bomal *et al*¹⁸ to compare the effectiveness of different silane coupling agents in silica-filled solution SBR compounds. Of particular interest was the interface between the rubber and the silica where it was found that in the absence of coupling agent, vacuoles, or voided regions were formed around the silica by the ingress of styrene. Initially, styrene is able to swell more easily regions of ‘weakness’ in the vulcanisate, ie the rubber – filler interface, which, during the subsequent polymerisation and phase separation process⁵, are retained as regions of unstained polystyrene. The volume fraction of the polystyrene filled void surrounding the silica particles could be quantified and was found to be inversely related to the amount of silane coupling agent used¹⁸. Where a full amount of silane coupling agent was employed, no voiding between the SBR network mesh structure and silica was found.

Figures 3 and 4¹⁵ show network visualisation TEM micrographs of silica-filled ENR-25 and NR vulcanisates, respectively. A stained vulcanized network mesh structure can be seen in each case with dark silica aggregates of some 50–100 nm diameter dispersed throughout each micrograph. Whilst the network mesh structure appears slightly different for each polymer, for reasons discussed previously¹⁷, attention should be directed to the silica particles and the surrounding network mesh. The reduced level of silica filler used here (20 phr) greatly improves the clarity of the micrographs, whilst leaving general conclusions that are drawn unaffected.

The contrast in appearance between Figures 3 and 4 is marked; whereas Figure 3 shows no polystyrene ‘void’ regions between the silica and ENR-25 network, ie the ENR-25 network is fully attached to the silica particles, voiding is clearly present between the silica and NR network in Figure 4. However, it can also be seen in Figure 4 that there are a small number of stained network strands connecting the silica particles with the surrounding rubber network mesh. The observation of a weak attachment of the NR network to silica provides direct evidence for interaction between NR and silica, albeit to the limited extent suggested by the bound rubber and volume swelling measurements (Table 3). In comparison, the ENR-25 network mesh is so strongly attached to the silica particles that localised distortion of the ENR-25 network mesh structure can be observed in Figure 3 around several of the larger silica aggregates. Thus, Figures 3 and 4 illustrate precisely the conclusions drawn from bound rubber and volume swelling data of the silica filled ENR-25 and NR compounds discussed above.

Figure 3 Network visualisation TEM micrograph of ENR-25 vulcanisate with 20phr silica.

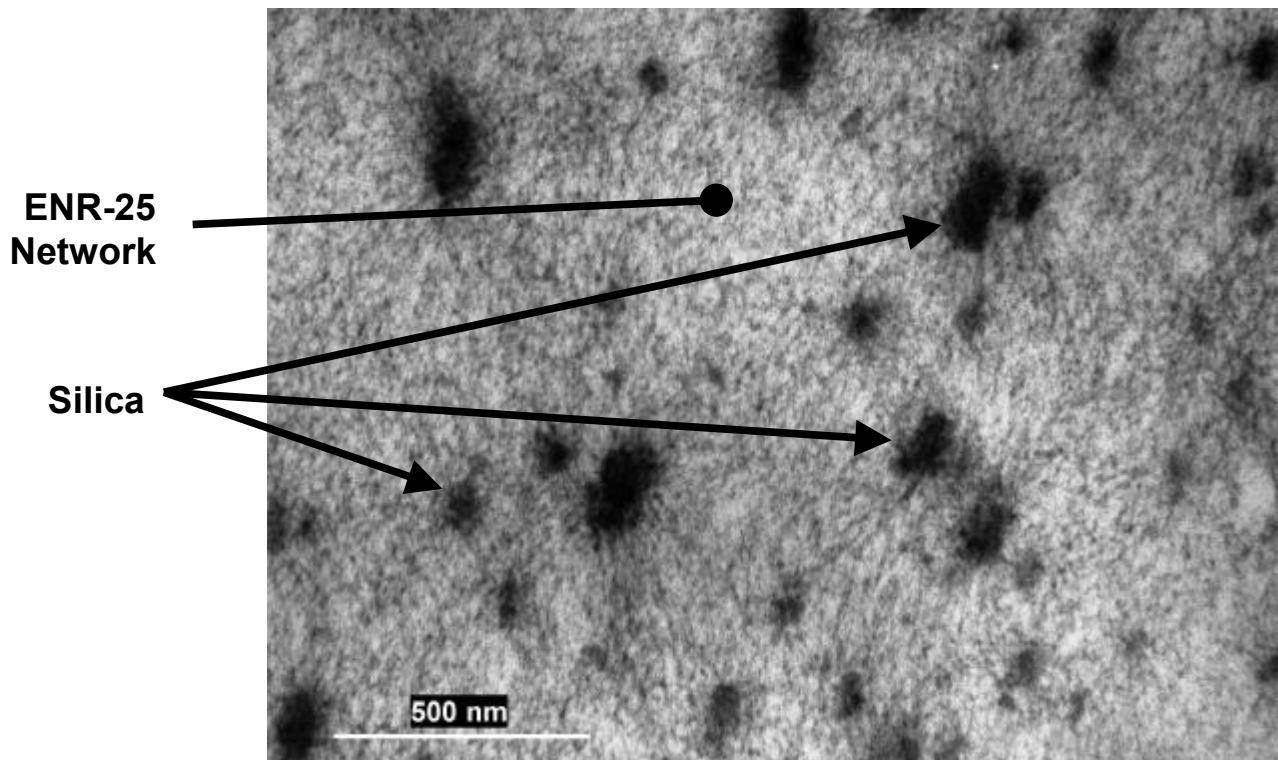
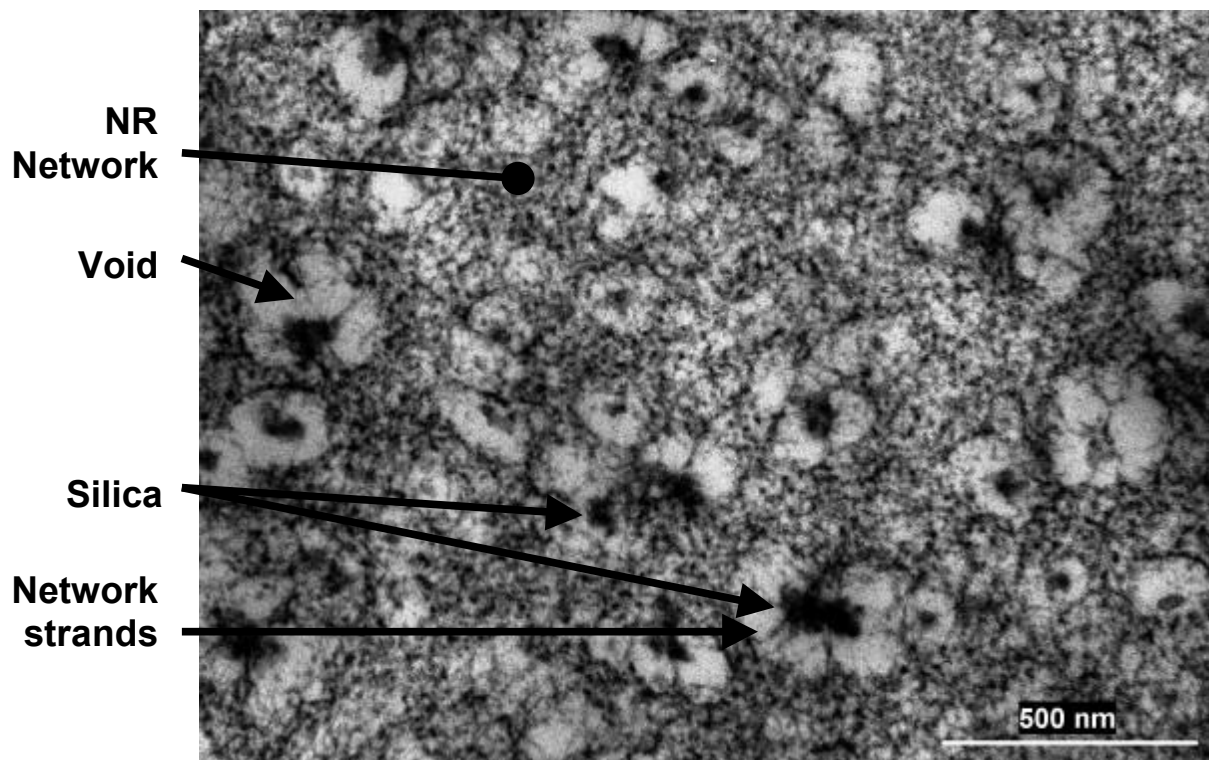


Figure 4 Network visualisation TEM micrograph of NR vulcanisate filled with 20phr silica.



Network visualisation TEM micrographs of silica-filled 70:30 ENR-25/NR and ENR-25/BR blend vulcanisates are shown in Figures 5 and 6¹⁵. Figure 5 shows that the ENR-25 phase contains silica and that there is no voiding present around the silica particles in this phase. In the NR phase of this blend, while some silica appears to be present within the NR regions, it mainly appears to be located at the phase boundary. In addition, the network mesh structure within the NR phase appears to be relatively incomplete, particularly at the phase boundary. These observations may be rationalized as follows: during blending the difference in strength of interaction between ENR-25 and silica and NR and silica is sufficient for much of the silica to be drawn to the phase boundary but not for the silica to be transferred completely to the ENR-25 phase.

Information may also be gained regarding the relative level of crosslinking in the NR phase of the blend as compared with that in the ENR-25 phase. The relative incompleteness of the NR mesh structure within the NR phase and at the phase boundary is a qualitative indication of low crosslink density within the NR phase and poor crosslinking across the ENR-25/NR phase boundary. This is thought due to preferential distribution of the sulphur into the more polar ENR phase

Figure 6 by comparison shows little or no silica to be remaining at all within the BR phase of the blend. This observation is consistent with the silica transferring to the ENR-25 from the BR phase during the blending process, the strength of interaction between BR and silica being insufficient to retain any silica in this phase. Figure 7 shows a recently acquired AFM image of the silica-filled ENR-25/BR blend¹⁵. The silica can clearly be seen distributed in the ENR-25 phase.

Figure 5 Network visualisation TEM micrograph of silica-filled 70:30 ENR-25/NR vulcanisate

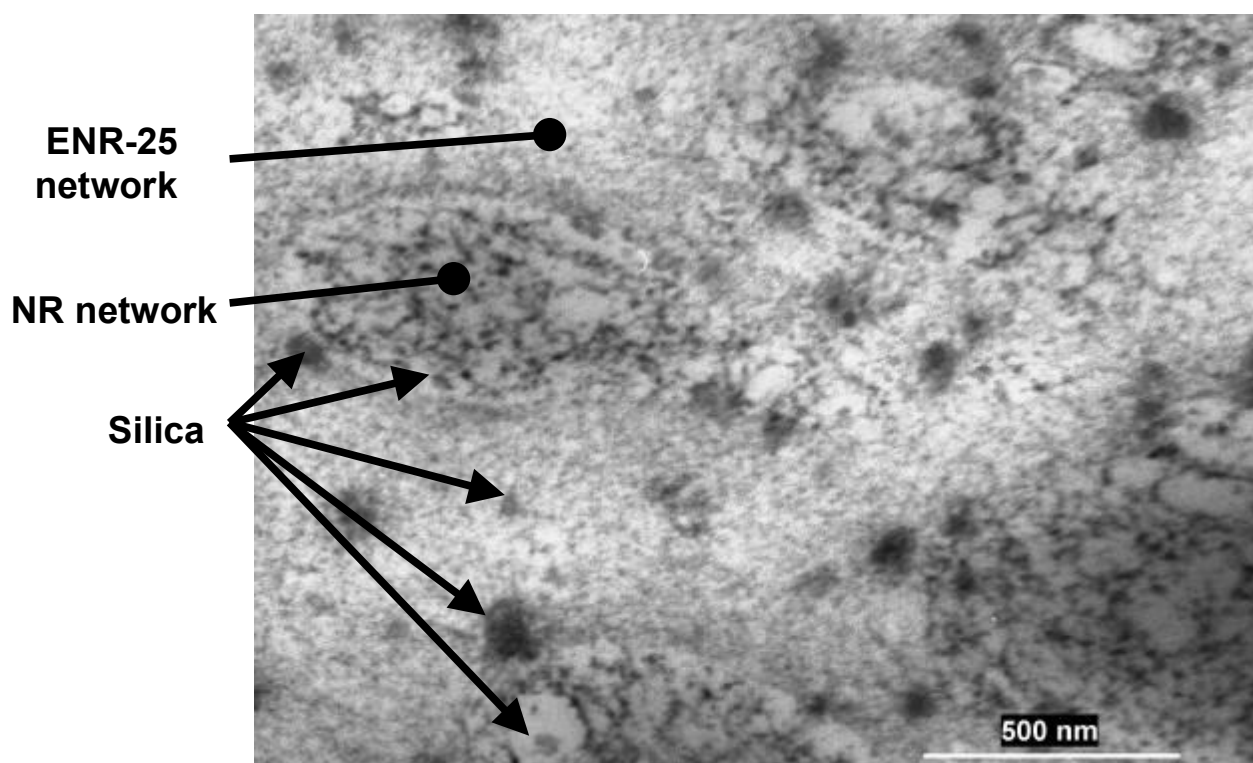


Figure 6 Network visualisation TEM micrograph of silica-filled 70:30 ENR-25/BR vulcanisate

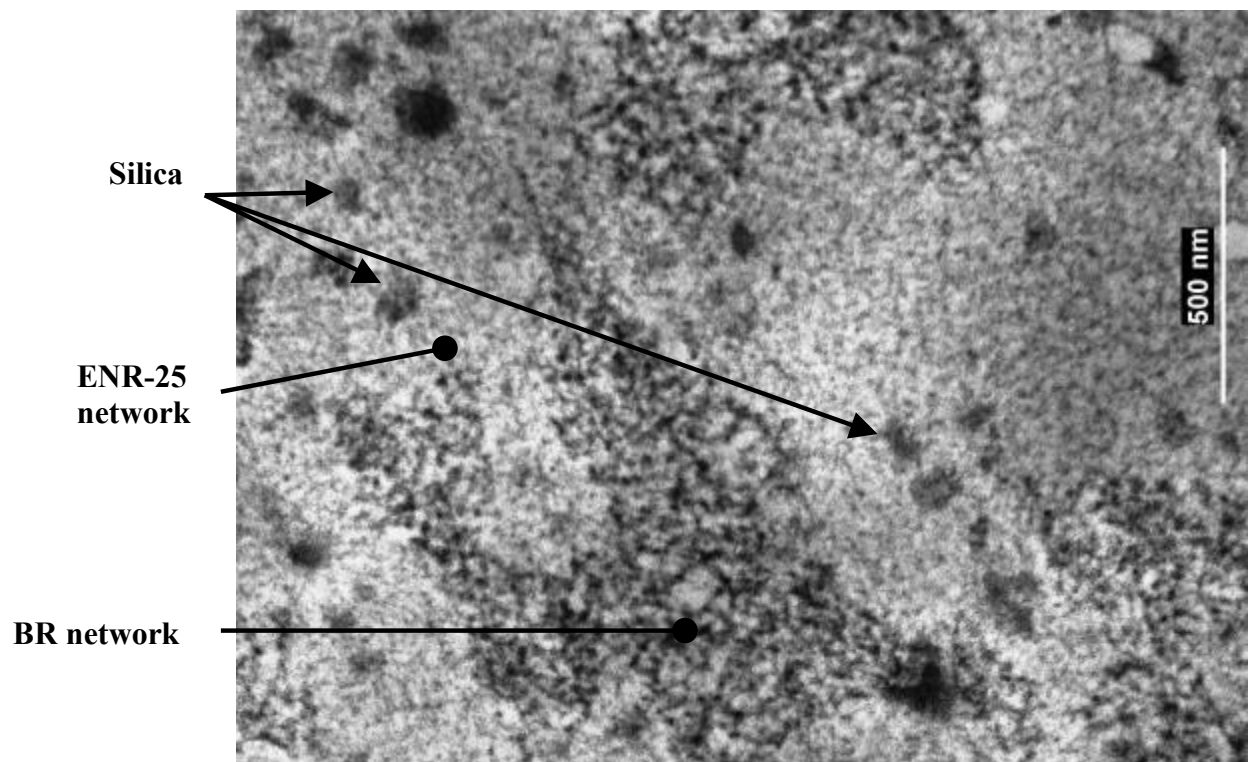
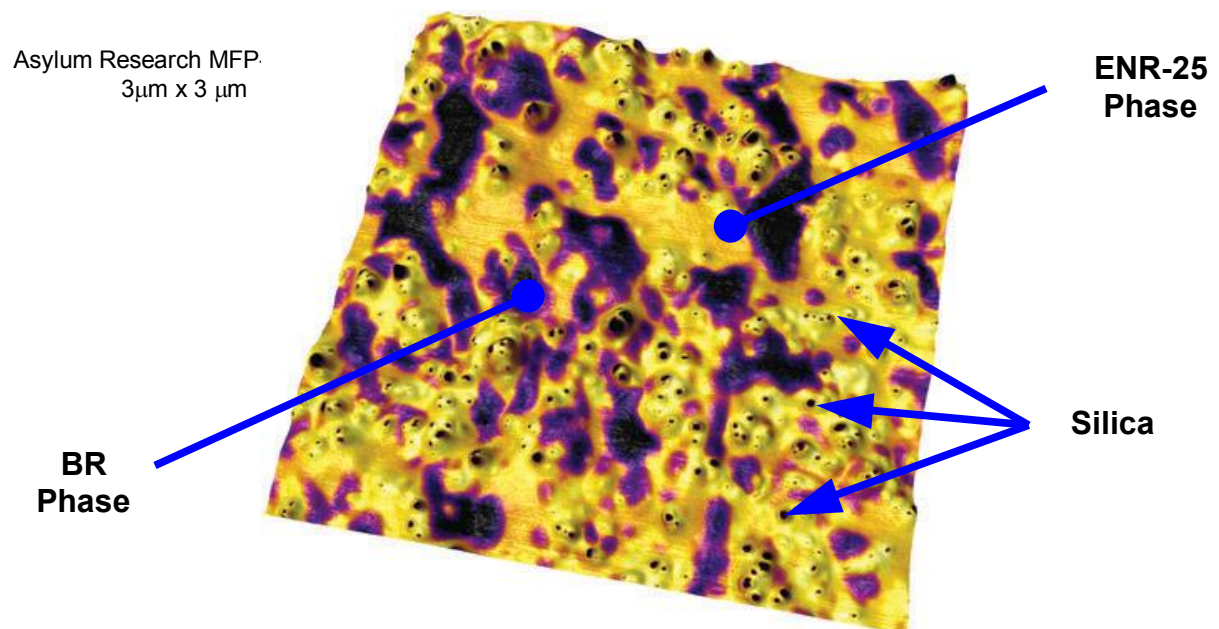


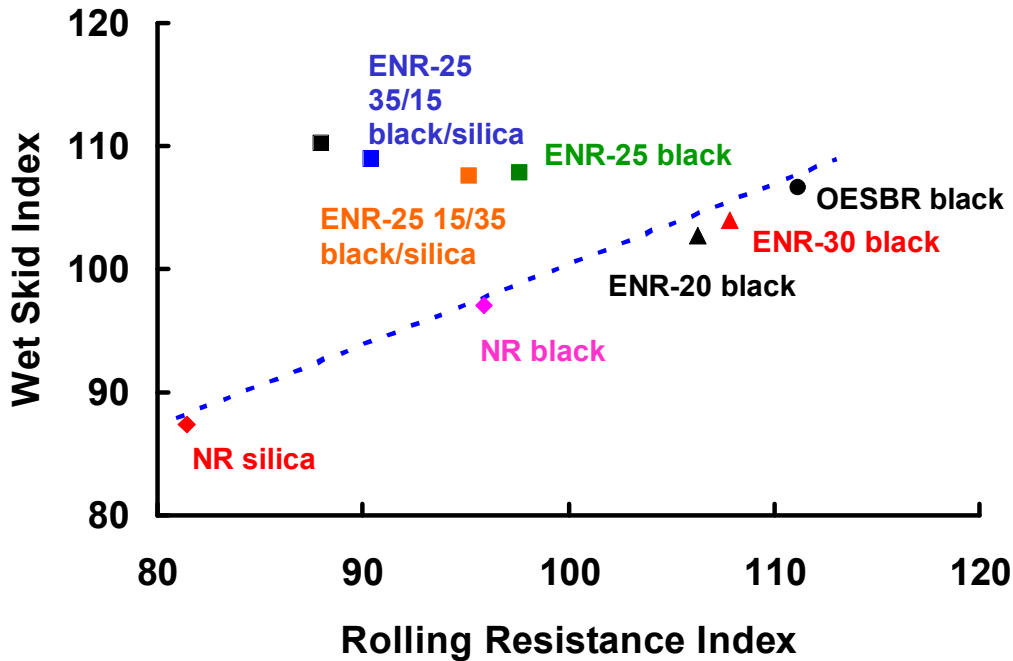
Figure 7 AFM dual-phase/topographic overlay image of silica-filled 70:30 ENR-25/BR vulcanisate



With a relatively high T_g but low resilience at higher temperatures, it was thought that ENR-25 would be suitable for tyre tread compounds. This was investigated at MRPRA (as TARRC was known then) about 20 years ago¹⁹. As shown in Figure 8²⁰, it was demonstrated that tyres

with treads made from silica-filled ENR-25 had both lower rolling resistance and better wet grip than comparable black-filled NR or SBR tread compounds. At that time however, the economic and environmental climate were not favourable to the commercialisation of silica-filled ENR tread compounds and so this technology remained dormant. This situation changed abruptly with SRI Dunlop's introduction in 2006 of the Enasave ES 801 tire and has led to renewed study of ENR-silica compounds at TARRC.

Figure 8 Wet grip (pebble surface) vs. rolling resistance of retreaded passenger car tyres



In a recent study at TARRC²¹, an ENR-25 – silica (50 phr Zeosil 165) tread compound was compared with 70:30 s-SBR/BR-silica (80 phr Zeosil 1165), with and without a silane coupling agent (TESPT – Si69), and also with a non-coupling silane (Dynasytan[®]). Black-filled (67.5 phr N234) 70:30 s-SBR/BR compounds were also included in the study, with and without reactive mixing to increase the rubber-black interaction. The basic physical properties and dynamic properties of the different compounds are compared in Tables 4 and 5. The higher tensile strengths and moduli in the silane-coupled s-SBR/BR-silica, reactively mixed s-SBR/BR-black and ENR-silica compounds indicate strong rubber-filler interactions in these systems. In stark contrast with ENR, in the s-SBR/BR blend there is little evidence of any silica-reinforcement unless a coupling agent is used. The dynamic data demonstrate the correlation between increased rubber-filler interaction and reduced hysteresis. Without coupling, heat build-up in the s-SBR/BR-silica vulcanisates is very high, whereas the uncoupled ENR-silica vulcanisates show exceptionally high resilience.

Table 4 Comparison of ENR-silica and SBR/BR tread compounds: Physical properties

	s-SBR/BR silica			s-SBR/BR N234		ENR-25 silica
	Unmod.	Mod. TESPT	Mod. Dynasytan [®]	Unmod.	Mod.	Unmod.
Hardness, IRHD	82	62	44	65	61	63
M300, MPa	3.9	8.4	1.5	7.6	7.9	9.5
TS, MPa	15.5	19.6	14.1	18.6	18.6	24.3
EB, %	780	515	840	600	555	550
Angle Tear, N/mm	39	36	24	43	37	40
Akron abrasion, vol loss, mm ³	41	13	25	12	12	<20

Table 5 Comparison of ENR-silica and SBR/BR tread compounds: Dynamic properties

	s-SBR/BR silica			s-SBR/BR N234		ENR-25 silica
	Unmod.	Mod. TESPT	Mod. Dynasytan [®]	Unmod.	Mod.	Unmod.
Dunlop resilience, % 23°C	44	55	44	38	46	67
Dunlop resilience, % 60°C	52	69	55	52	62	78
Goodrich HBU, °C	124	64	103	82	67	-

Figure 9 compares the temperature dependence of $\tan \delta$ of the different vulcanisates, determined DMTS measurements on double shear test pieces²¹. Coupling of the SBR/BR blend to silica reduces the hysteresis at 60°C, which correlates with reduced rolling resistance. Reactively mixing the black-filled s-SBR/BR blend has a similar effect. The lowest $\tan \delta$ at 60°C, however, is observed with the silica-filled ENR-25 compound. This also has a very high $\tan \delta$ at -30°C, which is indicative of good traction on ice. The wet grip performance of these compounds was evaluated using a British Portable Skid Resistance Tester. The results are compared in Figure 10²¹; they indicate that the ENR-silica compound will provide better wet grip.

Figure 9 Dependence of $\tan \delta$ on temperature, 1 Hz, 0.2% strain

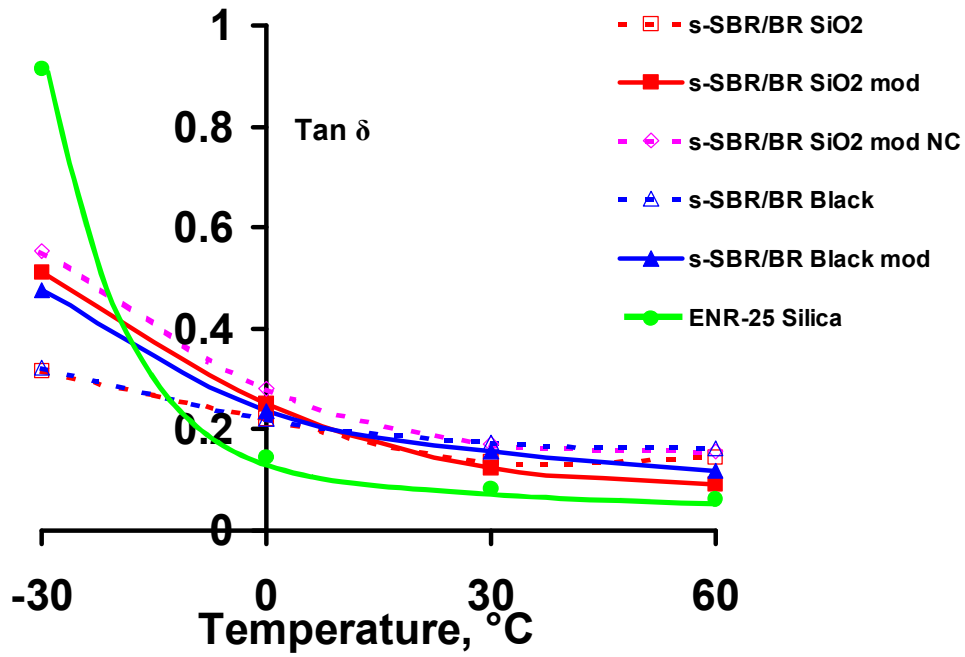
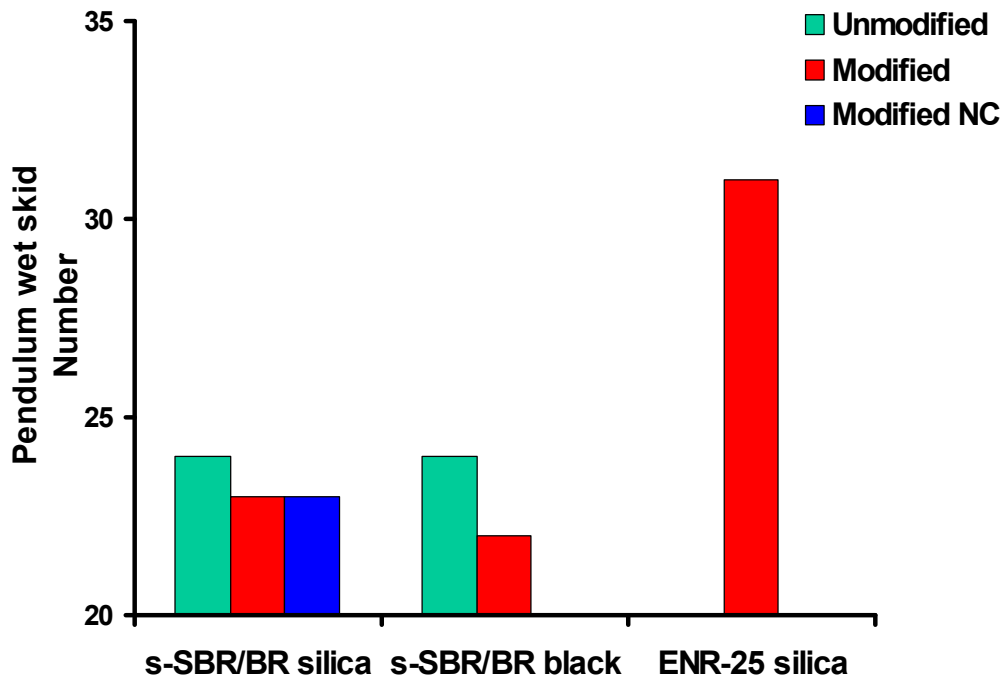


Figure 10 Comparison of the wet skid behaviour of different tread compounds



Thermoplastic elastomers based on NR and ENR

Thermoplastic elastomers (TPEs) aim to combine the speed, convenience and recyclability of plastic processing with physical properties approaching those of thermoset rubbers. Thermoplastic vulcanizates (TPVs) are a special class of TPEs, in which the rubber phase is crosslinked by dynamic vulcanization during blending with the thermoplastic polymer. TARRC has developed TPVs based on blends of polypropylene with NR (NRTPV²²) and ENR (TPENR²³). The rubber is dynamically vulcanised during a continuous mixing process in a twin-screw extruder, providing blends which have a co-continuous phase morphology over a wide hardness range²².

Although NRTPVs tend to have slightly lower modulus at a given hardness than other polypropylene-based TPVs, the basic physical properties of NRTPVs are similar to those of TPVs derived from other elastomers, as shown in Table 6. Even though, in terms of recovery performance, TPVs in general have been regarded as having rather inferior performance when compared with thermoset elastomers, the recovery characteristics of NRTPV compounds, including compression stress relaxation, have been found to excel those of commercially available TPVs based on other elastomers (See Table 7). This recovery behaviour, together with low fogging, good property retention after heat ageing at 135°C (Table 8) and good environmental resistance, indicates that NRTPV is suitable for a range of product areas, including automotive sealing applications and windscreen wipers.

Table 6. Basic physical properties of TPVs²²

Physical Property	NRTPV			EPDM TPV Santoprene® 201-64	EPDM TPV Sarlink® 3160
	53	61	73	64	63
Hardness, Shore A (15sec)	53	61	73	64	63
M50, MPa	1.5	2.0	2.9	2.4	2.4
M100, MPa	2.2	2.7	3.7	3.1	3.6
Tensile Strength, Mpa	4.2	4.8	6.2	5.6	6.8
EB, %	270	285	340	365	550
Tear Strength, N/mm	16.2	20.2	27	21	32

Table 7. Comparison of typical recovery properties of TPVs and thermoset rubbers²²

Property	NRTPV 59	EPDM TPV		NR Thermoset	EPDM Thermoset
		Santoprene® 101-55	Santoprene® 101-64		
Comp set, %					
1d/23°C	15	17	20	5	12
1d/100°C	31	33	38	21	23

Table 8. Comparison of property retention after hot air ageing²²

% Retention	NRTPV 59 3d/125°C	NRTPV 59 3d/135°C	NR Thermoset ^a 3d/125°C	EPDM Thermoset ^b 3d/125°C
M100	107	90	85	-
TS, MPa	97	85	50	124
EB, %	97	85	50	47

NR Thermoset^a Semi EV, engineering compound for moderate/elevated temperature applications with high resistance to set (TARRC Formulary)

EPDM Thermoset^b General Weatherstripping (Dupont Dow in ‘The Rubber Formulary’)

As shown in Tables 9-11, TPENR provides good general physical properties, combined with excellent heat and oil resistance. Indeed, the retention of properties at high temperatures is rather better than might be expected from a TPV based on an unsaturated elastomer. Thus, the resistance to heat ageing is similar to that of an EPDM-based TPV, while the oil resistance is much better and comparable to that of NBR. These properties make TPENR suitable for automotive “under the hood” applications.

Table 9 TPENR: Comparison of physical properties²³

Material	TPENR	EPDM TPV*	NBR
Hardness, Shore A, 15s	65	64	65
M100, MPa	3.7	4.6	3.0
Tensile strength, MPa	6.5	7.0	17.2
Elongation at break, %	240	310	420
Die C tear strength, N/mm	23	22	42
Compression set, %:			
1d at 23°C	24		9
3days at 23°C		22	
1day at 100°C	36	32	17
7days at 100°C	44	42	
3days at 120°C	49		33

* Santoprene 201-64

Table 10 TPENR: Volume swelling and property retention (%) after ageing (3d/125°C)²³

Ageing medium Material	Air		ASTM #3 oil	
	TPENR	NBR	TPENR	NBR
Volume swell	-	-	14	11
M100	101	202	94	117
TS	95	122	80	109
EB	99	65	80	88

Table 11 Property retention (%) after multicell oven ageing²³

Material	TPENR A	TPENR B	EPDM TPV [†]
7days/125°C			
M100	105	99	105
TS	93	96	98
EB	93	103	91
7days/135°C			
M100	119	102	105
TS	91	91	90
EB	81	95	86
7days/150°C			
M100	105	106	92
TS	71	74	76
EB	72	71	79

[†] Santoprene 101-64

Conclusions

NR and polymers based on NR can meet the increasing desire for products to be based on renewable materials. With its very uniform microstructure, NR has very low hysteresis and undergoes strain crystallisation, leading to very high tensile strength and resistance to tearing and abrasion. The high strength, tear resistance and resilience are suited to many engineering applications. Because of its low heat build-up and good green strength, tack, tear strength and adhesion to brass-steel cord, large amounts of NR are used in tyres, especially in larger tyres where NR dominates. NR latex provides high strength in unfilled thin-walled products, such as condoms and gloves.

Epoxidation of NR raises increases the polarity of the polymer and the glass transition temperature, while the ability to strain crystallise is retained up to about 50% epoxidation. ENR interacts strongly with silica, without the need for coupling agents. Because of these unique properties, ENR-25 in silica-reinforced tyre tread compounds provides low rolling resistance, together with high wet grip. Thus ENR, as well as being a renewable material, can contribute to reducing climate change by lowering vehicle fuel consumption.

Thermoplastic elastomers based on NR and ENR combine the use of renewable rubbers with the convenience and recyclability of thermoplastic processing. NRTPV, a dynamically vulcanised blend of NR and polypropylene, has similar basic properties to other commercially available TPVs, together with enhanced recovery behaviour, making it suitable for automotive sealing applications. TPENR, a dynamically vulcanised blend of NR and polypropylene, provides excellent heat and oil resistance, as well as good general properties, and is thus suitable for automotive applications likely to come in contact with heat, oil or fuel.

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