International Journal of Technical Innovation in Modern Engineering & Science (IJTIMES)
Impact Factor: 5.22 (SJIF-2017), e-ISSN: 2455-2585
Volume 5, Issue 01, January-2019

Future Prospects of Thermoplastic Elastomers and Thermoplastic Vulcanizates Based on Acrylonitrile Butadiene Rubber and Ethylene Methyl Acrylate co-polymer A Review

N.Murugan[1], S.T.Saravanan[2] J.Lingaraj[3]

[1] Senior Lecturer in Department of Plastic Technology,
V.S.V.N, Polytechnic College, Virudhunagar 626001, Tamilnadu, India,

[2] Senior Lecturer in Department of Plastic Technology,
V.S.V.N.Polytechnic College, Virudhunagar 626001, Tamilnadu, India.

[3] Senior Lecturer in Department of Plastic Technology,
V.S.V.N.Polytechnic College, Virudhunagar 626001, Tamilnadu, India.

Abstract: ***The purpose of this review is to describe the various aspects Thermoplastic elastomers (TPEs) which are class of materials that have industrial viability because of economical leverage that they offer by having the properties of cross linked elastomers without associated with costs of the chemical cross linking process. TPEs are two-phase in nature, a thermoplastic phase which accounts for their processing behavior and an elastomeric phase which accounts for their elastic behavior. The elastomer particles should be cross linked to promote elasticity. The best way to produce thermoplastic elastomeric compositions comprising vulcanized elastomer particles in melt processable plastic matrices is by dynamic vulcanization. The improvements in properties of blends resulting from dynamic vulcanization are numerous. This review paper covers the work being carried out from the last 20 years in the field of Acrylonitrile Butadiene Rubber (NBR) and its blends. The position of NBR as the standard polymer for rubber goods that are exposed to oils, liquid fuels, and greases is likely to be depending very much on the fuels of the future. Attempts have been made the possibility of developing NBR and Ethylene-Methyl Acrylate copolymer (EMA) grades and processing methods and working out new and more suitable recipes endeavoring to ensure the continued use of this material in such applications.***

*Key words: **blends; NBR; EMA; thermoplastic elastomers; dynamic vulcanization***

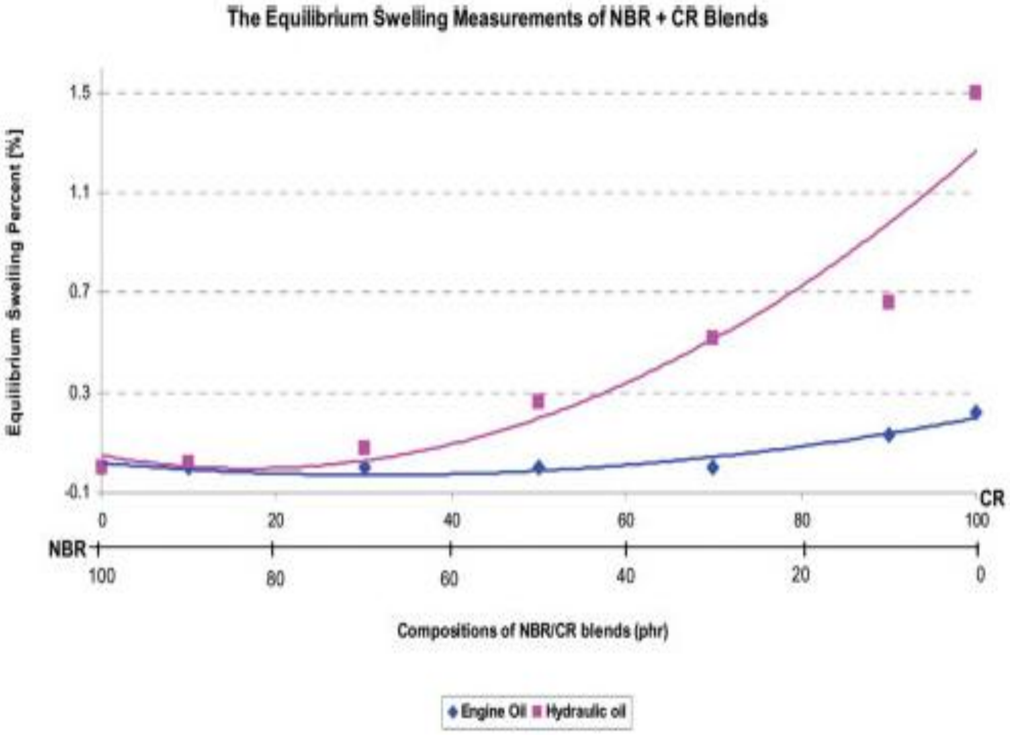
I. INTRODUCTION

TPEs can be prepared either by blending of two polymers, or by block polymerization process. In both cases the elastomer phase has no chemical interaction but some physical interaction occurs between the thermoplastic block segments and elastomeric domains. Simple blending of two polymers can only yield a technically adequate product if polymers based on the dynamic vulcanization principles first outlined by Hofmann and extended by Coran. Dunn *et al* have described a range of oil-resistant thermoplastic elastomers that are prepared by the dynamic vulcanization of blends of nitrile rubber and polyolefin resin. In order to overcome the gross incompatibility of these two polymers a compatibilizing mechanism needs to be introduced and it is suggested that the production of a block copolymer from the two incompatible polymers would be one way of achieving this.

1. GENERAL CHARACTERISTICS OF NBR:

The general characteristics of NBR are, Oil, fuel and grease resistance, Good processing characteristics, Variety of curing systems, Low permanent set, Good abrasion resistance, Low gas permeability, Moderate to good low temperature flexibility, Moderate ozone resistance, Moderate tack, Compatibility with polar thermoplastics (e.g. PVC, phenolics)

Swelling Resistance: The good swelling resistance of NBR is, of course, restricted to contact with non-polar or slightly polar substances, such as mineral oils, liquid fuels with low aromatic contents, and greases based on mineral oils. Polar substances, such as esters and ketones, initiate strong interactions and cause severe swelling of NBR; the same applies to aromatic hydrocarbons. NBR is resistant to fuels containing aromatic hydrocarbons, only if the fuels do not contain more than about 50 % aromatics. If liquid fuels containing aromatics are additionally modified with alcohols, the resistance to swelling suffers a further drastic reduction. Where contact with mineral oils is concerned the resistance to swelling does not merely depend on the oil’s viscosity and content of paraffinic, naphthenic, and aromatic hydrocarbons. Experiments with technical lubricating and hydraulic oils have shown that the resistance to swelling is also influenced by the types and amounts of additional additives, by the temperature and by the exposure period. These factors have been investigated systematically by Bertram and Brandt. It follows that a vulcanisate which has been found to resist certain technical lubricants will not necessarily resist others.



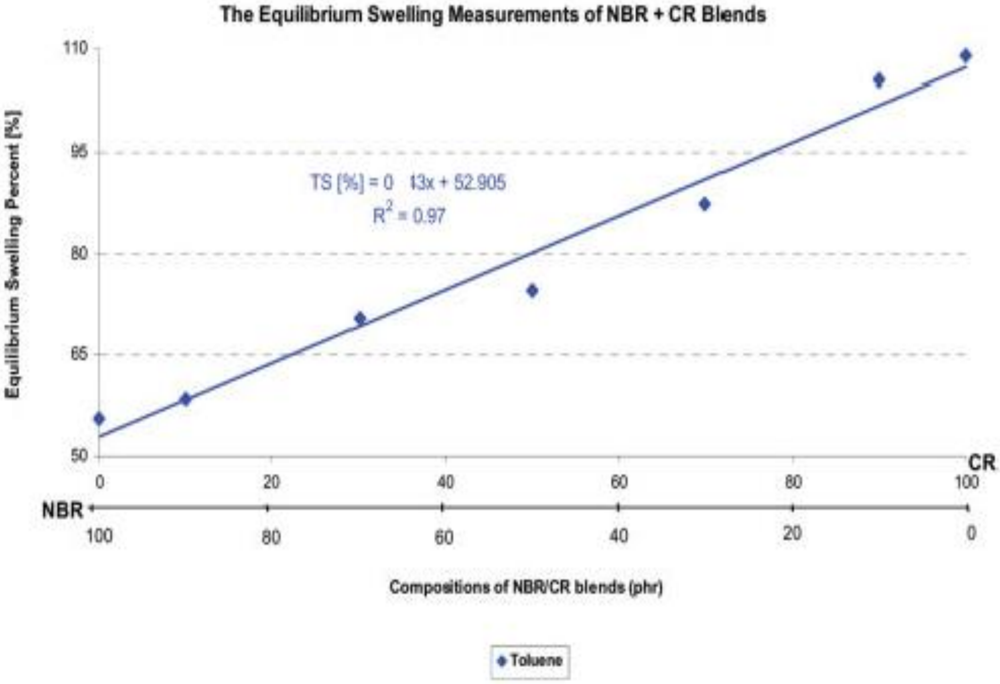
Resistance to Ozone: The ozone resistance of unprotected NBR is comparable with that of other diene rubbers. Unlike that of natural rubber and styrene—butadiene rubber, however, it cannot be greatly improved by including paraffinic hydrocarbons and antiozonants in the compound. In cases where increased thermoplasticity and reduced low-temperature flexibility are acceptable this difficulty is often overcome by blending PVC with the NBR. Although thermoplastic elastomers with other chemical compositions have already acquired considerable importance, no thermoplastic NBR is yet available. The state of development has been reviewed by Dunn *et al.* An interesting method of obtaining thermally or mechanically reversible crosslink sites has been proposed by Shen *et al.* and is described in several previous patents. The development of a technically satisfactory thermoplastic NBR is eagerly awaited.

2. MODIFICATION BY BLENDING WITH OTHER POLYMERS:

Blends of NBR with other rubbers or with thermoplastics or thermosetting resins have been known for several decades. Modification by blending is undertaken to reduce costs, to improve the rheological properties of material, or to confer specific physical or chemical properties to the end product. The fundamental characteristics of the end product are determined chiefly by the polymer which is present in the larger proportion of the blend. Thus a blend consisting mainly of NBR has, on the whole, the typical properties of NBR. A blend consisting mainly of a thermoplastic and containing only a small amount of NBR will have the fundamental characteristics of the thermoplastic, though certain of its properties (e.g. toughness) may have been substantially improved. The role of elastomers in rubber-modified plastics has been discussed at length by Dinges. The properties of all polymer blends depend on the effectiveness of the physical blending process; they also depend on whether the polymers are compatible or form a heterogeneous mixture, and therefore—in the latter case—on the morphology of the blend. Also of importance in the case of elastomer blends is the chemical process of crosslinking. This is very complex in heterogeneous blends because (i) different rubbers have different rates of crosslinking; (ii) the crosslinking system and plasticisers have different degrees of solubility in the various rubber phases; and (iii) the interactions between the rubber and filler differ according to the rubber concerned.

3. BLENDS OF NBR WITH OTHER RUBBERS:

NBR/NR and NBR/SBR Blends: These blends have been used in the rubber industry for several decades— NBR/SBR blends for reasons of cost or to meet certain swelling resistance requirements and NBR/NR blends because they have more tack than NBR alone.



NBR/CR Blends: NBR/CR blends are more resistant to ozone and fatigue than NBR alone, yet they retain good resistance to oils. They are, however, less resistant to ozone than NBR/PVC and NBR/EPDM blends.

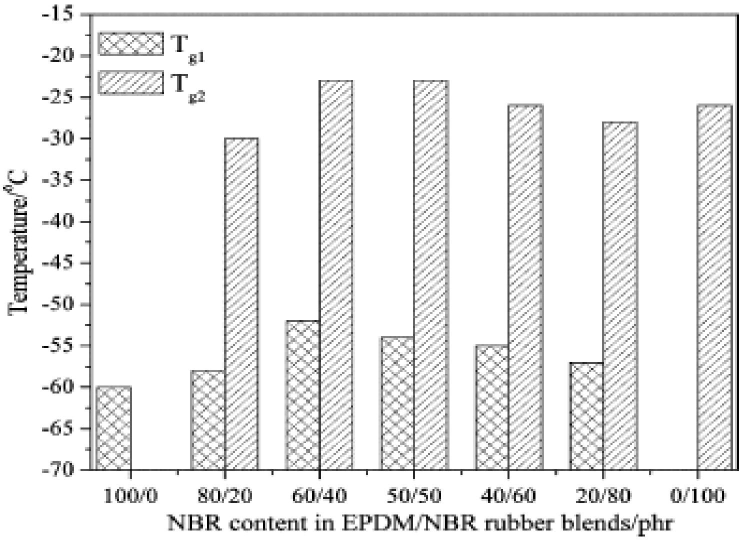
NBR/EPDM Blends: These blends, similarly to those consisting of NBR and PVC, are intended to combine the ozone resistance of EPDM with the oil resistance of NBR. NBR/EPDM blends lack a homogeneous phase because the difference in the polarity of the two materials is excessive. They are heterogeneous blends. With a view to obtaining a finer dispersion of the EPDM particles in the NBR they are mixed in lattice stage. It is not yet possible to assess the suitability of the resulting materials for their intended purposes. For good ozone resistance the EPDM must be dispersed as finely as possible. The blending conditions are therefore decisively important. In this connection Mitchell[42] recommends that carbon black, plasticisers, and activators be added exclusively to the EPDM. Other authors[43] recommend the addition of chemicals which have homogenising effects. Good resistance to ozone can be obtained with blends containing 30—35 % **EPDM** but in many cases, where resistance to swelling is important, the proportion of EPDM cannot exceed 20 %. Because of this waxes and anti-ozonants have to be included. The problems that arise from the different rates of crosslinking and accelerator solubilities have been investigated by many authors.[41,44,47] The classical thiuramdisulphide vulcanisation systems, possibly supplemented by sulphur donors, give the best overall results. Long-chain alkyl dithiocarbamates are also recommended as special accelerators. Peroxide crôsslinking gives good ozone resistance but the overall property pattern is only moderately good because the NBR is overcured and the EPDM undercured. In principle, NBR/EPDM blends can be used to combine the swelling resistance of NBR with the ozone resistance of EPDM.

NBR/BR Blends: Here again the differences in polarity make the polymer mixture heterogeneous. The inclusion of 10 % BR considerably improves the performance in the cold bending test (according to ASTM-D *736-57*T). At approximately 20 % BR the brittleness temperature is reduced considerably without the dynamic glass transition temperature being altered. Other effects of BR addition are an improvement of the flow behaviour in injection moulding and a reduction of the energy needed for extrusion. Certain adverse effects on the physical properties of the vulcanisates have to be accepted.

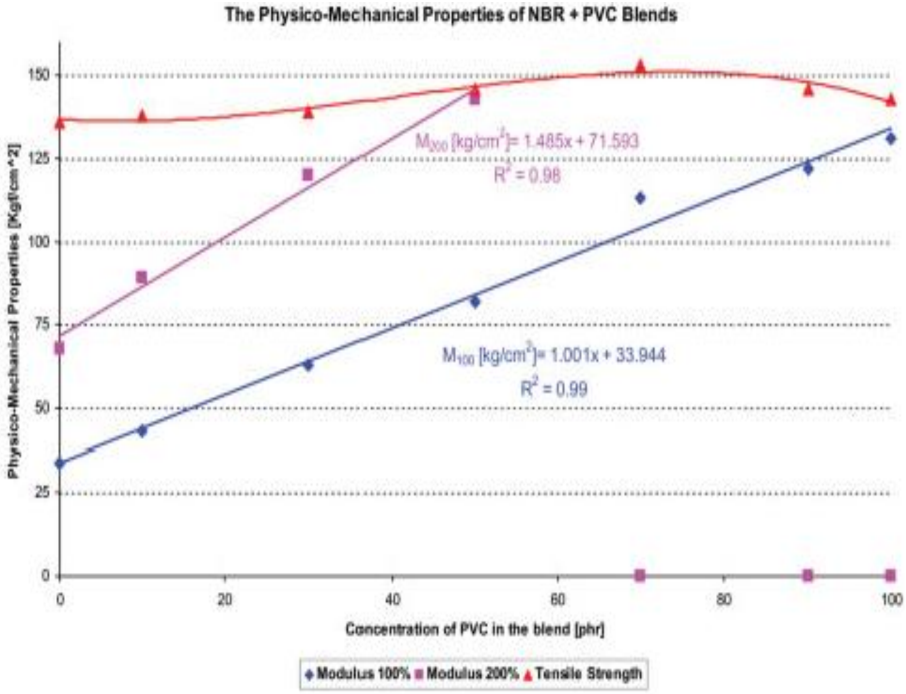
NBR/CIIR Blends: These blends, too, are heterogeneous. Good resistance to ozone is obtained. Applications of these polymers are aimed at the automotive, domestic appliance, fluid power and industrial hose industries, and although still not performing as well as conventional NBR on compression set, they could also find use in certain seals and gasketing applications. Without doubt this is one of the most interesting developments that has taken place in recent years and will surely be followed by further types from other manufacturers.

4. BLENDS OF NBR WITH PLASTICS:

Although small amounts of NBR are added to thermoplastic or thermosetting resins to improve certain properties of these, the following remarks are concerned mainly with blends in which the rubber predominates and which are processed and used similarly to rubber.



NBR/PVC Blends: Blends of NBR with PVC were developed to have combined properties of the ozone resistance of PVC with the cross-likability and oil resistance of NBR. With PVC it is possible to have two distinct types of blend ratios, firstly that where the PVC predominates and the resultant blend is processed as a thermoplastic and secondly that where the NBR predominates and the blend is subsequently processed as a vulcanizable elastomer. This second type of blend ratio was initially developed as a means of improving the ozone resistance of nitrile rubber, where it was used mainly as a competitor for polychloroprene rubber. The amount of PVC present in the blend can vary up to *50* parts, but to have any measurable improvement in weathering properties, at least *25* parts of PVC must be present in the blend. Nitrile rubbers have a range of *NBR/PVC* blends available, some of which are mechanically prepared, though most are manufactured from latex blends.



Comparison with Carboxylated NBR: The use of carboxylated NBR (XNBR) in blends with PVC has also been studied and the resultant blends exhibit increased tensile strength and modulus with improved abrasion resistance. The main draw back to the use of XNBR in such blends has been its tendency to crosslink during the fluxing stage of blend preparation; this has now been solved and proprietary blends can be obtained.

Blends of NBR with Polyvinyl Acetate (PVAC) and its Copolymers: Stollfuss investigated blends of NBR with polyvinyl acetate (PVAC) and its copolymers. The object was to obtain better low-temperature flexibility, compression set behaviour, and ageing resistance than that possible with NBR/PVC blends. Although the solubility parameters are similar in the two cases and the formation of a homogeneous phase was expected, only two-phase systems were found, except in the case of a vinyl acetate/maleic acid ester copolymer. All the mechanical properties, and also the resistance to ozone, were inferior to those of the NBR/PVC blends. Only the resistance to ageing was improved.

Blends of NBR with Cellulose Esters: According to the solubility parameters blends of NBR with cellulose acetate, propionate, or acetate butyrate should give a homogeneous phase. Owing to the formation of hydrogen-bridge bonds, however, the theory fails; the polymer blends consist exclusively of two phases and they have no resistance to ozone, even when the fluxing has been carried out at temperatures of around 180°C. The vulcanisates combine great hardness with good resilience, but the compounds are exceedingly viscous and therefore difficult to process.

Blends of NBR with Polyamides (PA): Despite the similarity of the solubility parameters, pronounced crystallisation and hydrogen-bridge bond formation by the polyamides (PA) prevent NBR/PA blends (6-PA, 6, 6-PA) from forming a homogeneous phase. Tolstukhina and Kolesnikova[86] found that the benzene resistance of gelled blends was considerably improved, but at the expense of the resistance to abrasion and elongation at break. It is assumed that the NBR is crosslinked by the polyamide.

Ozone Resistance :NBR vulcanisates are only moderately resistant to ozone. The ozone resistance can be increased effectively by blending the NBR with PVC or EPDM. If, for technical reasons, this is not possible all that can **be** done is to add large amounts of p-phenylenedimines or the- non-staining antiozonant AFD (which is based on enol ether) together with waxes. No explanation has yet been found for the fact that antiozonants have so little effect in NBR vulcanisates. Grades with low acrylonitrile contents can be given more protection than those containing large amounts of acrylonitrile.

II.ACRYLONITRILE BUTADIENE RUBBER AND FUTURE PROSPECTS

Blends of NBR with Other Special Rubbers: Propylene oxide rubber, shows depolymerisation phenomena at high ageing temperatures, whereas NBR undergoes further cross linking and becomes harder.

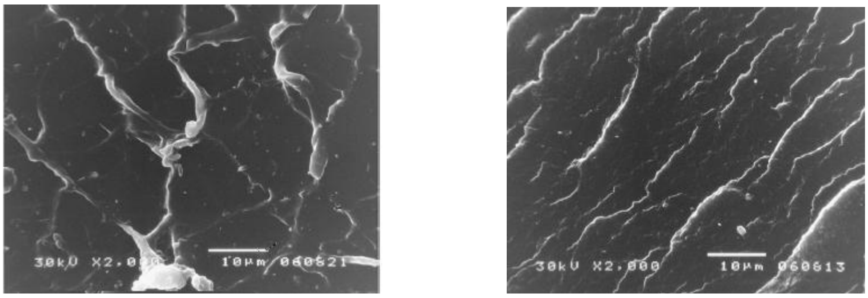


Figure 1: SEM micrographs of NBR rubber vulcanisates

The attempts that have been made to improve the ageing resistance of rubber by blending these two polymers with a view to combining their opposite tendencies have not been successful. Similarly, in cases where NBR has remained an important constituent of the polymer mixture it has not proved possible to increase the resistance of NBR vulcanisates to ageing by blending with epichlorohydrin

III} PRESENT PROBLEMS AND FUTURE PROSPECTS

Heat Resistance The opportunities for improving the heat resistance of NBR vulcanisates through the use of improved polymers and optimised compounds ensure that NBR will retain many automotive and general engineering applications in which improved heat resistance is necessary. The developments of recent years, which have given a new lease of life to an inexpensive and proven polymer, are investigated from the standpoint of motor vehicle manufacturers by Waker. Whether further substantial progress will be possible is uncertain. Improvements could result from the use of hydrogenated NBR, but it is not certain that this material will be produced industrially. The extent to which demands will become more exacting in the future is another unknown quantity.

Future Fuels: NBR has gained many of its applications through the ability of its vulcanisates to withstand liquid fuels. Future developments in fuels may therefore be of considerable importance.

Effect of Oil Scarcity: Although many different forecasts can be made, it is certain that oil will continue to become scarcer, with the result that its price will increase drastically and alternative fuels will become more important. Legislation in a number of countries has reduced the tetraethyl lead content of petrol. Aromatics are therefore being added to compensate for the reductions in octane numbers which would otherwise result. Low-lead petrol in the Federal Republic of Germany has an aromatics content of *40-45* %, whereas the corresponding figure in the United States is 33—36 %. Compared with American fuels, European fuels therefore exert a more pronounced swelling action on rubber goods. For reasons of industrial hygiene it is unlikely that further increases in the aromatic contents of petrol will be forthcoming.

Alcohol Addition: It is probable that methanol or ethanol will be used to some extent as a fuel substitute in order to raise octane numbers and save conventional fuels. A number of technical problems (arising from phase separation of fuels, increased vapour pressure values, and cold start difficulties) remain to be solved in this connection. In a hydrocarbon/methanol mixture the proportion of relatively stable hydrogen bonds is reduced. In addition, polar dipole—dipole interactions take place between the alcohol and the nitrile group of the rubber, with the result that NBR vulcanisates swell much more severely in hydrocarbon alcohol mixtures than they do in the individual fiuids.[47] Apart from this, all the diffusion processes are accelerated to the extent that the polymer network is loosened. Accordingly the addition of alcohols to hydrocarbon fuels may be expected to increase the extent to which liquid fuels diffuse through rubber goods. At the moment it appears that new fluoro rubbers, and possibly epichiorohydrin rubber, could offer a solution to these problems.

IV PROSPECTS AND CONCLUSION

In some of its applications NBR has been replaced by other special rubbers that are superior to it in individual respects, or in combinations of several properties. Thus acrylate, silicone, and fluoro rubbers have already been used for a number of years for many types of shaft oil seal, which were formerly made with NBR. The change was dictated by higher engine temperatures and speeds and alterations to the composition of lubricating oils, together with longer guarantee periods and intervals between oil changes. Even the use of NBR for certain rubber parts which come into contact with liquid fuels has been replaced by that of epichiorohydrin polymers, which offer more favourable combinations of resistance to swelling, low-temperature flexibility, and resistance to ozone. It is here, above all, that the future of NBR will depend very much on the fuels of the future. On the whole, however, the position of NBR as the standard polymer for rubber goods that are exposed to oils, liquid fuels, and greases is unlikely to be seriously challenged. In those applications where the goods are only just equal to the demands made on them, NBR manufacturers and the rubber industry are endeavouring to ensure the continued use of this material by developing new grades and processing methods and working out new and more suitable recipes.

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