Elastomer
Vol. 34, No. 2, pp. 177~182(1999)

The Use of Chemical Additives to Protect SBS Rubbers Against Ozone Attack

C. A. Moakes†
Rubber business Group, Research and Development 51368 Leverkusen, Germany
(Received May 21,1999)

ABSTRACT : SBS thermoplastic elastomers offer an inexpensive alternative to vulcanised rubbers for many undemanding applications. They are, however, particularly susceptible to attack from atmospheric ozone leading to cracking as soon as any strain is applied. In most rubber applications some strain is unavoidable. In this paper a compounding approach to protecting SBS thermoplastic rubbers against ozone is described. An explanation is offered for why a protective effect is observed only when certain combinations of additive are used.

SBS elastomers are the most affordable class of thermoplastic rubbers.To achieve finished products resistant to ozone and without compromising the light colours often demanded, recourse must be made to blending with other saturated elastomers or replacement by hydrogenated (SEBS) types. The latter is a significantly more expensive alternative.

Under laboratory conditions where the rate of ozone attack is increased by several decades, unprotected SBS begins to crack within a few hours. Several different protective agents are examined here, the best of which, a cyclic enol ether, Vulkazon® AFD, can extend the resistance to any cracking to several weeks by the use of a few percent by weight of additive. The systems reported neither discolour the polymer nor stain other materials with which it may be in contact.

Use of the protective systems described here could enable SBS elastomers to compete in many applications with the more expensive SEBS polymers.

Keywords : thermoplastic elastomer, ozone resistance, protection.

I. Introduction

Styrene butadiene block copolymers offer a cheaper alternative to vulcanised rubber for many moulded and extruded applications. The Market price for SBS is higher than for SBR but its significantly cheaper processing results in many products being produced cheaper overall in SBS than in vulcanised SBR. SBS thermoplastic elastomers are chemically the same as SBR rubber.

SBS also shares with SBR a facility for compounding to meet a wide variety of end product property requirements. Both rubbers also share

†대표저자(*e-mail : Colin-Adrian.Moakes.CM@bayer-ag.de*)

some disadvantages. They are susceptible to ageing and attack from atmospheric ozone. The latter ageing effect is a well understood process in vulcanised rubbers and much development work has been devoted to finding ways of preventing it. Most of the solutions involve the use of staining chemicals which would be unacceptable in many of the products where SBS is employed as these often exploit its purity of colour.

A product is made from rubber if it is expected to conform to deformation during its service life. As soon as rubber is deformed ozone attack can occur. Ozone is normally present in sufficient quantity in the atmosphere to initiate cracking.

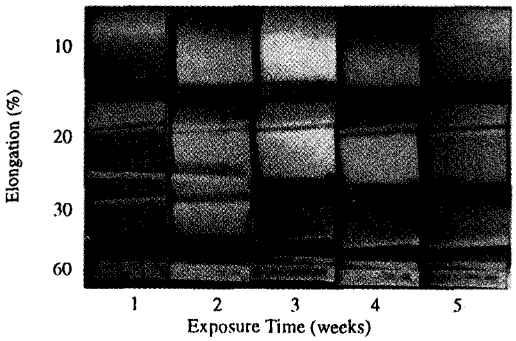

Fig. 1. Progress of ozone attack (Par. Wax 2, Cyclic acetal 2).

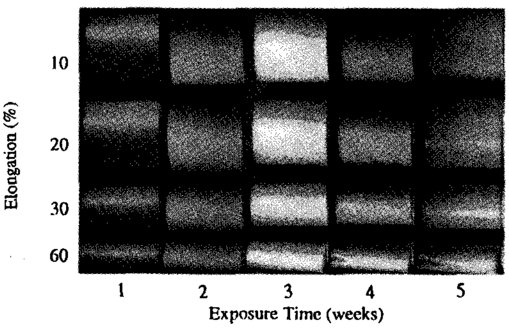

Fig. 2. Progress of ozone attack (Par. Wax 2, Enol ether 2).

Ozone cracks always grow perpendicular to the direction of the strain. When the conditions allow, ozone cracks can grow very quickly and lead to complete break of the product or test piece. Examples of this are shown in Figure 1, where unprotected SBS has been exposed to ozone under conditions chosen to accelerate considerably its effect. The improvement that can be achieved by inclusion of suitable chemical additives is seen in Figure 2. Here one of the most ozone resistant compounds in the present study is depicted.

Wilder[1] classified the ozone resistance of styrene block copolymers as similar to that of emulsion or solution SBR and recommends compounding with 20 to 30% of EPDM or EVM to improve resistance. Thorstad[2] and co-workers showed that both the amount of EPDM used and the type chosen are critical to achieving the necessary protection.

Xianglong[3] et al. have shown the importance of the morphology of EPDM in the blend with SBS. All of these recommendations are based on the addition of between 20 and 50% of the weight of SBS of an additional polymer, something which has a significant effect on many other properties of the material. Also the protection afforded is conditional on ensuring that the second polymer forms a continuous phase.

No mention has been found in the literature of attempts to protect SBS polymers from ozone attack by the use of chemical antiozonant. A possible explanation for this could lie in the generally poor protection offered by such agents, which is discussed in more detail below.

The protective mechanism of waxes against ozone attack in unsaturated general purpose rubbers has been studied in some detail. Best and Moakes[4] show the importance of the rate of migration and how this in turn is related to the type of wax used. Their experimental work was based mainly on natural rubber but enough testing was carried out to show that migration rates do differ considerably between different types of rubber. The ranking of migration rates of different types of wax is independent of the rubber type.

The utility of combining chemical antiozonants with protective waxes has been demonstrated for various types of vulcanised synthetic rubber.[5] The work described in this paper was devoted to finding a simple way of protecting SBS from ozone attack without disturbing the original colour or indeed other properties of the compound. It draws freely on the extensive body of knowledge of compounding vulcanised rubbers.

II. Experimental

A straightforward radial block SBS polymer was used throughout the test. A white test compound (Table 1) which could serve as a moulding or extrusion compound was prepared by an upside mixing procedure in a laboratory internal mixer with a nominal capacity of 1,5 litre. Separate mixes were prepared for each of the additives or additive combinations to be evaluated. In all cases no difficulty was encountered in preparing homogeneous compounds. A mixer temperature of 120°C was set as standard followed by milling at the same temperature. 4mm thick slabs were pressed in a mould at 150℃ for two minutes followed by cooling to 45℃ for three minutes. Basic physical properties were determined on appropriate samples produced under identical conditions. After ensuring that the slabs so produced were smooth and free from blemishes or marks test samples were punched out with the dimensions 45×55mm, for the higher extensions and 45×45mm for the 10% elongation. The samples were then arranged in a slotted rack as shown in Figure 3 with the long dimension running along the rack. The test method is a company internal standard method broadly

Table 1. Test Compound

Ingredient	Parts by Weight(phr)
Styrene butadiene block copolymer*	100
Precipitated Whiting	20
Paraffinic oil	50
Zinc stearate	0.8
Additives	
Vulkanox 4010 NA, N isopropyl N′, phenyl p-phenylene diamine(IPPD) Vulkazon AFS, bis(1,2,3,6 tetrahydrobenzaldehyde) pentaerithriteacetal (Cyclic acetal) Vulkazon AFD, Enol ether	2
Waxes	
Paraffin 3412	2 or 3
Microcrystalline (softening point 71°)	2 or 3

*Europrene Sol T 161B

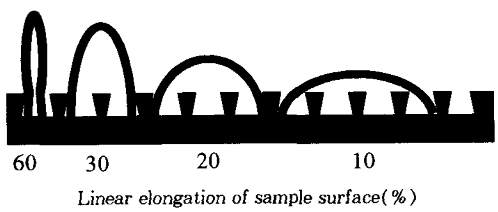

Fig. 3. Ozone test rack.

based on DIN 53509.

This gives linear static elongations of 10, 20, 30 and 60%. The extended samples were allowed to equilibrate in the laboratory conditions without being exposed to ozone for 72 hours before being put into the ozone chamber.

Ⅲ. Results and Discussion

In the field of vulcanised rubbers, the unsaturated general purpose rubbers, NR, SBR and BR are considered to have poor resistance to ozone attack. These three do not differ greatly in their susceptibility to attack. When allowance is made for the difference in tensile modulus between the compounds tested, the evidence[6] suggests that SBS polymers are more susceptible to attack by ozone than is SBR If this can be confirmed by more detailed study it is believed that an explanation lies in the different morphology as the two types of polymer are chemically similar.

1. Chemical Protection

Three different chemical additives (Table 1) which are widely used in vulcanised rubber applications were compared. One of these, the paraphenylene diamine (IPPD), stains the rubber dark brown and stains other painted or polymeric surfaces on contact. It is a widely used powerful antiozonant in vulcanised rubber products such as belts and hose. The other two chemicals cause neither discoloration nor contact staining and are often applied in vulcanised rubber products as antiozonants where the colour of the product is important.

Figure 4 summarizes the performance of these

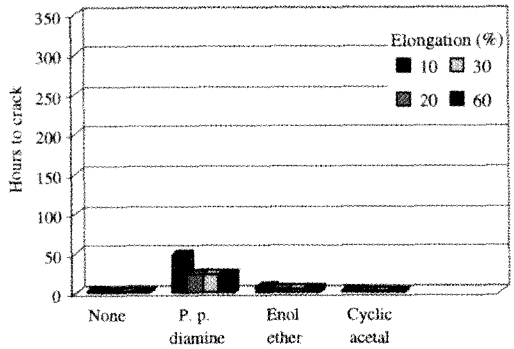

Fig. 4. Chemical additives.

three antiozonants in comparison with the unprotected compound. The discolouring paraphenylene diamine offers a measure of ozone protection over the range of elongations tested here. The enolether (Vulkazon® AFD) offers a small amount of protection over the full range of elongations. The cyclic acetal (Vulkazon® AFS) appears to offer no ozone protection under these conditions.

None of the three products tested achieved the improvement needed to be able to claim that SBS had been compounded to render it ozone resistant.

2. Protection by Waxes

Paraffin and microcrystalline waxes are widely used in vulcanised rubber to provide ozone protection. A fast migrating paraffin wax and a slow migrating, high melting point, microcrystalline wax were selected for evaluation alone and in combination. The selection was based on the reported migration behaviour in natural rubber.[4] This series of compounds was exposed to ozone in the same way as the previous series. Results of testing are summarised in Figure 5. The paraffin wax when 2phr were added gave hardly

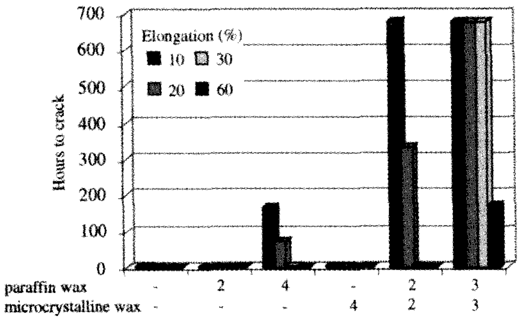

Fig. 5. Wax addition.

any improvement in ozone resistance. Increasing the dosage to 4phr protected the rubber from ozone for 170 & 72 hours respectively at the 10 and 20% elongations but achieved little above these levels. Four phr of the microcyrstalline wax, however, achieved only a marginal improvement in the time to crack. The blend of 2phr each of the two waxes protected at 10% and 20% elongation for more than 600 hours, a much better result than either of the two waxes used individually at the same overall dosage. Increasing the level of both waxes in the blend extends the protection to over 600 hours for the 30% elongation Waxes alone or in combination can be effective in protecting SBS copolymer from ozone attack. It is doubtful whether the level of protection seen here could be considered acceptable for those applications where lack of ozone resistance currently prevents SBS from being used. The level of wax addition needed to achieve protection, 6 parts of a combination of two waxes, is probably not acceptable in many thermoplastic rubber applications because of the unsightly surface bloom this causes.

3. Combination of Wax and Chemical Antiozonant

In the third part of this study the series of compounds with wax additions, from the second part, was repeated twice with the addition of 2 parts of each of the non staining chemical antiozonants from the first series. Thus the effect of combining each antiozonant with each of the various wax combinations can be seen. Figure 6 and Figure 7 show clearly how much the addition of 2 parts of chemical antiozonant improved the ozone resistance of the SBS compound beyond the improvement achieved

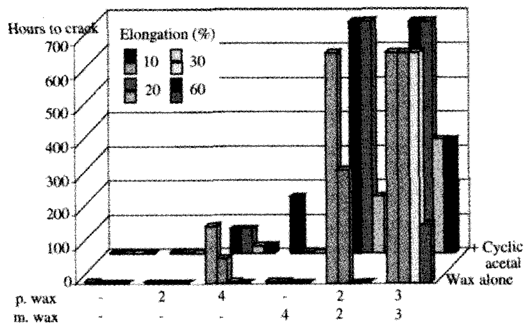

Fig. 6. Wax and cyclic acetal.

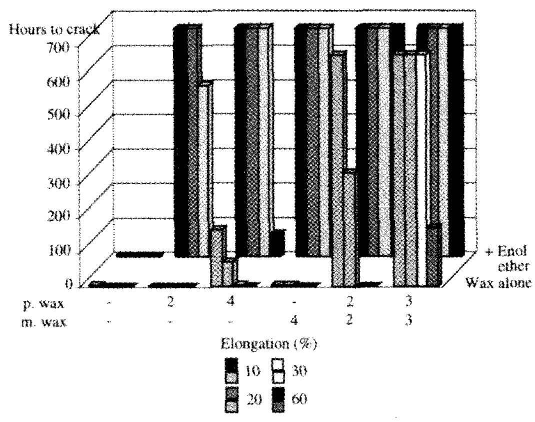

Fig. 7. Wax and enol ether.

by the addition of wax. Clearly the enol ether (Figure 7) offers a bigger improvement in ozone protection than the acetal. The cyclic acetal improved protection in the compound with 4 parts of microcrystalline wax at 10% elongation.

Because the two non staining antiozonants do not protect SBS from ozone attack when used alone but protect for long periods when used in combination with either paraffin or microcrystalline wax, it is concluded that the wax is operating as a carrier to deliver the antiozonant to the surface.

The strongest or longest lasting effects are seen when microcrystalline wax is used in combination with the enol ether. Probably the slower migration of this wax serves to replenish supplies of the antiozonant at the rubber surface, where it is needed, over a longer period.

Even two parts of paraffin wax, which alone do not protect the rubber, give several weeks of ozone protection at up to 30% elongation when combined with the enol ether.

V. Conclusions

SBS thermoplastic rubbber is particularly sensitive to ozone attack. The addition of chemical antiozonants has little or no effect in protecting SBS against ozone. Paraffin wax offers some protection if 4 parts are added but inadequate protection at 2 parts. Microcrystalline wax on its own offers no protection under these conditions. When these two waxes are added in combination a protective effect is seen.

The ozone test conditions applied in this study are far more severe than the service conditions that rubber articles would normally meet. The best combinations of protective materials found here where several weeks total protection have been seen should provide several years of protection under normal conditions of use.

Particularly the enol ether (Vulkazon(r)AFD) with even small amounts of paraffin or microcrystalline wax protects SBS thermoplastic elastomer against ozone attack under these severe test conditions. This chemical additive, when combined with a carrier, which ensures that it is delivered to the rubber surface, is shown to have a powerful protective effect.

References

1. C. R. Wilder, (1988), in Handbook of Elastomers (edited by Bhowmick, A. K.), Marcel Dekker Inc., New York., p. 319.
2. T. Thorstad, P. F. McNally, R. Delme, A. Leclerc, (April 1981) Butadiene-Styrene Thermoplastic Rubbers.. Brochure from Phillips Petroleum Company.
3. W. Xianglong, Improvement in the Ozone Resistance of SBS by the Addition of EPDM, Int. Rubber Conference, Gothenburg, Sweden, June 3-6 (1986).
4. L. L. Best, and R. C. W. Moakes, *Trans. I. R. I.*, **27**, No. 2 (1951).
5. N. G. Harmsworth, C. A. Moakes, *Kaut. Gummi Kunst.*, **49**, 597-606 (1996).
6. Unpublished work.