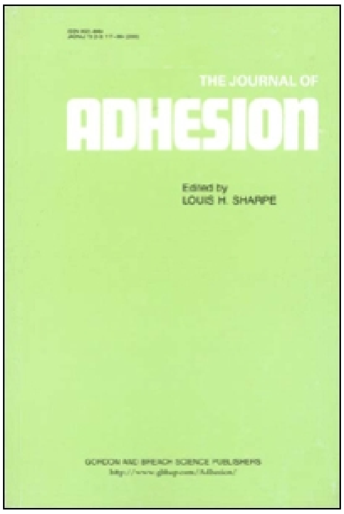

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New Pretreatment for Elastomers to Enhance Adhesion

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New Pretreatment for Elastomers to Enhance Adhesion

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The effects of various chemical pretreatments on the surface chemistry and adhesion performance of an additive-free styrene-butadiene block copolymer and an additive-free ethylene-propylene elastomer have been studied. Most of the powerful oxidising agents that are effective with hydrocarbon plastics were ineffective in enhancing the adhesion to elastomers despite causing major changes to their surface chemistries. The poor adhesion was attributed to the existence of weak boundary layers. Chlorinated agents were also examined and a new pretreatment for elastomers containing carbon-carbon double bonds has been identified. It was found that a mildly acidified dilute aqueous suspension of Chloramine-T was very effective at enhancing the adhesion performance of styrene butadiene copolymers.

Keywords: Elastomers; Solvent-free pretreatments; Aqueous Chloramine-T; Styrene-butadiene block copolymers (SBS); Surface analysis; X-ray photoelectron spectroscopy (XPS); Static secondary ion mass spectrometry (SSIMSC)

INTRODUCTION

There are many applications which require bonding of rubber to other substrates. In many cases this may be achieved by carrying out the bonding process during vulcanisation. However, this is not always

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Address correspondence to D. M. Brewis, Institute of Surface Science and Technology, Loughborough University, Loughborough LE11 3TU, UK. E-mail: d.m.brewis@lboro.ac.uk possible and the bonding process may have to be carried out after vulcanisation or, in the case of thermoplastic rubbers, on the fully formulated material after moulding. To achieve satisfactory bonds with both vulcanised elastomers and thermoplastic rubbers it is frequently necessary to pretreat the rubber prior to bonding. Some of the more important pretreatments for polymers are summarised in Table 1.

Pretreatments for plastics are often not suitable for elastomers and *vice versa*. Thus corona, flame, and plasma treatments are effective with most plastics but are not normally used with elastomers. On the other hand, trichloroisocyanuric acid and sodium hypochlorite are effective with many elastomers but not with plastics. Pretreatments may be subdivided into two broad categories; namely, those based on physical methods such as solvent or detergent cleaning or surface abrasion and those involving chemical attack on the surface. Whereas the former mainly act by removing cohesively weak material from the polymer surface, the latter may also remove or solubilise such low molecular material by, for example, oxidation but also act by introducing chemical groups into the polymer surface that can then interact more effectively with the adhesive than in the case of the unmodified elastomer. This is of particular importance in the pretreatment of hydrocarbon-based elastomers, such as styrene-butadiene block copolymers (SBS) and ethylene-propylene-dimer terpolymers (EPDM), which have relatively low surface energies and do not interact readily with most adhesives. Similar considerations apply to the pretreatment of hydrocarbon-based plastics such as polyethylene (PE) and polypropylene (PP), which have been studied far more extensively than the corresponding elastomers largely because the former contain fewer additives. For example, Chew *et al.* [1] showed that

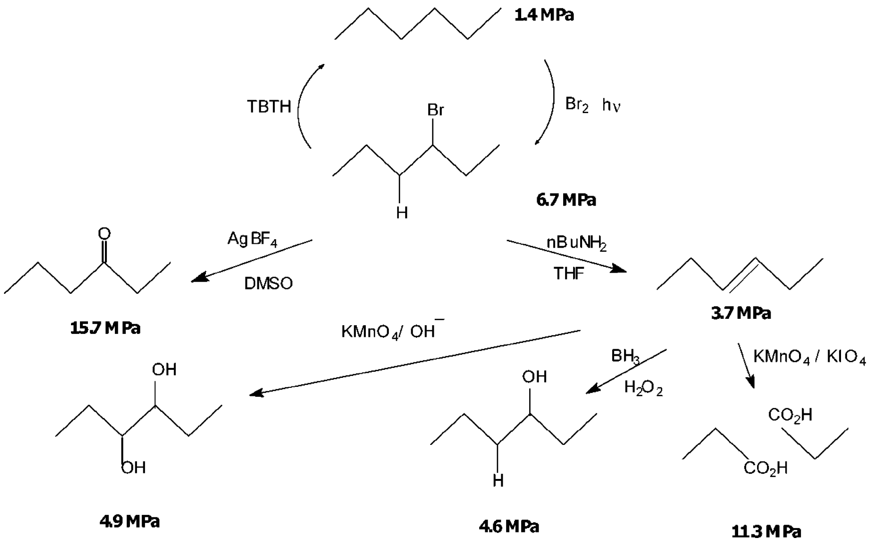
TABLE 1 Methods Available for the Pretreatment of Plastics and/or Elastomers

Plastics	Elastomers
Abrasion	Abrasion
Solvent cleaning	Solvent cleaning
Corona*	Conc. sulphuric acid*
Flame*	Trichloroisocyanuric acid*
Plasma*	Halogen gases*
Reactive gases,* e.g. fluorine/inert gas mixtures	Acidified sodium hypochlorite*
Specific reagents* e.g. sodium in liquid ammonia	UV irradiation*
UV irradiation*	

*Treatments resulting in chemical reactions with the surface regions.

the introduction of several discrete functional groups into the surface of LDPE resulted in a very large increase in the adhesion of this polymer in lap shear tests using an epoxy adhesive as shown in Scheme 1.

The pretreatments of elastomers, with particular emphasis on the chemical changes involved, have been reviewed by Brewis [2]. Most of the work reported involved the pretreatment of fully formulated rubbers or vulcanised materials. There appear to be very few effective pretreatments for rubbers with only a small amount of unsaturation, such as EPDM, whereas highly unsaturated rubbers, such as styrene-butadiene rubber (SBR) and SBS, require treatment with solvent-borne chlorinating agents such as trichloroisocyanuric acid (TCICA) or with relatively hazardous acidified sodium hypochlorite solution. The presence of numerous additives renders analysis of the surface changes induced by the pretreatments very difficult. The present study was undertaken with the aim of investigating the surface chemical changes produced by various solvent-free or aqueous chemical pretreatments of additive-free SBS and EPDM rubbers. Particular emphasis has been placed on the use of an aqueous suspension of acidified Chloramine-T to pretreat elastomers. This agent has been previously used to treat elastomers when applied from organic solvents but, to the authors' knowledge, has not been applied from an aqueous medium.



SCHEME 1 Effect of various functional groups on the adhesion of LDPE.

EXPERIMENTAL

The rubbers used were additive-free SBS, Kraton® Type D-1102, kindly supplied by Shell Chemicals (Chester, UK), and additive-free EPDM, Nordel® Type IP4725, kindly supplied by Du Pont (Londonderry, UK). The elastomers were pressed at 140°C into sheets 0.1 to 0.5 mm thick. Initial adhesion tests were performed on single lap shear joints prepared by bonding the elastomer films between two solvent-degreased, grit-blasted, aluminium strips (2 × 20 × 60 mm) with a 10 mm overlap using Araldite® 2011, supplied by Huntsman, (Duxford, UK). This adhesive is based on a formulated bisphenol A epoxy resin hardened with a formulated polyaminoamide preparation. The assembled joints were cured for 12 h at room temperature followed by a further 1 h at 60°C. The assembled joints were pulled apart at a rate of 6 mm per min using a Hounsfield Type H 20K-W tensometer (Redhill, Surrey, UK). Peel tests were performed on fully-compounded SBS, kindly supplied by SATRA, Kettering, UK, and moulded into test strips 3 × 20 × 150 mm. The adhesive used was supplied by Bostik UK (Stafford, UK) and consists of a two-part polyurethane-based aqueous suspension of Aquagrip® 626 mixed just prior to use with 6% (wt/wt) Fixadur® 66 Blue. The adhesive was applied to the first 100 mm of the test strip by means of a spatula and allowed to air dry at room temperature overnight. The test pieces were activated in an oven at 82°C for 2–3 min and pressed together by a hand roller while still hot and left to cool to room temperature. Peel tests were carried out on a Lloyds Instruments Type 10000 tensometer (East Farham, UK) at a test speed of 100 mm min^{-1}. Surface analysis was performed using a VG ESCALAB Mk1 XPS spectrometer (VG Instruments, Hastings, UK) using an Al Kα x-ray source. Scanning electron microscopy was carried out on a Cambridge Instruments Stereoscan® 360 electron microscope. Time of flight secondary ion mass spectrometry (ToFSIMS) was carried out using a Physical Electronics Instruments 7200 spectrometer (Ismaning, Germany) using a Cs^+ ion source.

The chemical pretreatments were carried out by immersing the elastomer samples in the appropriate solutions for the specified times and at the temperatures as described below:

For treatment with Fenton's reagent the sample was placed in a solution of ferrous chloride, 0.4 g in 120 ml of water. 100 volume ($\sim$30%) hydrogen peroxide, 20 ml, was added slowly at a rate corresponding to the overall treatment time. Treatment with Chloramine-T was performed by immersing the rubber in a stirred suspension of the N-chloro-p-toluenesulphonamide prepared by addition of 10%

sulphuric acid, 50 ml, to a solution of Chloramine-T, 1 g in 50 ml of water. The oxidation with acid dichromate was performed using a solution of potassium dichromate, 7 g in water, 12 ml, and sulphuric acid, 82.5 ml. A solution of silver(II) nitrate was generated by the electrochemical oxidation of a solution of silver(I) nitrate in dilute nitric acid as described elsewhere [3]. The SATREAT treatment was carried out by applying a 2% solution of TCICA in ethyl acetate by brush. The samples were then left for 20 min and excess reagent removed by wiping with ethanol. Deposits of manganese dioxide after the permanganate treatments (see Tables of a and b) were removed by reduction with a dilute solution of sodium metabisulphite and excess sulphonamide was removed by rinsing the Chloramine-T treated samples with dilute (5%) sodium hydroxide solution.

Irradiation with ultraviolet (UV) light was performed using either two 11 W Germicidal lamps 22 W total output (Philips, Croydon, Surrey, UK) or a single 400 W mercury cadmium halide lamp (UV Light Technology Ltd Type UV-F400, Birmingham, UK). Both of these lamps emit most of their radiation at ~250 nm. In some experiments benzophenone was used as sensitiser, as first suggested by Bragole [4], by immersing the elastomers in a 1% solution of the ketone sensitiser in either ethanol or diethyl ether prior to irradiation.

RESULTS AND DISCUSSION

Treatments of Additive-free Elastomers with Various Oxidising Agents

It is well established that the treatment of hydrocarbon-based polymers such as PP and PE with powerful oxidising agents such as aqueous potassium permanganate, solutions of potassium dichromate in sulphuric acid or dilute acidic solutions of silver(II) nitrate results in the introduction of oxygen-containing functional groups into the polymer surface. This is accompanied by a large increase in the bondability of these polymers even for relatively low oxygen concentrations of the order of 3–4 atom percent [3, 5]. Exposure of SBS and EPDM to these oxidising agents also resulted in the introduction of substantial amounts of oxygen into the surface of these elastomers as shown in Table 2.

The results presented in Table 2 suggest that most of the oxidising agents known to be effective for the pretreatment of hydrocarbon plastics yield similar, if not higher, levels of oxygen when used with elastomers. A series of alternative oxidising agents that were considered to offer potentially more cost effective pretreatments were also investigated (Table 3). Two of these reagents, Oxone® (potassium

TABLE 2 Surface Composition After Treatment of Elastomers with Strong Aqueous Oxidising Agents

		Surface composition (atom%)				
Treatment	Elastomer/time	C	O	S	K	Cr
1% $KMnO_4$ (H+) 70°C	SBS 1 m	94.4	5.6			
1% $KMnO_4$ (H+) 70°C	EPDM 1 m	95.4	4.6			
1% $KMnO_4$ (alk)	SBS 1 m	94.5	5.5			
1% $KMnO_4$ (alk)	EPDM 1 m	98.0	2.0			
1% $KMnO_4$ (neutral)	SBS 5 m	96.2	3.8			
1% $KMnO_4$ (neutral)	EPDM 5 m	97.7	2.3			
$K_2Cr_2O_7$ H^+ 70°C	SBS 1 m	78.0	19.9	1.48	0.3	0.32
$K_2Cr_2O_7$ H^+ 70°C	EPDM 1 m	92.8	7.2			
Ag(II) H^+	SBS 5 m	76.7	22.3			
Ag(II) H^+	EPDM	91.1	8.9			

All experiments were carried out at room temperature unless indicated otherwise

monoperoxysulphate compound) and hydrogen peroxide in the presence of tungstic acid, were expected to react specifically with the alkene moieties, whereas Fenton's reagent, which involves the formation of hydroxyl radicals, was expected to be effective with both SBS and EPDM. As shown in Table 3, the results obtained are broadly in line with these expectations.

According to the literature [6] irradiation of hydrocarbon polymers with UV light in the presence of benzophenone as sensitiser results in enhanced adhesion of paint to such surfaces. As can be seen from Table 4, irradiation of SBS and EPDM with low intensity (22 W) short wavelength (approximately 250 nm) UV-C light for extended periods of time results in the uptake of substantial amounts of oxygen in the case of SBS but considerably less oxygen is introduced into the surface of

TABLE 3 XPS Surface Composition of Elastomers Treated with Various Alternative Oxidizing Agents

			Surface composition (atom%)			
Reagent	Conditions	Elastometer/time	C	O	Cl	Other
Fenton's	20°C	SBS 1 m	90.5	8.2		Fe 1.3
Fenton's	20°C	EPDM 5 m	92.5	6.7	0.4	Fe 0.4
20% Oxone®	5% H_2SO_4/90°C	SBS 1 m	91.5	7.7	0.8	
20% Oxone®	5% H_2SO_4/90°C	EPDM 1 m	97.9	2.1		
H_2O_2	WO_3/50°C	SBS 5 m	89.0	9.9		W 1.1
H_2O_2	WO_3/50°C	EPDM 5 m	97.0	3.0		

TABLE 4 XPS Data for the Surface Pretreatment of Elastomers by Exposure to Low Intensity (22 W) UV Light in the Presence and Absence of Benzophenone as Sensitiser

		Surface composition (atom%)	
Treatment	Elastomer/time	C	O
UV 250 nm BP* Et_2O	SBS 15 m	90.6	9.4
UV 250 nm BP* Et_2O	SBS 15 h	71.6	28.4
UV 250 nm No BP	SBS 15 h	75.8	24.2
UV 250 nm BP* Et_2O	EPDM 15 m	97	3.0
UV 250 nm BP* Et_2O	EPDM 15 h	90.8	9.2
UV 250 nm No BP*	EPDM 15 h	98.2	1.8

*BP-benzophenone

EPDM. The amount of oxygen introduced into the surface of EPDM is increased significantly in the presence of benzophenone but its presence has little effect in the case of SBS. The long exposure times may lead to creation of low molecular weight material, but more intense light sources, which could have been effective at shorter irradiation times, were not available to the authors.

The results obtained so far are encouraging in that many of the treatments introduce appreciable amounts of oxygen into the surface of SBS and, to a lesser extent, into that of EPDM. A number of adhesion tests were, therefore, carried out on the treated elastomers in order to establish whether or not there is a relationship between the amount of oxygen introduced and the adhesion levels attained with the use of an epoxy adhesive. Examination of Tables 5 and 6 clearly show that no such simple relationship exists for the majority of treatments considered so far. It should be noted that no visible roughening of the surface had taken place for any of the aqueous halogenating agents used in this study. Changes in the microroughness may play a role but would require further study.

Although the UV treatments result in the introduction of substantial amounts of oxygen into the elastomer surface, only in the case of SBS irradiated with low intensity UV-C light was there a substantial increase in failure load. The same may be said for the other oxidative pretreatments, most of which introduce considerable amounts of oxygen but only in the case of acid dichromate is there a significant improvement in failure load. (See Table 6.)

It appears, therefore, that in terms of adhesion promotion, hot acid dichromate is the only effective oxidative pretreatment for SBS and to a lesser extent EPDM. The use of chromium(VI) is, however,

TABLE 5 Results of Lap Shear Adhesion Tests of Unformulated SBS and EPDM after Surface Pretreatment by Irradiation with 250 nm UV Light in the Presence of Benzophenone Using Either the 400 W or 22 W Light Source

		Surface composition (atom%)			Failure stress (MPa)	
Elastomer	Treatment	C	O	Other		Mode
SBS	None	99.0	1.0		1.0	I*
EPDM	None	100.0			2.2	I*
SBS	UV-400W 2 m	82.5	17.5		2.2	I*
EPDM	UV-400W 2 m	93.0	7.00		2.5	I*
SBS	UV-22W 20 h	72.3	27.7		8.1	I/C*
EPDM	UV-22W 20 h	72.0	27.1	N0.9	2.5	I*

*I-apparent interfacial, C-cohesive failure.

unacceptable on environmental grounds. An investigation into the use of aqueous and solvent-based chlorine donors was, therefore, undertaken.

Treatment of Additive-free Elastomers with Halogenating Agents

Acidified solutions of sodium hypochlorite [7] and solutions of trichloroisocyanuric acid (TCICA) in organic solvents [8] such as ethyl acetate

TABLE 6 Results of Lap Shear Adhesion Tests of Unformulated SBS and EPDM after Surface Pretreatment with Various Oxidising Agents

		XPS surface composition (atom%)			Failure stress (MPa)	
Elastomer	Treatment	C	O	Other		Mode
SBS	none	99.0	1.0		1.0	I*
EPDM	none	100			2.2	I*
SBS	KMnO4 1 m 60°C	66.7	25.5	Mn7.8	1.1	I*
EPDM	KMnO4 1 m 60°C	92.1	6.5	Mn1.4	2.8	I/C*
SBS	KMnO4 5 m 60°C $Na_2S_2O_5$	91.7	7.1	Na1.2	1.1	I*
EPDM	KMnO4 5 m 60°C $Na_2S_2O_5$	94.9	5.1		1.5	I*
SBS	Fenton's 1 m	90.5	8.2	Fe1.3	1.1	I*
EPDM	Fenton's 5 m	92.3	6.9	Cl0.4, Fe0.4	1.2	I*
SBS	$K_2Cr_2O_7H^+$ 1 m 70°C	78.0	19.9	S1.48, K0.3,Cr0.3	13.1	C*
EPDM	$K_2Cr_2O_7H^+$ 1 m 70°C	92.8	7.2		5.3	I*
SBS	Ag(II) H^+ 20 m 60°	84.4	11.6	Cl2.6, Ag1.4	2.1	I*

*I-apparent interfacial, C-cohesive failure.

were found to be effective for the pretreatment of SBR and SBS but not EPDM. Both of these pretreatments are far from ideal, in that the former releases free chlorine and the latter solvent vapours into the environment. Both reagents appear to introduce both oxygen and chlorine into the elastomer surface. In the case of the hypochlorite treatment this almost certainly involves electrophilic attack on the olefinic double bond [9]. The precise nature of the predominant electrophile depends on the pH of the hypochlorite solution [10]. The relatively weakly electrophilic hypochlorous acid predominates between pH 10 and 11. At lower pH the more powerful electrophile H_2OCl^+ and, under acidic conditions, molecular chlorine become the predominant species. It is, therefore, to be expected that the rate of reaction and the proportion of chlorine relative to oxygen introduced into the surface should increase as the pH of the hypochlorite solution is decreased. This is confirmed by the results presented in Table 7.

The mechanism of the TCICA process is more complex and, according to the literature, both addition and substitution take place [11]. In view of the proven effectiveness of these reagents alternative chlorinating agents were investigated that neither require organic solvents nor release toxic chlorine during use. We found that immersion of SBS in an aqueous suspension of a mixture N-chloro-p-toluenesulphonamides produced by acidifying a dilute aqueous solution of N-chloro-N-sodio-p-toluenesulphonamide (Chloramine-T) results in the introduction of considerable amounts of chlorine and oxygen into the surface of SBS. The reagent can be used over the temperature range of 20–80°C and short immersion times of 1 min are

TABLE 7 XPS Data for the Surface Pretreatment of SBS with Sodium Hypochlorite Solution (1% Active Chlorine) at Various pH and Room Temperature

		Surface composition (atom%)				
Treatment	Treatment time	C	O	Cl	Si	Br
NaOCl pH 10.2	5 m	87.2	7.5	1.7	3.2	0.4
NaOCl pH 10.2	10 m	87.7	4.9	2	5.4	
NaOCl pH 8	1 m	86.0	6.4	6.6		1.0
NaOCl pH 8	10 m	78.4	10.8	10.8		
NaOCl pH 4.2	1 m	79.3	6.0	14.7		
NaOCl pH 4.2	3 m	74.3	7.1	18.6		
NaOCl pH 4.2	10 m	72.9	7.7	19.4		

TABLE 8 Results of Lap Shear Adhesion Tests of Unformulated SBS after Surface Pretreatment with a) 2% TCICA in Ethyl Acetate, b) 1% Dispersions of Chloramine-T in Dilute Sulphuric Acid (CT), or c) Acidified Sodium Hypochlorite Solution (NaOCl)

Treatment	Surface composition (atom%) C	O	Cl	other	Failure stress MPa	Mode
2% TCICA	71.4	11.8	11.6	N5.2	4.3	I/C*
1% CT 1 m 80°C	78.0	9.6	9.0	N3.4	11.3	C*
1% CT 1 m 60°C	67.2	13.5	8.0	Br2.4, N3.7, S5.2	16.1	C*
1% CT 1 m RT	72	13	7.0	N3, S3, Na2	19.6	C*
1% CT 10 m RT	77.4	10.6	7.0	N2, S2, Br1	14.9	C*
NaOCl pH 4.2 1 m	72.1	11.5	16.4		12.3	C*
NaOCl pH 4.2 5 m	64.6	13.8	21.6		8.7	C*

*I-apparent interfacial, C-cohesive failure.

generally sufficient to produce significant increases in the adhesion of SBS when used with an epoxy adhesive. The surface composition and failure loads obtained for various chlorinating species are compared in Table 8.

The failure loads observed for the treatment of SBS with the chlorinating agents are generally much higher than those found for treatments with aqueous solutions of a number of strong oxidising agents. There is, again, no obvious relationship between the surface concentration of polar groups such as oxygen or chlorine (or their sum) and the observed failure loads. There is no satisfactory explanation for this behaviour at present. It is likely that the two major factors involved are the formation of weak boundary layers and the formation of specific functional groups capable of interacting with the adhesive, although other factors such as strengthening of the surface by, for example, crosslinking may also play an important part [8], particularly in the case of unvulcanised materials. Weak boundary layers are almost certainly involved when SBS is treated with potassium permanganate solution. A dense, brown layer rich in manganese compounds is readily visible with the naked eye and both sides of the failed joint exhibit this same colour. This suggests that failure must have occurred within this weak layer. A scanning electron micrograph of a permanganate-treated surface is shown in Figure 1. Weak boundary layers are the most likely explanation for the other cases where chemical modification has been substantial but the adhesion is poor.

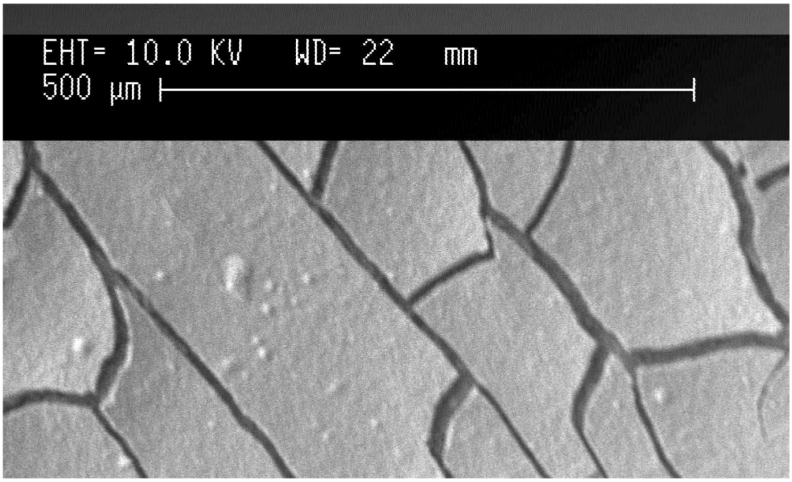


FIGURE 1 SEM of the surface of SBS after treatment with an acidic potassium permanganate solution for 2 h at 60°C.

The C1s spectrum of this surface shows the presence of carboxyl groups as evidenced by the smaller peak at approximately 289 eV. This implies chain scission brought about by attack of the oxidising agent on the olefinic double bonds. The resultant low-molecular-weight material intimately mixed with manganese dioxide is then the main constituent of the weak boundary layer observed in the adhesion tests. The C1s spectrum of this layer is shown in Figure 2.

It is a simple matter to completely remove this layer by immersing the sample in dilute sodium metabisulphite solution for a few minutes. XPS analysis of the decolourised surface reveals the complete absence of manganese compounds and only a small amount (1–4 atom%) of residual oxygen. It is probable that a similar explanation applies for the treatment of SBS with silver(II) ion and may also account for the lack of adhesion observed when either SBS or EPDM is exposed to 255 nm UV radiation where, again, the C1s spectrum shows evidence for the presence of carbonyl and carboxyl groups as shown in Figure 3. Further discussion of the high resolution spectra will be given in a later publication.

Treatment of SBS with chlorinating agents appears to involve mainly addition to, rather than oxidation of, the olefinic double bond. For example, prolonged exposure of SBS to the Chloramine-T reagent does introduce a considerable quantity of oxygen into the surface but there is little evidence for the formation of carboxyl groups in the corresponding C1s spectrum shown in Figure 4.

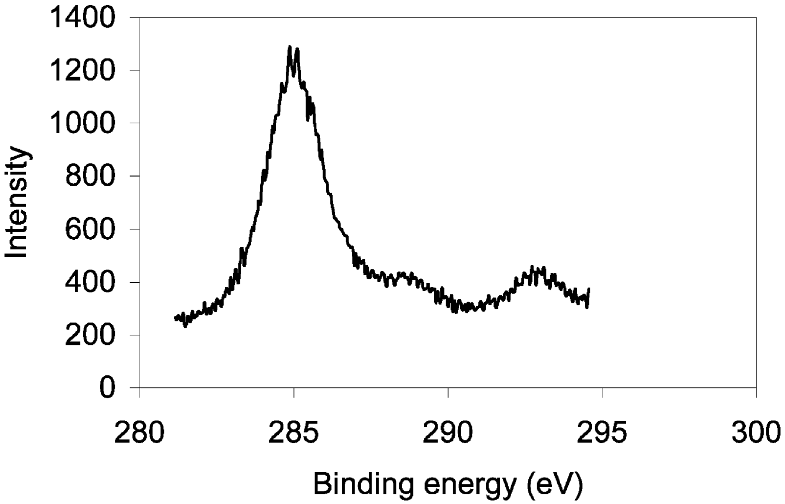


FIGURE 2 C1s spectrum of SBS treated with neutral potassium permanganate for 25 h at room temperature.

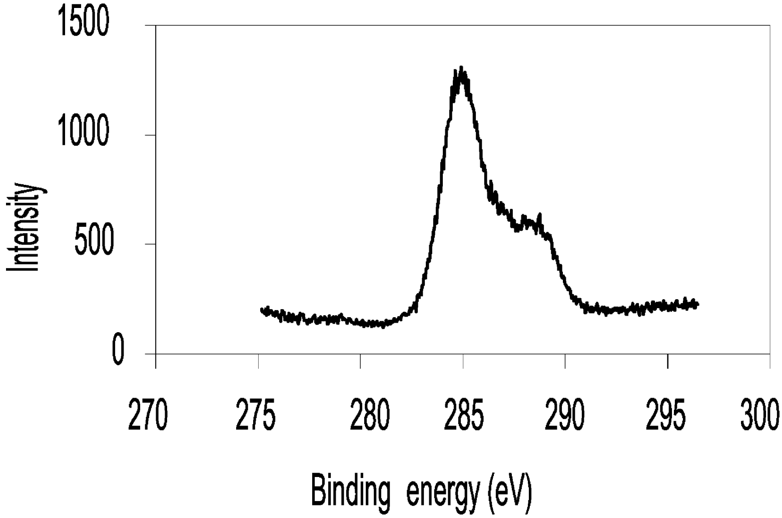


FIGURE 3 C1s spectrum of EPDM after irradiation with 250 nm UV radiation for 20 h.

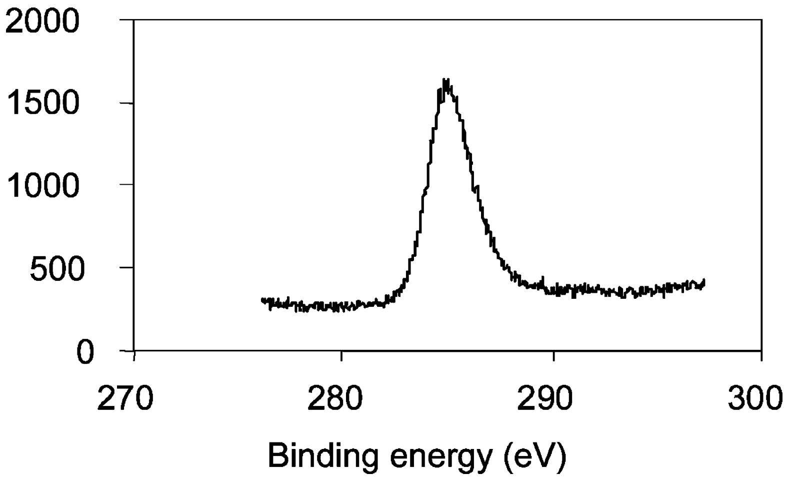


FIGURE 4 C1s spectrum of SBS after treatment with Chloramine-T for 105 min at room temperature.

Pretreatments of Fully Formulated Elastomers

As expected, the peel strengths obtained with untreated fully-formulated SBS and EPDM are poor. However, if fully formulated SBS is treated with Chloramine-T, large increases in peel strength occur and the locus of failure changes from apparent interfacial (with no treatment) to failure deep within the elastomers. The results in Table 9 indicate that the Chloramine-T treatment is superior to the existing commercial treatment for SBS, that is, trichloroisocyanuric acid (TCICA) in ethyl acetate. The new treatment obviously has the advantage of being solvent free.

As noted above, Chloramine-T was not effective with EPDM. Apart from chromic acid, none of the oxidising agents examined resulted in good adhesion with EPDM in a reasonable time. The most effective treatment examined in the present programme was a triphenylisocyanate applied from an organic solvent (Table 9).

The mode of operation of the isocyanate will be discussed in the Mechanisms section.

Mechanisms

Many studies of plastics such as polypropylene have shown that a wide variety of pretreatments that introduce oxygen-containing groups greatly improve the bondabilities of the plastics. For example, introducing about 4 atom % of oxygen into polypropylene by means of a flame

TABLE 9 Peel Tests of Fully Formulated SBS[a] + EPDM

Polymer	Treatment	Peel strength (N mm^{-1})
SBS	None	0
SBS	2% TCICA in ethyl acetate	4.5
SBS	1% CT, 5% H_2SO_4 10 m at rt	8.8
EPDM	None	0
EPDM	Isocyanate primer	2.6

[a] Bonded with Aquagrip 626® containing 6% Fixadure 66 Blue® dried at RT and activated at 80°C.

Test speed 100 mm min^{-1}.

treatment would typically increase joint strength by a factor of 5 or more. This is in marked contrast to the results in Table 2 which show that SBS and EPDM may be extensively functionalised by oxygen-containing groups without achieving significant improvements in adhesion. The only logical explanation for this observation is that a region of low cohesive strength exists on the pretreated elastomers and this cannot be absorbed by the adhesive. Chromic acid is a clear exception in that it does lead to large improvements in the bondability of SBS and EPDM. Presumably, in this case, cohesively weak layers are removed by chromic acid; this is in line with the known high etching rates of hot chromic acid. It appears that Chloramine-T is able to modify chemically and to solubilise any cohesively weak material or, alternatively, crosslink this material to long polymer chains. Chloramine-T can only be effective if carbon-carbon double bonds are present. Therefore, as expected, Chloramine T is ineffective with EPDM. The use of an isocyanate primer was moderately successful with EPDM. The most likely explanation is that the isocyanate diffuses into the EPDM while introducing polar groups into the polymer surface.

Secondary ion mass spectrometry (SIMS) has provided some useful pointers as to the mechanism of the Chloramine-T, chromic acid, and potassium permanganate treatments of SBS. The counts of hydrocarbon fragments (HC), fragments containing one oxygen atom (CHO), and those containing two oxygen atoms (CHO_2) in the mass range 29–85 Daltons account for a very high proportion of the total ion count for SBS treated with the above reagents. The normalised area ratios of the oxygen containing fragments relative to the total area of all of the hydrocarbon fragments in the above mass range are presented in Table 10. The data show that the Chloramine-T treatment results in the formation of a much larger proportion of oxygen-containing fragments than either the permanganate or the chromic acid treatment. The proportion of fragments containing two oxygen

TABLE 10 Normalized Positive Ion Counts of Oxygen-Containing Fragments Relative to the Total Hydrocarbon Intensities in the Mass Range 29–86 Daltons in the SSIMS Spectra of SBS Treated with Chloramine-T, Potassium Permanganate, or Chromic Acid

	Untreated	KMnO4 (BR)	KMnO4 (WH)	CT	CA
Total CHO	1	5.27	6.11	21.19	5.11
Total CHO2	1	1.46	3.90	10.29	2.24
Total O (CHO + CHO2)	1	4.98	5.94	20.34	4.89

atoms is somewhat greater for the permanganate treatment (after removal of inorganic matter) compared with the dichromate treatment. Because such fragments are most likely formed by chain scission, it may be inferred that the extent of chain scission in the case of the chromic acid treatment is less than that obtained for the permanganate treatment. This could be caused by extensive crosslinking or cyclisation initiated by electrophilic attack of, for example, an acidic species on the double bonds, resulting in sulphonation of the elastomer. This is supported by the presence of peaks at 64 and 48 Daltons in the negative ion spectrum of chromic acid treated SBS characteristic of SO_2 and SO. Negative ion peaks at 45 Daltons due to HCO_2^- are most abundant in the potassium permanganate treated samples by a factor of 12 compared with the CT and CA treated samples. Removal of manganese oxides with sodium bisulphite lowers their relative intensity by a factor of 6. This is in agreement with the XPS data and provides further evidence for extensive chain scission in the permanganate treatment. The relatively low molar mass carboxylic acids obtained in this way are retained by the manganese oxides to form the weak boundary layer mentioned earlier. Removal of the oxides with aqueous sodium bisulphite releases the acids, which enter the aqueous phase, thereby lowering the surface concentration of oxygen.

Chloramine-T is fully dissociated in aqueous solution as shown in Equation (1) of Scheme 2. Upon acidification a white precipitate is formed, consisting of a mixture of p-toluene sulphonamide ($TosNH_2$) and N,N-dichloro-p-toluene sulphonamide, also known as Dichloramine-T ($TosNCl_2$), plus other products, as shown in Scheme 2 [12]. Possible oxidising or chlorinating species present in acidic Chloramine-T solution are $TosNC1^-$, TosNHCl, $TosNCl_2$, HOCl, and $TosNH_2Cl^+$.

It is suggested that the attacking species is Dichloramine-T ($TosNCl_2$) produced in reaction 3. This species is likely to act as a powerful electrophile which is, moreover, likely to be soluble to some

$$\mathrm{TosNClNa} \rightleftharpoons \mathrm{TosNCl^-} + \mathrm{Na^+} \quad (1)$$

$$\mathrm{TosNCl^-} + \mathrm{H^+} \rightleftharpoons \mathrm{TosNHCl} \quad (2)$$

$$2\mathrm{TosNHCl} \rightleftharpoons \mathrm{TosNCl_2} + \mathrm{TosNH_2} \quad (3)$$

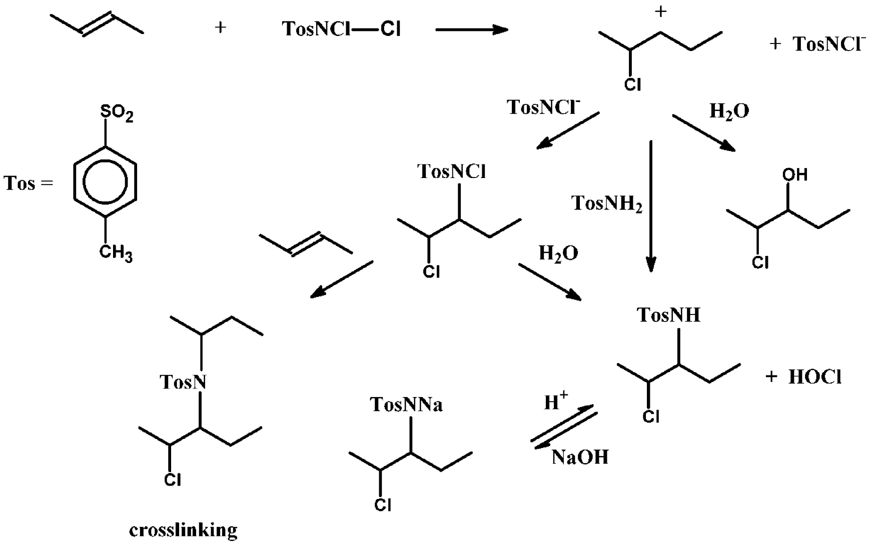
$$\mathrm{TosNHCl} + \mathrm{H^+} \rightleftharpoons \mathrm{TosNH_2Cl^+} \quad (4)$$

$$\mathrm{TosNHCl} + \mathrm{HO_2} \rightleftharpoons \mathrm{TosNH_2} + \mathrm{HOCl} \quad (5)$$

SCHEME 2 Reactions of Chloramine-T in acidic solution [12].

extent in the elastomer and capable of introducing chlorine as well as sulphur and nitrogen into the elastomer; in addition, it can initiate crosslinking as shown in the proposed Scheme 3.

This mechanism is supported by the XPS and SSIMS data that show the presence of chlorine, nitrogen, and sulphur as well as sodium.



SCHEME 3 Reaction of Chloramine-T with SBS under acidic conditions.

CONCLUSIONS

In conclusion, it appears that none of the oxidising agents which have been used successfully for the treatment of hydrocarbon-based plastics are effective for EPDM and SBS with the exception of acid dichromate, which does bring about a useful improvement in adhesion to these elastomers. In practically all cases, substantial amounts of oxygen-containing functional groups are introduced, which is one of the characteristic features of the successful pretreatments of hydrocarbon-based plastics. The poor adhesion is due to the formation of cohesively weak oxidation products which form a weak boundary layer on the elastomer surface. In the case of SBS this is probably due to the ease of cleavage of the olefinic double bond. Reagents that add to the double bond or possibly substitute at allylic or benzylic positions provide effective pretreatments for SBS. Acidified Chloramine-T, a reagent that has not been used before as an oxychlorinating agent of polymers in an aqueous medium, as far as we are aware, is particularly effective as a pretreatment for SBS. The reagent appears to be environmentally acceptable and is applied from a dilute aqueous dispersion at room temperatures. Independent tests carried out at SATRA confirm the effectiveness of this reagent for the pretreatment of fully formulated SBS and SBR [13].

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