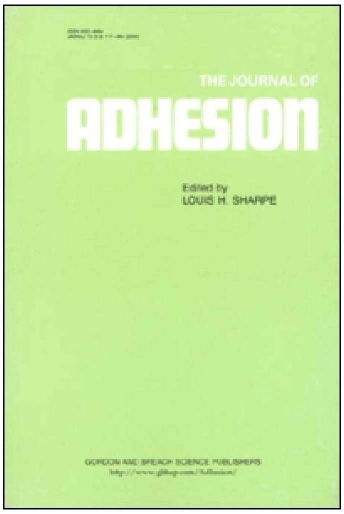


The Journal of Adhesion
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713453635

Surface Modification of Elastomers for Bonding

D. Oldfield[a]; T. E. F. Symes[a]
[a] Department of Defence, Materials Research Laboratories, Ascot Vale, Victoria, Australia

To cite this Article Oldfield, D. and Symes, T. E. F.(1983) 'Surface Modification of Elastomers for Bonding', The Journal of Adhesion, 16: 2, 77 — 95

To link to this Article: DOI: 10.1080/00218468308074907

URL: http://dx.doi.org/10.1080/00218468308074907

J. Adhesion, 1983, Vol. 16, pp. 77–96
0021-8464/83/1602-0077 $18.50/0

Printed in the United Kingdom

Surface Modification of Elastomers for Bonding†

D. OLDFIELD and T. E. F. SYMES

Materials Research Laboratories, Department of Defence, P.O. Box 50, Ascot Vale, Victoria 3032, Australia

(*Received March 24, 1983; in final form May 10, 1983*)

This paper describes detailed studies on the chlorination of vulcanized elastomer surfaces by an organic chlorine donor and the bonds obtained between such surfaces using a polyamide-cured epoxy adhesive. The bonds produced with a range of commercially important elastomers were found to retain their strength during extended seawater immersion better than those produced using the earlier surface treatments. The practical parameters of this technique have been investigated to establish the requirements for reliable and effective bonding. The chlorinated elastomer surfaces have been examined and explanations are offered for the changes observed.

INTRODUCTION

Despite the advances made in the use of adhesively bonded structures in the aerospace industry, problems are still encountered in bonding elastomeric components in underwater sonar equipment. In particular there is a need to be able to bond vulcanized elastomeric components, such as sonar windows or specialized antifouling elastomers, to steel or other surfaces which may then be continuously submerged in seawater for several years. This paper describes investigations of factors which influence the bondability of vulcanized elastomer surfaces. The problems of producing durable elastomer to metal bonds will be dealt with in a subsequent publication.

Vulcanized elastomers generally require some form of surface treat-

---

† This paper was presented at the Thirteenth Australian Polymer Symposium held at the Australian National University, Canberra, Australia, August 1982.

ment before they can be successfully adhesively bonded. Recommended surface treatments[1] range from simple solvent cleaning, through mechanical abrasion to chemical reactions such as chlorination or cyclisation. The ease with which elastomers may be bonded increases with their polarity; non-polar elastomers such as butyl rubber still present difficult bonding problems.

Chlorination was recognized as an effective way to improve adhesion to elastomers, but the chlorinating solutions had disadvantages for factory use where release of chlorine into the atmosphere was not desirable.[2] To overcome these objections the concept of using an organic chlorine donor was developed[3] specifically to aid the bonding of elastomeric shoe soles to uppers made from leather and other materials. This procedure has been further developed[4] for a range of different shoe soling materials bonded with polyurethane or polychloroprene adhesives.

This paper shows that the use of an organic chlorinating agent, trichloroisocyanuric acid (TCICA) dissolved in ethyl acetate, to treat vulcanized elastomer surfaces produced strong and durable bonds with a polyamide cured epoxy adhesive. The durability of bonded specimens was assessed by measuring their peel strengths after immersion in seawater at 60°C for up to 12 months. Those specimens produced from elastomers treated with TCICA retained their peel strength better than any other surface treatment investigated.

The practical parameters of the technique, such as optimum chlorinating agent concentration and time allowable between treatment and bonding have been assessed so that good adhesive bonding can be routinely achieved. The surfaces of treated vulcanizates have been investigated in detail by several techniques to explain the large increase in bond strength produced by this chlorination procedure.

EXPERIMENTAL

Materials

The materials and suppliers used in this investigation are detailed in Table I, however other materials comparable in chemical composition and activity should be equally satisfactory. The formulations of the vulcanizates, which are typical of good quality commercial elastomer stocks, are shown in Table II.

TABLE I
Materials

Material	Trade name	Supplier
Antioxidant A	Permanax B	Vulnax International Ltd.
Antioxidant B	Santoflex 13	Monsanto Aust. Ltd.
Antioxidant C	Flectol H	Monsanto Aust. Ltd.
Aromatic oil	Mobisol 30	Mobil Aust. Pty. Ltd.
Bromobutyl rubber	Bromobutyl X2	Polysar Ltd.
Butyl rubber	Butyl 301	Polysar Ltd.
Carbon black	Acarb FEF	Australian Carbon Black Pty. Ltd.
Coumarone resin	Polymer 300	Union Carbide Aust. Ltd.
N-cyclohexyl-2-benzothiazyl sulphenamide (CBS)	Vulcafor CBS	Vulnax International Ltd.
Diphenyl guanine (DPG)	DPG	Monsanto Aust. Ltd.
Epoxy resin	Epirez 828	Epirez Australia Pty. Ltd.
Dibenzthiazyl disulphide (MBTS)	Vulcafor MBTS	Vulnax International Ltd.
Natural rubber	SMR 20	Malaysian Rubber Bureau
Naphthenic oil	P857	Shell Chemical Pty. Ltd.
Nitrile rubber	Krynac 3450	Polysar Ltd.
Polyamide hardener	Versamid 125	A. C. Hatrick Pty. Ltd.
Styrene-butadiene rubber	Austrapol 9705	Australian Synthetic Rubber Pty. Ltd.
Tetramethyl thiuram disulphide (TMTD)	Thiurad	Monsanto Aust. Ltd.
Trichloroisocyanuric acid (TCICA)	Trichlor	Brooke Barmer Chemicals Pty. Ltd.
Zinc diethyl dithiocarbamate (ZDC)	Vulcafor ZDEC	Vulnax International Ltd.

Vulcanizate preparation

Compounding was performed in a small internal mixer and curing agents were added on a laboratory two roll mill (200 mm × 75 mm). The curing characteristics of each formulation were determined on a Monsanto LSD Rheometer and test sheets were moulded in a single cavity mould (250 mm × 250 mm × 6.35 mm) in an electrically heated press at 160°C for the time taken to reach 90 percent of the maximum torque in the Rheometer.

Surface treatment

Solvent wipe the vulcanized elastomer surface was wiped with a paper tissue moistened in toluene then allowed to dry for at least 24 h before bonding.

Abrasion the elastomer was mechanically abraded by an open

TABLE II
Elastomer formulations

Ingredients	Formulation number						
parts by weight[a]	1	2	3	4	5	6[b]	7
Butyl rubber							100.00
Natural rubber	100.00					100.00	
Bromobutyl rubber		100.00					
Nitrile rubber			100.00		100.00		
Styrene-butadiene rubber				100.00			
Stearic acid	2.50	1.00	1.00	2.00	1.00	2.00	1.00
Zinc oxide	3.00	3.00	3.00	3.00	3.00	3.00	5.00
Carbon black	70.00	70.00	70.00	70.00	70.00	50.00	70.00
Antioxidant A	1.00	1.00	1.00				
Antioxidant B				2.00		2.00	
Antioxidant C					1.00		
Aromatic oil				5.00		10.00	
Coumarone resin			10.00		10.00		
Naphthenic oil							20.00
Wax						2.00	
TMTD	0.30	0.50	2.00	0.25	1.00	0.30	1.90
CBS	1.20	3.00	1.00		2.00	1.20	
Sulphur	0.50	0.30	0.30	1.50	0.30	1.25	1.00
DPG	0.50						
MBTS				1.25			
ZDC							0.60

[a] See Table I for full identification.

[b] Commercial natural rubber compound believed to be made to this formulation or similar, carbon black used was probably N300 series.

structure aluminium oxide grinding wheel rotating at 1,440 rpm. Surface debris was subsequently removed from the elastomer by wiping with a toluene moistened paper tissue.

Aqueous chlorination the elastomer was immersed for 5 min in a solution consisting of concentrated hydrochloric acid (2 ml), sodium hypochlorite solution (4 ml, 15% w/v) and water (100 ml). The elastomer was then rinsed well in distilled water and allowed to dry.

Cyclisation the vulcanizate was immersed in concentrated sulphuric acid for one to two minutes then rinsed in distilled water and allowed to dry. The surface was flexed before bonding to induce the formation of fine cracks in the hardened surface layer.

Organic chlorination the vulcanizate surface was wiped successively with clean paper tissues moistened in ethyl acetate, trichloroisocyanuric acid (TCICA) in ethyl acetate and finally acetone. The surface was allowed to dry for at least 4 h before bonding. The discarded paper tissues soaked in TCICA solution were dampened with water before disposal to avoid spontaneous combustion as TCICA is a strong oxidizing agent.

Peel specimens

A bead of adhesive, mixed from epoxy resin and polyamide hardener in the ratio from 1 : 0.5 to 1 : 2 parts by weight, as noted in the results section, was spread down the centre of the treated surface of an elastomer strip (100 mm × 25 mm × 6.35 mm). A second similar strip was placed on top with masking tape at one end between the surfaces to leave a non-bonded area (25 mm × 25 mm). A rectangular steel bar weighing about 500 g was placed on each specimen which was then allowed to stand at 20°C for at least 96 h before testing. Bond thickness was typically about 0.125 mm and was assumed to be the same for all specimens.

Specimens immersed in seawater were stored in screw topped glass jars in an oven at 60°C.

Peel strength

The bonded specimens were trimmed to 19 mm wide with a parallel-bladed cutter and the mean force required to peel the two adherends at an angle of 180° was measured on an Instron 1026 tensile testing machine using a crosshead speed of 50 mm/min.

Internal reflectance spectroscopy (IRS)

IRS was performed on a Perkin Elmer 580B computer assisted infrared spectrophotometer using a germanium crystal.

Contact angle

Contact angles were measured in a NRL goniometer manufactured by Rame-Hart Inc., Mountain Lakes, N.J.

Scanning electron microscopy

Treated surfaces were examined in a Cambridge Stereoscan Mk II scanning electron microscope fitted with a Link 860 energy dispersive X-ray analysis system.

X-ray fluorescence

A Philips PW1400 sequential X-ray spectrometer with a chromium X-ray tube was used. The sample discs (24 mm diameter) were placed into the evacuated spectrometer with the chlorinated surfaces facing the X-ray beam. The emitted X-rays were separated by a pentaerythritol crystal and the intensities of chlorine K_α and background radiation were measured for 10 seconds by a gas flow proportional counter. A sample of polychloroprene was measured with each group of samples as a reference.

RESULTS AND DISCUSSION

Adhesive composition

The overall programme was intended to elucidate the influence of various elastomer surface treatments on bond strength and durability. Bonds to flexible substrates, such as elastomers, fail most readily when subjected to peeling forces. Thus if systems could be developed which would produce good peel strength, as measured by 180° peel tests with two flexible elastomeric adherends, then those results should be generally applicable to the bonding of elastomers either to rigid or flexible substrates. The properties seen as important in the adhesive included good adhesion to the elastomer, flexibility and resistance to water immersion. A polyamide cured epoxy resin was chosen as being most likely to meet these requirements.

Preliminary work indicated that for natural rubber adherends (formulation no. 1) the peel strength increased as the ratio of epoxy resin to polyamide changed from 1:0.5 to 1:1 and then decreased as more polyamide was added. The adhesive composition for the specimens immersed in seawater for 12 months was equal parts by weight of epoxy resin and polyamide. Subsequent work with a different natural rubber (formulation no. 6) indicated an optimum epoxy to polyamide ratio of 1:0.8 whilst for a nitrile rubber (formulation no. 5) the optimum appeared to be 1:0.6. The adhesive composition used in each case is identified in the Tables, and each column of results was derived from specimens made with the same batch of adhesive at the same time. The results within any column may therefore be compared to see the effect of a particular variable on peel strength. The criterion of good bonding adopted throughout was that failure should occur in the elastomer adherends rather than adhesive failure at the adhesive interface.

Provided this criterion was met variations in measured peel strength to achieve this result between specimens made at different times, with different batches of adhesive and by different operators, were not considered of great importance. Those surface treatments which resulted in cohesive elastomer failure, or rubber tear as it is sometimes known, were judged to be the most satisfactory.

The peel strengths of nominally identical specimens were found to vary by up to 30 percent from the mean value even where rubber tear resulted. Cutts[5] recently noted the large scatter in peel strengths of rubber to metal bonds and remarked that the ratio of standard deviation to mean was typically up to 20 percent but that values greater than 50 percent were not uncommon. He described the typical saw tooth form of the peeling force trace which was also observed in the present work. Estimation of the mean peeling force from such a trace is not easy.

The type of elastomer surface treatment or even the concentration of TCICA in the chlorinating solution was observed to produce different failure patterns in the torn rubber surfaces and a range of peel strengths. These patterns ranged from fine-grained shallow tearing in the rubber close to the adhesive bond line to a deep chunky appearance where large amounts of rubber were torn from one of the adherends. A similar series of failure patterns was reported by Cutts.[5]

Comparison of surface treatments

The peel strengths for specimens of four different elastomers with five surface treatments and bonded with adhesive consisting of epoxy resin and polyamide hardener in the ratio of 1 : 1 by weight are presented in Table III. The initial peel strengths, measured after allowing the adhesive to cure for at least 96 h at 20°C, show that the performance of the different surface treatments depends on the elastomer chosen. For natural rubber (formulation no. 1) the two chlorination treatments were the only ones which resulted in good bonding leading to rubber tear. These results were maintained during immersion of the specimens in seawater at 60°C for up to 12 months. Throughout the trial the organic chlorine donor (TCICA) gave higher peel strengths than the aqueous chlorination procedure.

Bromobutyl rubber is considered to be difficult to bond in the vulcanized state and this is borne out by the low peel strengths obtained for all surface treatments except TCICA. However TCICA treatment resulted in bonds which produced failure in the elastomer both initially and after up to 12 months in seawater at 60°C.

TABLE III
Peel strengths

		Peel strength, kN/m[e]			
Elastomer[a] type and formulation no.	Surface[b] treatment	Original	After immersion in seawater at 60°C for 1 month	After immersion in seawater at 60°C for 6 months	After immersion in seawater at 60°C for 12 months
Natural rubber (1)	A	0.1[c]			
	B	1[c]			
	C	10[d]	10[d]	14[d]	12[d]
	D	1[c]			
	E	18[d]	12[d]	16[d]	16[d]
Bromobutyl rubber (2)	A	1[c]			
	B	1[c]			
	C	3[c]			
	D	0.1[c]			
	E	20[d]	12[d]	15[d]	11[d]
Nitrile rubber (3)	A	8.0[d]	5[c]	3[c]	4[c]
	B	5[c]			
	C	8[d]	10[d]	14[d]	15[d]
	D	18[d]	6[d]	3[c]	5[c]
	E	21[d]	14[d]	16[d]	11[d]
Styrene-butadiene rubber (4)	A	0.2[c]			
	B	1[c]			
	C	12[d]	8[d]	8[d]	6[d]
	D	12[d]	10[d]	8[d]	6[d]
	E	11[d]	9[d]	6[d]	6[d]

[a] See Table II, (formulation number).

[b] See experimental; A solvent-wipe, B abrasion, C aqueous chlorination, D cyclisation, E organic chlorination, 3.0% TCICA.

[c] Rubber/adhesive failure.

[d] Cohesive failure in rubber.

[e] Adhesive used epoxy resin: polyamide hardener 1 : 1 w/w. Mean of 3 specimens in each case.

Styrene-butadiene rubber proved to be easier to bond than natural rubber with both chlorination methods and cyclisation giving bonds of similar strength. The relative performance of the three systems did not show much change during 12 months immersion.

Nitrile rubber proved to be the easiest rubber to bond, in accordance with practical experience. The highest initial peel strength was shown by the TCICA treatment and this was maintained for up to 6 months immersion but after 12 months the aqueous chlorination treatment appeared stronger. However, even in this case, TCICA treatment was still producing cohesive elastomer failure on peeling after 12 months seawater immersion.

Table III clearly shows that TCICA treatment produced strong and durable bonds with all four elastomers and the aqueous chlorination treatment would be placed second best overall. It should be emphasized, however, that TCICA was the only successful surface treatment for bromobutyl rubber. The TCICA treatment is considered to be the most convenient and reliable chemical surface treatment of those studied and its general applicability indicated that the process should be investigated in more detail to establish the practical limits.

Effect of chlorinating agent concentration

Peel strengths of specimens prepared from five elastomers after surface treatment with solutions containing different concentrations of TCICA are given in Table IV. The standard pre-treatment with ethyl acetate and post-treatment with acetone were applied as described in the experimental section. For each elastomer the peel strength increased with increasing TCICA concentration up to the point at which cohesive failure in the elastomer occurred. Surface treatment with more concen-

TABLE IV
Effect of TCICA concentration on peel strength

TCICA concentration in chlorinating solution %	Peel strength, kN/m[a]				
	Natural[b] rubber (6)	Bromobutyl[c] rubber (2)	Nitrile[d] rubber (5)	Styrene-[c] butadiene rubber (4)	Butyl[b] rubber (7)
0	0.2[e]	3[e]	3[e]	0.2[e]	0.5[e]
0.1	0.2[e]	2[e]	3[e]	0.3[e]	–
0.2	2[e]	3[e]	2[e]	0.4[e]	2[e]
0.4	7[e]	6[f]	2[e]	1[e]	1[e]
0.8	10[f]	6[f]	10[e]	1[e]	7[f]
1.6	12[f]	5[f]	12[f]	2[e]	13[f]
3.0	10[f]	5[f]	14[f]	5[f]	9[f]
5.0	11[f]	6[f]	12[f]	7[f]	11[f]

[a] Formulations as in Table II (formulation number) results mean of 3 specimens.
[b] Adhesive used, epoxy resin : polyamide hardener 1 : 1.
[c] Adhesive used, epoxy resin : polyamide hardener 1 : 0.8.
[d] Adhesive used, epoxy resin : polyamide hardener 1 : 0.6.
[e] Rubber/adhesive failure.
[f] Cohesive failure.

trated solutions maintained cohesive failure with no change or only slight decreases in measured peel strengths. For practical applications on any of the five elastomers studied TCICA concentration of between 1.6% and 3% appeared most satisfactory. Some evidence was obtained that TCICA solutions stored for 3 months after using part of the amount in the brown bottle lost up to half their chlorinating ability. TCICA liberates chlorine on contact with water and therefore the solutions should be prepared as required to avoid slow loss of activity from reaction with atmospheric moisture.

Post chlorination treatment

When TCICA reacts as a chlorinating agent, cyanuric or isocyanuric acid is produced as a by-product[6] which may be deposited on the elastomer surface where it could contaminate the bonding surface. Peel specimens were prepared from natural rubber strips (formulation no. 6) which had been wiped with ethyl acetate followed by 3.0% TCICA solution then either no further treatment or an acetone wipe or a 3-hour soak in distilled water or a wipe with a 25% solution of ethanol in water. The strongest bonds, for natural rubber, were obtained after wiping the treated surface with a 25% ethanol solution. This is not surprising as cyanuric and isocyanuric acids are soluble in water and ethanol respectively.[7] Ethanol may help the solution to wet the treated surface better than water alone. The specimens which were immersed in seawater for up to 12 months were prepared from elastomers wiped with acetone after chlorination, therefore although this treatment appeared to be less satisfactory than 25% ethanol the bonds produced proved in practice to have good durability.

Safe elapsed time

In a practical situation it is important to know how long the treated surface may be stored under clean conditions between treatment and bonding. For natural rubber (formulation no. 6) there were no significant changes in peel strengths for specimens which had been stored for between 4 hours and 4 weeks in clean polyethylene bags before bonding but the results after 6 weeks storage were much lower. The natural rubber vulcanizate used for this series was a good quality commercial conveyor belt cover stock formulation such as may be encountered in a practical application. The material contained wax and antidegradents which, whilst quite normal in commercial practice, could reduce the adhesion to the vulcanizate by blooming to the surface. The reduction in peel strength noted after 6 weeks storage was probably due to bloom and could be avoided if the surface was re-wiped with a suitable solvent before bonding.

Internal reflectance spectroscopy by infra red (IRS)

The surfaces of a natural rubber vulcanizate (formulation no. 6) treated with increasing concentrations of chlorinating agent were examined by IRS. Natural rubber was selected due to the chemical homogeneity of the polymer, being more than 98% cis-polyisoprene. The most prominent changes in the surfaces on chlorination were decreases in the absorbance at 900 cm^{-1} due to the cis double bond and the appearance of a new absorbance at 835 cm^{-1} ascribed to a pendant double bond. These changes are shown in Table V where it appears that for the surface treated with 0.8% TCICA about 50% of the unsaturation was in the form of pendant double bonds. This was the minimum TCICA concentration which gave good bonding of natural rubber (Table IV).

The chlorination of butyl rubber (a copolymer of isobutylene and up to about 3% isoprene) has been reported to result in chlorinated isoprene

TABLE V
Internal reflectance spectroscopy by infra red[a]

Chlorinating solution used, TCICA concentration, %	Relative[b] absorbance due to cis double bond at 900 cm^{-1}
0	100
0.1	97
0.2	84
0.4	57
0.8	51
1.6	38
3.0	28
5.0	21

[a] Natural rubber formulation number (6) vulcanizate.

[b] Calculation of relative absorbance for cis double bond = $\dfrac{A_1}{A_1 + A_2} \times 100\%$

where A_1 = absorbance at 900 cm^{-1}
A_2 = absorbance at 835 cm^{-1}

units containing tertiary and secondary allylic chlorides.[8] One of the secondary allylic chlorides proposed contained a pendant double bond and a similar reaction may lead to the changes observed above. The bromination of butyl rubber has been said to result in up to 90% substitution in the allylic position to give a product with a pendant double bond.[9]

Chlorinated layer thickness

Specimens of a natural rubber vulcanizate (formulation no. 6) treated with different concentrations of TCICA were examined in a scanning electron microscope. The treated surfaces appeared identical to an untreated surface with no cracking or crazing, in contrast to an earlier report[2] where cracks were observed. The chlorine contents of cross sections of the specimens were examined by an energy dispersive X-ray analyser fitted to the microscope. It was found that chlorine could be detected at different depths from the treated surfaces depending upon the TCICA concentration. The chlorine penetration for 0.4% TCICA was less than 1μm, that for 0.8% TCICA was about 2μm and the depths for 1.6%, 3.0% and 5.0% TCICA were between 4μm and 5μm.

X-ray fluorescence (XRF)

Treated elastomer surfaces were examined by XRF with the results shown in Table VI. A polychloroprene vulcanizate containing about 22% chlorine registered approximately 200,000 counts per second under the same conditions. Based on the composition of the polychloroprene vulcanizate and the energy of the incident X-rays it can be calculated, according to Beer's Law, that the outer 5 μm of the material contributed about 10% of the observed chlorine signal. This suggests that a layer of polychloroprene 5μm thick should record about 20,000 counts/s. The chlorine contents of the treated surfaces which were shown above to be less than 5 μm thick were estimated in this way. The results, with the chlorine emission of the untreated surface subtracted, are shown in Table VII. The high chlorine signal for untreated styrene-butadiene rubber is undoubtedly due to residues from the sodium chloride coagulant used in the manufacture of this polymer.

The chlorine content of each vulcanizate assuming one atom of chlorine has been added for each double bond in the polymer has been calculated and included in Table VII.

TABLE VI
Chlorine content by X-ray fluorescence

	Chlorine emission, counts/sec[a]				
Chlorinating solution used, TCICA concentration, %	Natural rubber (6)	Bromobutyl rubber (2)	Nitrile rubber (5)	Styrene-butadiene rubber (4)	Butyl rubber (7)
0	260	240	750	2490	500
0.1	480	290	860	2620	–
0.2	2070	500	1140	2830	800
0.4	4120	530	1030	3280	510
0.8	6940	950	4700	5040	1190
1.6	13340	1540	10280	8130	1210
3.0	15480	1510	15740	17180	2700
5.0	33080	1240	19080	17030	2540

Polychloroprene standard = 200 000 counts/sec.

[a] Formulations as in Table II.

TABLE VII
Estimated chlorine content of surface

	Chlorine content of elastomer, % w/w[a]				
Chlorinating solution used, TCICA concentration, %	Natural rubber (6)	Bromobutyl rubber (2)	Nitrile rubber (5)	Styrene-butadiene rubber (4)	Butyl rubber (7)
0	0	0	0	0	0
0.1	0.2	0	0.1	0.2	–
0.2	2.0	0.2	0.5	0.4	0.3
0.4	4.2	0.3[b]	0.3	0.9	0
0.8	7.3[b]	0.7	4.4	2.8	0.8[b]
1.6	14.4	1.4	10.5[b]	6.2	0.8
3.0	16.7	1.4	16.5	16.1[b]	2.4
5.0	36.1	1.1	20.2	16.0	2.2
	23[c]	0.5[c]	19[c]	22[c]	0.5[c]

[a] Based on chlorine emission from polychloroprene, formulations as in Table II.

[b] Minimum TCICA concentration which produced cohesive elastomer failure (Table IV).

[c] Calculated chlorine content in vulcanizate for addition of 1 chlorine atom/double bond, % w/w.

Contact angles

The advancing contact angles of water, formamide and epoxy resin on chlorinated vulcanized elastomer surfaces are presented in Tables VIII and IX. These surfaces were similar to those used earlier for the peel

TABLE VIII
Contact angles on natural rubber[a]

Chlorinating solution used, TCICA concentration, %	Advancing contact angle, degrees			Work of adhesion[b] mJ/m^2
	Water	Formamide	Epoxy resin	
0	120	101	87	45
0.2	117	94	90	42
0.4	113	89	76	60
0.8	92	67	38	76
1.6	91	64	34	80
3.0	85	59	27	80
5.0	75	57	26	70

[a] Formulation no. 6.

[b] Calculated by the harmonic mean method[12] using advancing contact angles for water and formamide together with surface parameters for epoxy adhesive.[13]

TABLE IX
Contact angles

Elastomer	Chlorinating solution used, TCICA concentration, %	Advancing contact angle, degrees		
		Water	Epoxy resin	Formamide
Natural rubber (6)	0	120	87	101
	3.0	85	27	59
Bromobutyl rubber (2)	0	108	80	
	3.0	87	66	
Nitrile rubber (5)	0	88	82	
	3.0	74	40	
Styrene-butadiene rubber (4)	0	112	75	
	3.0	86	45	
cis-polyisoprene[a]		106		96
Chlorinated[a] cis-polyisoprene		86		68

[a] From reference 11.

specimens. In all cases the contact angle of a given liquid was lower on chlorinated than on untreated surfaces of the same elastomer, thus the wettability of the surface was improved by chlorination.

Table VIII illustrates the effects of increasing TCICA concentration on the contact angles of a natural rubber vulcanizate (formulation no. 6). Large decreases in the contact angles of water, formamide or epoxy resin were observed for the surface treated with 0.8% TCICA as compared with weaker solutions. Higher concentrations had a smaller effect as illustrated in Figure 1 where the cosine of the advancing contact angle cos θ_A, is plotted against TCICA concentration.

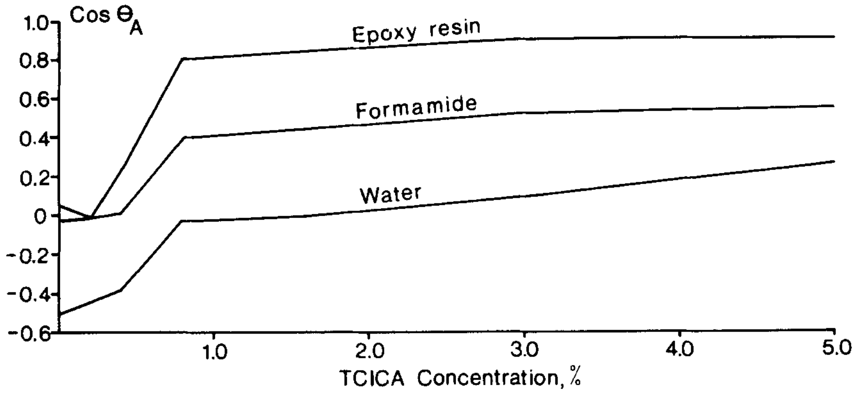


FIGURE 1 Plot of cosine of advancing contact angle, cos θ_A, vs. TCICA concentration.

Zisman[10] demonstrated the relationship between the molecular structure of a surface and the contact angles of liquids on that surface. The concept of the critical surface tension of a solid equivalent to the surface tension of that liquid which would just spread on the solid surface was developed. Substitution of chlorine for hydrogen in polymer surfaces produced large increases in critical surface tension, poly(vinyl chloride) had a value of 39 mN/m compared to 31 mN/m for polyethylene. Additional chlorine substitution had a much smaller effect than that of the first atom in each repeat unit. The results shown in Figure 1 are consistent with this earlier work. The changes of cos θ_A with increasing TCICA concentration may indicate that the natural rubber surface treated with 0.8% TCICA consisted of one chlorine atom to each isoprene unit.

Contact angles on four vulcanizates are given in Table IX together with values reported[11] on purified unvulcanized films of cis-polyisoprene and chlorinated cis-polyisoprene. The contact angles on the untreated natural rubber vulcanizate were higher than those on the purified cis-polyisoprene film, probably due to the presence of wax, stearic acid and other compounding ingredients in the vulcanizate. Water and formamide were reported[11] to have contact angles of 86° and 68° respectively on chlorinated cis-polyisoprene. Table VIII shows that the natural rubber surfaces which had similar contact angles were those treated with 3% TCICA for water and 0.8% TCICA for formamide.

The work of adhesion of an epoxy adhesive to the treated natural rubber surfaces was calculated by the harmonic mean method[12] using the parameters for the epoxy adhesive previously reported.[13] When the results shown Table VIII, are compared to the peel strengths of equivalent surfaces from Table IV, it appears that a work of adhesion greater than 70 mJ/m^2 is necessary to produce strong rubber tearing bonds with this particular vulcanizate. The actual values of work of adhesion should be regarded as tentative as the curing agent used in the present study differed from that reported earlier[13] which would probably affect the surface properties of the adhesive.

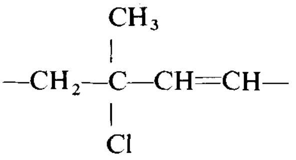
Salomon[14] found that the lap shear strength of joints with a variety of steel surface treatments and a common epoxy adhesive varied in the same direction as the cosine of the contact angle of the epoxy adhesive on the steel surface. The peel strengths of natural rubber specimens (from Table IV) can be compared with the values of cos θ_A for the epoxy resin in Figure 1. The peel strengths and cos θ_A both increased with increasing TCICA concentration thus improved wetting of the surface leads to higher peel strengths.

Chlorination by TCICA

TCICA is known to be both a chlorinating[6] and oxidizing[15] agent towards a range of organic compounds. Chlorination can proceed under both ionic and free radical conditions and highly coloured charge-transfer complexes were postulated[6] as intermediates in the chlorination of aromatic compounds such as aniline and phenol. Coloured products were observed when chlorinated elastomer surfaces were subsequently wiped with acetone and these were probably due to reaction with substituted para-phenylenediamine antidegradents in the vulcanizates. Allylic chlorination of cyclohexene by TCICA gave 3-chlorocyclohexane[16] and chlorination of phenyl allyl sulphides[17] took place at 5°C to give almost quantitative yields of the corresponding 1-thiophenoxy-3-chloroalkenes. TCICA can thus be seen to be an effective chlorinating agent under quite mild conditions.

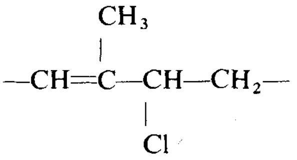
Chlorination of natural rubber in solution[18] produces a complex product containing up to 65% chlorine as a result of addition and substitution of chlorine, together with some cyclisation of the cis-polyisoprene. This suggests that by reaction with TCICA a complex surface may be produced if an excess of reagent is available.

In the chlorination of butyl rubber[8] three types of chlorinated isoprene units were produced (1, 2 and 3 below) in the proportions 1:2:2.



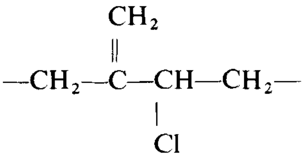
$$-CH_2-\underset{\underset{Cl}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH{=}CH- \qquad (1)$$

Tertiary allylic chloride



$$-CH{=}\overset{\overset{CH_3}{|}}{C}-\underset{\underset{Cl}{|}}{CH}-CH_2- \qquad (2)$$

Secondary allylic chloride



$$-CH_2-\overset{\overset{CH_2}{\|}}{C}-\underset{\underset{Cl}{|}}{CH}-CH_2- \qquad (3)$$

Secondary allylic chloride

Structure (3) is consistent with the changes observed by IRS of chlorinated natural rubber surfaces (Table V) where increasing concentrations of TCICA produced increasing absorbance due to the presence of a pendant double bond and decreased absorbance attributable to the original cis double bond.

The available evidence does not allow any firm conclusions to be drawn about the types of chemical structures formed during the chlorination of vulcanized elastomer surfaces by TCICA. The information supplied by contact angles, IRS and XRF would not be expected to be in exact agreement due to the different depths of material examined by the three techniques. Thus whilst contact angles are primarily influenced by the monomolecular surface layer,[10] IRS was affected by a layer of up to 0.7 μm deep, whereas XRF observed the whole thickness of the chlorinated layer.

The surface of a natural rubber vulcanizate treated with 5% TCICA was observed to develop fine cracks when cut with a sharp knife. This suggested that hardening of the surface due to cyclisation had occurred but this did not appear to have had any significant effect on peel strength (Table IV).

The increases in peel strength due to chlorination by TCICA can be correlated with the improved wetting of the surface by the epoxy resin. The advantages of this treatment over aqueous chlorination or cyclisation by concentrated sulphuric acid are convenience and reliability of application together with general effectiveness for a range of commercially important elastomers.

CONCLUSIONS

Chlorination of vulcanized elastomer surfaces by an organic chlorine donor, trichloroisocyanuric acid, has proved to be a simple and effective method of improving the bondability with an epoxy adhesive. The technique can be used for commercially important elastomers such as natural rubber, butadiene copolymers and bromobutyl rubber. The chlorinated surfaces produced bonds which retained a large proportion of their original strength during immersion in seawater at an elevated temperature. The improved bond strengths produced by chlorination can be related to the increased wettability of the treated surfaces by the epoxy adhesive used.

Acknowledgements

Thanks are due to B. E. Woods and M. Troy for experimental assistance and to P. J. Jackson, R. Zugno and A. Camilleri for compounding, moulding and testing the elastomers. The assistance of R. G. Davidson for infra red spectrophotometry, I. G. McDonald and G. Cumming for XRF and V. Silva and S. D. Boyd for SEM is gratefully acknowledged.

References

1. E. M. Petrie, *Handbook of Plastics and Elastomers*, C. A. Harper, Ed. (McGraw-Hill, New York, 1975). Chap. 10, pp. 10–55.
2. D. Pettit and A. R. Carter, *J. Adhesion* **5**, 333 (1973).
3. The Shoe and Allied Trades Research Association Brit. Pat. 1295677 (1972).
4. The Shoe and Allied Trades Research Association U.S. Pat. 4110495 (1978).
5. E. Cutts, *Developments in Adhesives—2*, A. J. Kinloch, Ed. (Applied Science, London, 1981). Chap. 10.
6. E. C. Juenge, D. A. Beal and W. P. Duncan, *J. Org. Chem.* **35**, 719 (1970).
7. R. C. Weast, *Handbook of Chemistry and Physics*, 51st ed. (The Chemical Rubber Co., Cleveland, 1970), pp. C-253, C-347.
8. N. E. Odam, *J.I.R.I.* **5**, 140 (1971).
9. The Bromobutyl Handbook (Polysar Ltd, Sarnia) A-1.
10. W. Zisman, in *Contact Angle, Wettability and Adhesion*, F. M. Fowkes, Ed. (American Chemical Society, Washington, D.C., 1964). Chap. 1.
11. L-H. Lee, *J. Polym. Sci. A-2*, **5**, 1103 (1967).

12. S. Wu, *Polymer Interface and Adhesion* (Marcel Dekker, Inc., New York, 1982), p. 178.
13. R. A. Gledhill and A. J. Kinloch, *J. Adhesion* **6**, 315 (1974).
14. G. Salomon, in *Adhesion and Adhesives, Vol. 1*, R. Houwink and G. Salomon, Eds. (Elsevier, Amsterdam, 1965), p. 108.
15. E. C. Juenge, M. D. Corey and D. A. Beal, *Tetrahedron* **27**, 2671 (1971).
16. K. Ziegler *et al.*, *Justus Liebig's Ann. Chem.* **551**, 80 (1942).
17. A. J. Mura Jr., D. A. Bernett and T. Cohen, *Tetrahedron Lett.* 4433 (1975).
18. J. I. Cunneen and M. Porter, *Encyclopedia of Polymer Science and Technology*, H. S. Mark, Ed. (Interscience, New York, 1970), **12**, 304.