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The Interphase in Rubber-Metal Moulding: The Influence on Adhesion of Sulphur-Containing Emulsifier Residues in Nitrile Rubber*

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When compounds based on nitrile rubber (NBR) are vulcanised in a mould a complex interfacial layer is formed at the surface of the mould. The components of the layer include vulcanisation and processing aids as well as residues of the NBR manufacturing process. When the moulding is removed parting occurs within the inter-layer; its constituents exert a dominant effect on the adhesion.

Rubber-mould adhesion has been studied by measuring the mould sticking index with a TMS rheometer and investigating the surfaces formed by X-ray photoelectron spectroscopy. This paper is concerned with the effects of organic sulphonate or sulphate emulsifier residues, which are common constituents of the interphase.

The adhesion has been measured of rubber compounds prepared with differing concentrations of sulphonates or sulphates included, and by use of rubber coagulated from latices stabilised with different emulsifiers. The presence of these residues generally increases adhesion, probably because of strong adsorption of the polar sulphony groups on the surface of the mould steel, producing an interfacial layer which is not easily sheared. In some experiments a tendency was observed for the adhesion to fall off at high sulphony residue concentration; this could be associated with weakness in shear of thicker layers of these compounds.

KEY WORDS adhesion; coagulant residues; emulsifier residues; interfacial layer; interphase; mould release; nitrile rubber; sulphates; sulphonates; TMS rheometer; XPS; sulfates; sulfonates.

INTRODUCTION

In the most obvious engineering applications of the science of adhesion, a bond of high strength and durability is required. In contrast, the moulding of rubber provides an example where the requirements are for low adhesion of brief duration. From the manufacturer's point of view, consistency in the level of adhesion—consistent mould release behaviour—is important, particularly where the moulding oper-

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ation is automated. The study of factors which influence these low adhesion levels provides an interesting scientific challenge.

Commercial rubber is usually a complex, multi-component material. The base rubber polymer is compounded with a range of ingredients, depending on its intended use. These will include a cure system and usually stabilisers and a filler.¹ Even a simple commercial compound is likely to comprise more than half a dozen components. The compounded rubber is moulded to shape and heated to cure [crosslink] the material.

Mould release problems occur sporadically in the rubber processing industry. They are often associated with particular compounds and particular mouldings. High processing temperatures and parts of moulds where there are high shear rates in the flowing rubber are often involved. A widespread palliative is to apply a release agent to the mould surface. The vast number of such agents described in the patent literature is a demonstration that none is completely satisfactory. There are, moreover, mouldings where the use of a mould release agent is undesirable for fear of contaminating the surface of the moulding or of affecting its properties. Such considerations might be crucial in the context of mouldings for use in the food industry or in applications where good long-term fatigue characteristics were essential to human safety.

OBJECTIVES

This paper is concerned with the adhesion that occurs when compounds based on nitrile rubber (NBR)—an acrylonitrile butadiene copolymer—are vulcanised against the mould surface in the *absence* of a mould release agent. Considerable variation of adhesion can be observed, even with similar rubber compounds. This variation is associated with several separate factors, the chemical composition and surface characteristics of the mould steel, the formulation of the rubber compound and the nature of the base rubber polymer.^{2,3} None of these influences is, in principle, surprising as it is now well recognised that the “strength” of an adhesive joint is determined by the interaction of the properties of the adhesive, the substrate and the interfacial regions [interphase]. What is perhaps surprising is the variation in adhesion exhibited by ostensibly the *same* material moulded against the *same* mould steel.

Table I shows the mould sticking indices of four nitrile rubber (NBR) compounds moulded under similar conditions against a steel surface. The NBR specification is the same for all the compounds and all the compounds involved are based on the *same* formulation, yet the adhesion, measured by the mould sticking indices (*v. infra*), ranges from 80 to 153 kPa. Equivalent grades of polymer are used in all compounds, the only difference is the manufacturer of the base NBR.

What is the reason for these differences in adhesion between ostensibly similar surfaces? They are of evident practical interest, as differences in mould adhesion like these can occur inadvertently in normal manufacturing practice. This paper is one of a series in which investigations of the reasons for such variation in mould adhesion are reported.

TABLE I
Moulding of equivalent NBR compounds against Stavax-420 steel:
(i) mould sticking indices, (ii) mole percent of sulphur detected by XPS
at binding energies of 164 eV and 169 eV on steel surface,
(iii) weight percentage sulphur in the base rubber

Compound	N5	N1	N6	N2
Mould sticking index kPa	80	98	103	153
S 164 eV %	0.06	0.25	—	—
S 169 eV %	0.2	0.48	2.0	0.58
S in base NBR	0.22	0.21	0.45	0.20

EXPERIMENTAL APPROACH

The low levels of adhesion involved are not easily measured in the laboratory in a manner which realistically reproduces industrial moulding practice. We have made use of a TMS (Turner, Moore and Smith) rheometer.

The TMS rheometer consists of a transfer chamber above a cavity in which is located a biconical rotor, giving a cone and plate configuration.⁴ The rotor represents the mould surface. The uncured rubber is placed in the transfer chamber and then moulded against the stationary rotor surface where it is cured. The rotor is then started and the peak stress which occurs when the rotor breaks free of the moulded rubber is taken as the "mould sticking index"⁵ (*cf.* Table I). For reproducible results the rotor has to be conditioned in the rubber; full experimental details are given in the references cited.

The chemical nature of the surfaces formed on parting the rubber from the rotor has been extensively investigated by surface analysis, especially XPS.^{6,7} This shows that when the rubber is removed from the mould parting takes place in a complex interlayer—an *interphase*—in which residues from the polymerisation and cure reactions can be found. The composition of the interphase affects the level of mould adhesion, and depends upon the base polymer used and the rubber compound employed. The detailed nature and origins of the components of the interlayer are discussed elsewhere.^{2,6,7} Typical elements detected include metals, such as Zn, Ca, Na and Mg, oxygen and sulphur compounds giving signals from 2p electrons at binding energies of *ca.* 164 eV and 169 eV. Standard sources⁸ indicate that a binding energy of 164 eV is associated with sulphur bonded to carbon or hydrogen and that of 169 eV with sulphur bonded in an organic compound to oxygen. This paper is concerned with the origin of these sulphur compounds and their influence on mould adhesion.

EXPERIMENTAL DETAILS

Materials

Six different **nitrile rubber** (NBR) polymers were used. Polymer K contained 35% acrylonitrile and had a Mooney viscosity¹ of 34 (ML 1 + 4 min. at 100 deg C). Those

designated 1, 2, 5 and 6, which were obtained from different manufacturers, would normally be regarded by rubber processors as *equivalent* materials as their specifications [28% acrylonitrile; Mooney viscosity 50 (ML 1 + 4 min. at 100 deg C)] were the same. These polymers were commercially available materials. In addition, some work was done with a specially prepared NBR latex of polymer containing 34% acrylonitrile which is designated AB. The principal residual elements determined by conventional elemental analysis are shown in Table II.

TABLE II
Residual elements in NBR (p.p.m.)

Polymer	Na	K	Ca	Mg	S
1	99	#	570	6	2100
2	246	#	880	24	2000
5	25	#	55	700	2200
6	89	#	1465	7	4500
K	25	#	2470	<10	910
AB¶	14	9.6	1340	#	#
AB*	15	11.2	260	#	#
AB§	15	7.7	235	#	#

¶, *, §—different emulsifiers used, v. Table VII. # not analysed for

The two rubber **compounds** used are given in Table III. Different polymers were used in compound N: the polymer employed is indicated by referring to N2, N-AB etc. In some experiments additional emulsifiers were added to compound N1 before vulcanisation. No polymer other than K was used in compound K9. Two alloy **steels** were used: 080M40 (also designated EN8) and Stavax-420. Their compositions are given in Table IV.

Rheometer

Details of the use of the TMS rheometer for measuring adhesion were briefly described above. Full details can be found in Reference 5.

TABLE III
Rubber compounds used (parts by weight)

Compound	N	K9
Nitrile rubber	100	100
Carbon black	55	30
Zinc oxide	2.5	—
Stearic acid	1	—
DOP	25	—
Sulphur	0.25	—
TMTD	1.5	—
MBTS	1.5	—
Dicumyl peroxide	—	1

DOP—dioctyl phthalate (plasticiser);
TMTD—tetramethylthiuram disulphide;
MBTS—2,2'-dithiobisbenzothiazole

TABLE IV
Composition of the mould alloys (manufacturers' specifications: wt %, balance Fe)

	C	Mn	Cr	Si	V	S	P
S-420	0.38	0.5	13.6	0.8	0.3	—	—
EN8 (080M40)	0.4	0.6 to 1.0	—	0.05 to 0.35	—	0.06	0.06

Electron Spectrometer

A VG Escalab mk. II X-ray photoelectron spectrometer was used, operating at 12.5 kV and 440 mA with an anode producing Al K_{α} radiation.

As the TMS rotors were much too large to get into the spectrometer, a special rotor with removable inserts was used for this purpose. The surfaces were exposed just before insertion into the spectrometer.

RESULTS

Origin of the Sulphur Compounds

Elemental sulphur and organo-sulphur compounds are common constituents of rubber compounds. Metallic sulphides have been shown to be formed from them during some vulcanisation reactions.⁹ None of these sulphur atoms would be expected to give rise to 2p electrons of binding energies as high as 169 eV; this expectation was confirmed by analysis of model compounds, Table V.

TABLE V
Sulphur 2p binding energies (eV) of model compounds measured by XPS

TMTD*	MBTS*	Sulphur	ZnS	FeS	Al ₂ (SO ₄) ₃
163.45	163.55	165.7	165.9	167.2	171.2

*v. note to Table III

It is possible that some of these sulphur compounds could become oxidised during vulcanisation, giving rise to higher binding energy electrons, but this does not give a satisfactory explanation of the 169 eV signal because it is also observed with peroxide-cured formulations (which contain no added sulphur) and on the surface of the uncompounded rubber. Indeed, elemental analysis of the base rubbers shows that they often contain sulphur residues, v. Table I & II.

Nitrile rubber is produced by an emulsion polymerisation process.¹⁰ The monomer emulsion is stabilised with the use of surface active molecules such as carboxylic acids, but which may be organic sulphonates or sulphates. At the end of the polymerisation the latex is coagulated by addition of a coagulant, typically an acid, an inorganic salt of metals such as sodium, calcium or magnesium or combinations of both. The polymer is then washed and dried. Thus, NBRs derived from different plants, or even from different batches, may have emulsifier and coagulant residues which differ in nature and extent. These sulphony compounds give rise to the XPS signal at 169 eV.

Another possible source of sulphur in the material is an inorganic sulphate introduced as the counter-ion in a coagulant containing a cation such as aluminium. As the result given in Table V shows, inorganic sulphates give S_{2p} electrons with higher binding energies than those in question.

Residues and Adhesion

The relationship between the composition of the interlayer and the mould adhesion is complex. The particular cations present and the chain length of the fatty acid residues are among the factors which have an influence.^{7,11} The work reported in this paper concentrates on the effects of sulphur-containing emulsifier residues.

In order to study the effect of sulphonate and sulphate residues on adhesion a series of experiments was conducted where increasing amounts of typical residues were added to the rubber compound before cure. Table VI shows the effect of addition of sodium dodecyl benzene sulphonate [NaDBS] and the sodium salt of sulphated oleic acid to the NBR formulation N1 [Table III]. In both cases there is a progressive increase in adhesion to Stavax-420. In some other examples there was an indication that, after an initial increase, the mould sticking starts to fall at higher emulsifier concentrations. This has been observed for an EN8 alloy with the N1/NaDBS compound for which other results are given in Table VI, and also for EN8 with a simple peroxide cured NBR (compound K9, Table III) to which sodium lauryl sulphate had been added at concentrations of $\frac{1}{2}$, 1 and 1.5 phr.

TABLE VI
Effect of addition of emulsifier to NBR compound N1
on mould sticking index (kPa) to Stavax-420

Emulsifier phr	NaDBS*	NaSOI#
0.5	110	
1	120	90
1.5	122	
1.75		118
2	130	
3		148
4		157

phr—parts by wt. per hundred parts of rubber.

*sodium dodecyl benzene sulphonate

#sodium salt of sulphated oleic acid,
 $C_9H_{18}(OH)(SO_3Na)C_8H_{15}COONa$

Further indications of the association of sulphony emulsifiers with high mould sticking were obtained from complementary experiments starting with latices of a NBR which contained 34% acrylonitrile. Latices of the same NBR polymer [designated AB] were stabilised at a nominal level of 1 phr with three commercially plausible emulsifiers: "tallow acids," a naturally-occurring mixture of fatty acids [e.g. C16 to C18], and two sulphonates. The sulphonates were sodium dodecyl benzene sulphonate and " α -olefin sulphonate." The latter is obtained by sulphonation of an α -olefin petroleum fraction centred on C14.

The latices were coagulated with calcium chloride and washed. After drying, the

rubber was compounded according to formulation N [Table III], and the mould sticking indices measured. Considerable higher adhesion was associated with the two sulphonate emulsifiers than with the fatty acid emulsifier, Table VII.

TABLE VII
Effect of change of emulsifier on the adhesion of otherwise similar NBR compounds (compound N-AB) to Stavax-420

Emulsifier	Tallow acids ¶	NaDBS *	α -OS §
Mould sticking index kPa	44	80	60

¶ Mixture of fatty acids *e.g.* C16 to C18

* sodium dodecyl benzene sulphonate

§ α -olefin sulphonate

DISCUSSION

The adhesion of nitrile rubber to a mould is a complex phenomenon in which many factors play a part, the nature of the mould alloy and its surface condition, the formulation of the rubber compound and the residues in the base polymer. In this paper attention has been directed at just one of these factors, the organic sulphonate or sulphate emulsifier residues the presence of which in the interphase is shown by the XPS S_{2p} signal at around 169 eV binding energy.

It has been shown that the presence of these residues generally increases adhesion. It is possible to speculate that strong adsorption of the polar sulphony groups occurs on the surface of the mould steel. This produces an interfacial layer which, by contrast with that which *may* be formed from fatty acids residues,^{7,11} is not easily sheared. In some experiments a tendency was observed for the adhesion to fall off at high sulphony residue concentration: this could be associated with weakness in shear of thicker layers of these compounds.

CONCLUSIONS

During moulding of a NBR-based compound, a complex interfacial layer is formed at the steel surface. This interphase exerts a dominant effect on the adhesion of the rubber to the mould. When the moulding is removed parting occurs within this layer. The nature of the layer depends both upon the rubber compound and on the base polymer used. Coagulant and emulsifier residues in the polymer and zinc compounds from the cure reaction are among the components of this layer.

The adhesion of NBR to mould steels depends on the nature of the interlayer formed: coagulant cations and sulphonate and sulphate emulsifier residues tend to be associated with high adhesion, fatty acids and zinc compounds with low adhesion. The composition of the layer can, to some extent, be controlled by alterations to the compound formulation. The residues in the base polymer employed can, however, still exert an important effect.

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