

Direct Bonding of Natural Rubber to Nitrile Rubber

R.P. CAMPION*

Strong bonds can form between natural rubber (NR) and nitrile rubber compounds when held together during vulcanisation if the former is modified by the addition of liquid polybutene as a compatible extender. Successful bonding is also dependent on the vulcanisation systems employed.

It is suggested that the phenomenon be regarded as one of liquid-solid contact. A NR compound thus modified is sufficiently fluid to wet, under moulding pressure, a high-viscosity nitrile rubber surface (notionally a solid) before vulcanisation is well-established. As the NR compound possesses the lower surface tension (or energy), the system is thermodynamically favourable.

Regarding the vulcanisation systems, a fast-curing nitrile compound is required to maintain the 'notional solid' role. Bond strengths decrease progressively as the NR vulcanisation system is changed from conventional through semi-EV to EV; high strengths are apparently associated with the many polysulphidic crosslinks which form, for conventional systems, during early stages of vulcanisation. It may require the relatively long lengths of polysulphidic crosslinks to traverse the bond interface. An alternative suggestion is that bond formation arises from the maturation reactions of polysulphidic crosslinks near the interface.

Bonds were not affected by immersion in either sea water or ASTM No. 3 oil for thirty days at room temperature. The polybutene levels used did not reduce the NR's high tearing energy characteristics and reduced hardness and modulus by only 10%.

The direct bonding of natural rubber (NR) and oil-resistant rubber compounds could benefit the manufacture of oil-transporting hoses. Oil-resistant rubbers such as acrylonitrile-butadiene copolymer (NBR) tend to be deficient in fatigue and tear properties, and for this reason these hoses are constructed as composites with layers of other, more durable, rubbers (together with textile and steel wire plies as reinforcements) bonded outside an oil-resistant lining rubber. When NR is used in the outer region of the hose wall construction to utilise its good fatigue resistance, bondability or low water uptake properties, it is usual to build outwards from the liner with several intermediate compound layers, each successive layer (frequently a blend) being nearer to NR in compatibility. In this way, components at each interface are sufficiently

compatible to bond together and oil resistance decreases gradually outwards through the hose wall construction.

As hose manufacturing techniques improve through the use of one-piece extruded liners and better bonding to end-fittings, the chance of oil leakage through 'micro-corridors' in butt joints or wrapped interfaces is reduced. Natural rubber could be employed next to the liner, provided that good bonding between NR and NBR could be achieved; this is not normally possible because the two rubbers are incompatible. This paper describes a technique whereby NBR compounds can be bonded directly to NR-based compounds; the early stages of the bonding process are regarded as the wetting of one component by the other rather than as a mutual

*Malaysian Rubber Producers' Research Association, Tun Abdul Razak Laboratory, Brickendonbury, Hertford, United Kingdom

(Present address: Materials Engineering Research Laboratory, Tamworth Road, Hertford, United Kingdom)

interaction occurring for reasons of compatibility.

THEORY

Successful bonding under pressure between adjacent surfaces of two elastomers requires initial intimate interfacial contact (termed *Stage 1* of the bonding process). For good vulcanised inter-elastomer bonding, bonds similar to crosslinks must then form between the elastomers during vulcanisation (*Stage 2*). Bonding is normally achieved by using 'compatible' rubbers of sufficient tack for *Stage 1* to take place. Compatibility can be defined in terms of the solubility parameter δ i.e. the square root of the cohesive energy density¹⁻⁴. The requirement for tack is that polymer chain packing gives sufficient free volume, suitably distributed between chains, to allow two-way diffusion of chain portions across the interface into large enough holes⁵⁻⁸.

When two tacky rubbers which satisfy the conditions for compatibility are brought into contact by viscoelastic flow due to moulding pressure, spontaneous interdiffusion ensures that the contact is maintained (*Figure 1a*). In addition, the presence in the bulk of the second elastomer of diffused chain portions of the first elastomer will facilitate *Stage 2*: normal crosslinking reactions can link these portions with chains of the second elastomer. The high tack of NR, apparently related to its chain structural features⁸, makes it particularly suitable for bonding in this way to a similar rubber.

The question then arises as to when two elastomers are compatible or not. An estimation (*Appendix A*) of the thermodynamic requirements at equilibrium conditions for compatibility i.e. for a reasonable amount (say 0.1 mole %) of interdiffusion (molecular interfacial mixing) to occur between two polymers 1 and 2 of molecular mass $\sim 10^5$ at a pre-vulcanisation moulding temperature of 110°C is that

$$(\delta_1 - \delta_2) < ca. 0.25 \text{ cal}^{1/2}\text{cm}^{-3/2} \quad \dots 1^*$$

In reality, this value is probably an underestimate, especially when considering compounds of rubbers (*Appendices A and B*). For elastomer pairs which do not satisfy *Equation 1*, little interdiffusion can occur, and these elastomers can be termed incompatible. Measurements of δ obtained by solubility parameter spectroscopy^{2,9,10} for typical compounds of NR and NBR are $8.6 \text{ cal}^{1/2}\text{cm}^{-3/2}$ and $10.3 \text{ cal}^{1/2}\text{cm}^{-3/2}$ respectively, values well outside the limits imposed by *Equation 1*.

However, the unique material properties of polymers provide an alternative approach to the bonding of incompatible pairs by considering *Stage 1* as a liquid/solid wetting phenomenon rather than liquid/liquid mixing. Although the outline of the suggested approach given here is probably an oversimplification of the actual processes involved, it has led to successful bonding being achieved between compounds of NR and NBR.

The critical surface tension γ_c of a solid surface is an empirically-based term pioneered by Zisman¹¹. Only liquids with a surface tension $\gamma_l < \gamma_c$ will wet that solid i.e. spontaneously spread over its surface indicating that the solid/liquid inter-molecular forces are higher than the liquid/liquid forces. This phenomenon is well utilised in adhesives technology¹². It is proposed that, for two incompatible elastomers to make such contact, the elastomer of lower viscosity is termed a 'notional liquid' and that of higher viscosity a 'notional solid'; if the surface tension of the former is less than that of the latter, intimate contact by wetting is permitted thermodynamically.

As γ_l and γ_c are generally accepted as being similar for the same material¹³, tabulated values of the latter¹⁴ can be employed. In practice, these thermodynamic considerations are over-ruled in the short term by the high viscosity of the notional liquid compared with normal liquids: the time required to achieve wetting will be very long, even when favourable thermodynamic conditions are augmented by

*The units $\text{cal}^{1/2}\text{cm}^{-3/2}$ are equivalent to $(\text{MPa}/4.184)^{1/2}$ in the S.I. system.

FOR SUCCESSFUL BONDING

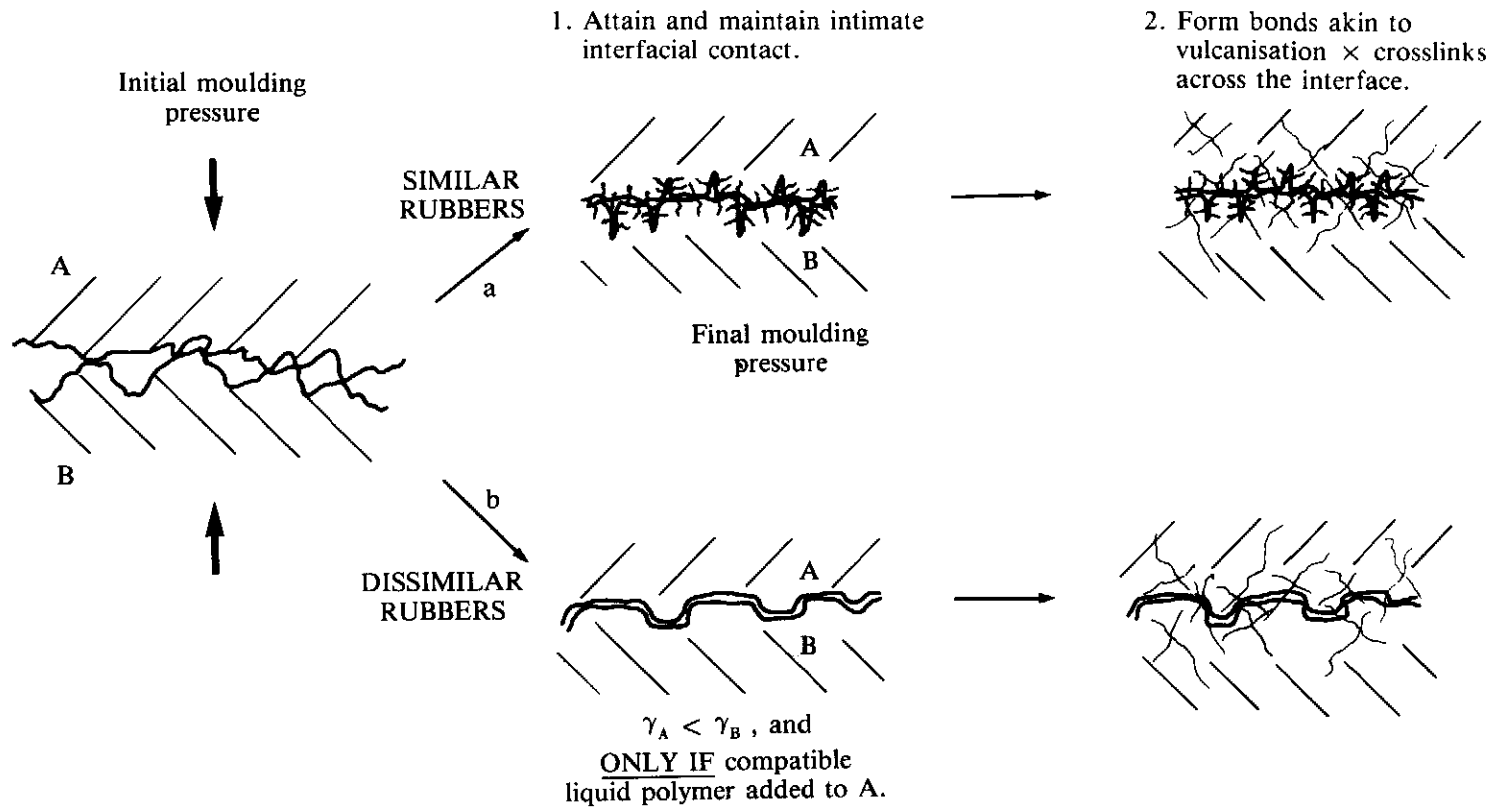


Figure 1. Schematic illustration of inter-elastomer bonding.

the considerable moulding pressures normally met during rubber processing. A reasonable means of overcoming the problem (*Figure 1b*) is by increasing the fluidity of the notional liquid by incorporating a compatible low molecular-mass polymer, *i.e.* a true liquid. (In this context, compatibility is defined as a solubility parameter difference of less than $\sim 0.8 \text{ cal}^{1/2} \text{ cm}^{-3/2}$ when using reasonable proportions of rubber and low molecular-mass polymer. The calculation (*Appendix B*) is considerably influenced by molecular mass.

Literature values¹⁴ of γ_c for NR and NBR are 31 dyne.cm^{-1} and 37 dyne.cm^{-1} (or mNm^{-1}) respectively; the NR compound must, therefore, be chosen as the notional liquid in the wetting process. The low molecular-mass polymer employed to increase fluidity was a polybutene of $M_n = 1300$ (designated PB1300), with a δ value¹⁰ of $8.0 \text{ cal}^{1/2} \text{ cm}^{-3/2}$, so that

$$\delta_{\text{NR}} - \delta_{\text{PB1300}} = 0.6 \text{ cal}^{1/2} \text{ cm}^{-3/2}$$

This difference satisfies the condition for compatibility noted above so that NR and PB1300 can be considered to be compatible. The value of γ_c for PB1300 may be taken as near to 27 dyne.cm^{-1} , the value for butyl rubber¹⁴, so that the nitrile surface should be wetted by either NR or PB1300. The work described in

this paper has shown that a NR compound containing PB1300 is sufficiently fluid to allow this thermodynamically predicted wetting of NBR to occur under moulding conditions well within practical vulcanisation times, giving good bonding between the elastomeric compounds.

The development of significant bond strength during vulcanisation — *Stage 2* of the bonding process — suggests that crosslinks must form across the interface despite the absence in this system of significant interfacial interdiffusion. Such crosslinking is presumably possible because of the closeness of contact between the NBR and PB-extended NR surfaces. Experimental data on this point are also given below.

EXPERIMENTAL

Materials

Natural rubber-based formulations are shown in *Table 1*. *Compounds 1-3* contained no polybutene and differed only in vulcanisation systems: *1* contained a conventional sulphur system, *2* a semi-EV and *3* an EV system. *1* and *2* differed only in minor detail from formulations fully described in *Natural Rubber Engineering Data Sheets EDS18* and

TABLE 1. NATURAL RUBBER-BASED COMPOUNDS

Formulation	Parts by weight						
	1	2	3	4	5	6	7
NR (SMR 10)	100	100	100	80	75	75	75
N330, HAF black	50	50	50	50	50	50	50
Process oil ^a	5	5	5	—	—	—	—
Zinc oxide	5	5	5	5	5	5	5
Stearic acid	2	2	2	2	2	2	2
Sulphur	2.5	1.5	0.4	2.5	2.5	1.5	0.4
CBS	0.6	1.5	6	0.6	0.6	1.5	6
Antioxidant/antiozonant ^b	2	2	2	2	2	2	2
Polybutene ($M_n = 1300$) ^c	—	—	—	20	25	25	25

^aLow viscosity naphthenic, Petrofina 2059

^bSantoflex 13 (Monsanto)

^cHyvis 30, kindly supplied by BP Chemicals Ltd

EDS40, respectively. Compounds 4-7 contained some PB1300 and no process oil: 4 and 5 resembled 1 with 20 p.p.h.r. and 25 p.p.h.r. respectively of NR replaced by PB1300; similarly 6 and 7 resembled 2 and 3 with 25 p.p.h.r. NR replaced by the polybutene.

The NBR formulation used is shown in Table 2. The accelerated sulphur-donor vulcanisation system was much faster than those in the NR-based formulations. This ensured that during bonding the NBR remained notionally 'solid' relative to the notionally 'liquid' extended NR compounds until completion of cure.

TABLE 2. ACRYLONITRILE-BUTADIENE COPOLYMER COMPOUND

Formulation	Parts by weight
NBR ^a	100
Plasticiser ^b	10
N330, HAF black	50
Zinc oxide	5
Stearic acid	2
Sulphur donor ^c	2.9
CBS	1
Antioxidant/antiozonant ^d	1

^aAcrylonitrile-butadiene copolymer, Krynac 34-50 (Polysar)

^bDiallylphthalate

^cDipentamethylenethiuram tetrasulphide Robac P25, oiled (5% oil) (Robinson Brothers Ltd)

^dSantoflex 13 (Monsanto)

Bonding and Test Details

Bond strengths were measured by a reinforced 180° peel test. The reinforcing material was rubberised tyre fabric supplied by Dunlop Aviation Division, Birmingham, United Kingdom. Tests were carried out on specimens vulcanised in a long plunger (follow-on) mould. A suitably-sized slab (4 mm) of each compound was compression moulded for 5 min at 100°C-110°C between sheets of polyester film, then well cooled. Two rectangles of tyre fabric were

cut to the same shape with the cords running lengthways: when bonding to NBR, one surface of one rectangle was treated with consecutive brush-coatings of *Chemlok* 220 and 205 with suitable inter-coat drying. The polyester sheets were removed and the slabs each backed with the tyre fabric pieces, the *Chemlok*-treated fabric surface contacting the NBR. The other two faces of the slabs were brought into contact, with a small metal-foil insert at each end to form tabs for gripping when testing. The composite structures were press-cured, using the plunger mould, at an actual pressure of 11.4 MPa (1660 p.s.i.) for 45 min at 150°C; a shorter cure would have sufficed.

Two 25-mm wide testpieces were cut from the vulcanised composite slab so as to avoid edge effects. The 180° peel test was carried out using a Zwick tensile tester with a jaw separation speed of 50 mm per minute.

Durability Tests

Several testpieces were submerged in either ASTM No. 3 oil or (synthetic) sea water for thirty days at room temperature before testing.

RESULTS AND DISCUSSION

The form of the trace obtained from the peel test depends on the magnitude of the separative force. Figure 2 shows typical traces depicting low bond strength (unextended NR to NBR) and high bond strength (NR/PB1300, Compound 5, to NBR). In the former case, the peel load rises to the point where adhesive separation occurs at a constant value. In the latter the recorded force is variable, reflecting 'stick/slip' behaviour when the separative peel force is close to the rubbers' bulk strength in this mode. To quantify this behaviour a representative value (F) was taken as indicated by the broken line in Figure 2.

As with the fracture of rubbers generally, adhesion failure is best represented energetically. The ideal case of increasing (by peeling) an adhesive fracture by a small length for a flexible (rubber) strip bonded to an unyielding metal strip was considered by Lindley¹⁵. For a rein-

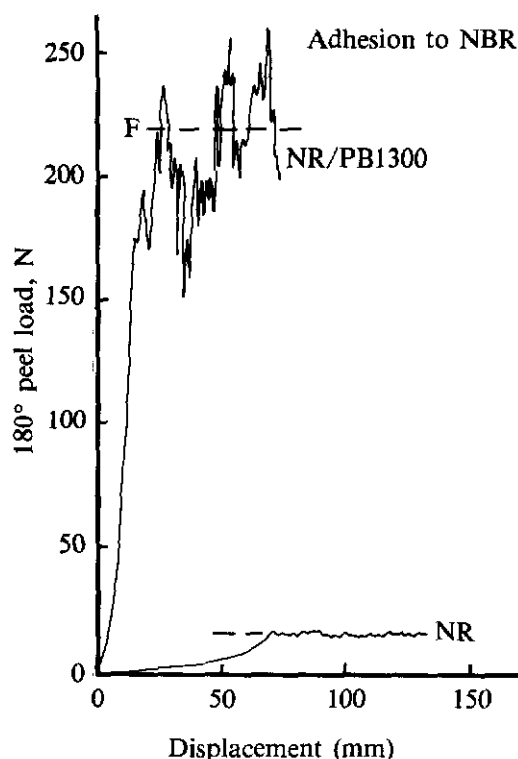


Figure 2. Typical peel adhesion strength traces.

forced testpiece peeled at 180°, the equation derived reduces to

$$P = 2F/w \quad \dots 2$$

where P is the peel adhesion energy, F the peel force and w the testpiece width. On applying Lindley's approach to the situation of two flexible, bonded strips under peel test, the general equation differs slightly from the original. However, the modified equation also reduces to the form of Equation 2 for reinforced testpieces peeled at 180°, and this equation was used to convert peel forces to peel energies.

The peel energies obtained are shown logarithmically as histograms in Figure 3, each histogram being the mean of four measurements. The NR-NR bond (Compound 1 to itself) gave a peel adhesion energy of 100 kJm⁻². Compound 1 bonded to NBR gave only 1½ kJm⁻²; adhesion was non-existent. Com-

pound 5, NR:PB1300 (75:25) to NBR, gave a value of about 15 kJm⁻². Photographs of the testpieces (Figures 4-6) confirm that NR-NBR adhesion is non-existent, but suggest that both NR-NR and NR/PB1300-NBR are high-adhesion systems. The latter conclusion arises from the shape of the separated surfaces and the obvious occurrence of cohesive failure in the rubber in both cases, but especially for NR-NR bonds. Compound 4, NR:PB1300 (80:20) to NBR, also gave a peel adhesion energy of 15 kJm⁻² (Figure 3).

Use of Equation 2 for very low adhesion systems with the testpieces employed is an oversimplification. The textile reinforcement used to prevent extension of the gripping tabs during testing gave rise to strips relatively stiff in the peeling mode. Thus a minimum interfacial bond strength was necessary for the testpiece to be pulled into the position shown in Figure 4 (180° bond separation) at the start of each test. For adhesion levels below this minimum, bond separation occurred during the early motion so that 180° separation was never achieved (as shown in Figure 5) and therefore Equation 2, based on 180°, did not apply. As the present work was concerned with achieving good adhesion, the refining of low adhesion measurements by recording actual separation angles and producing a more suitable equation, was not performed.

Furthermore, with the highest adhesion systems, the energy dissipated as rubber fracture normal to the direction of separation (*i.e.* branching) is not accounted for in the original analysis: the value of 100 kJm⁻² for the NR-NR bond (Figure 4) includes contributions from many such fractures into the strips and is thus an over-estimate of the interfacial peel adhesion energy. This conclusion is supported by the observation by Stevenson¹⁶ that the tearing energy of bulk NR (measured by crack growth fatigue testing) is only about 40 kJm⁻². Nevertheless, Equation 2 provides a convenient, reasonable, means of expressing bond strengths, as most results are away from these extremes.

The bond strengths to NBR obtained with NR/PB1300 compounds containing semi-EV

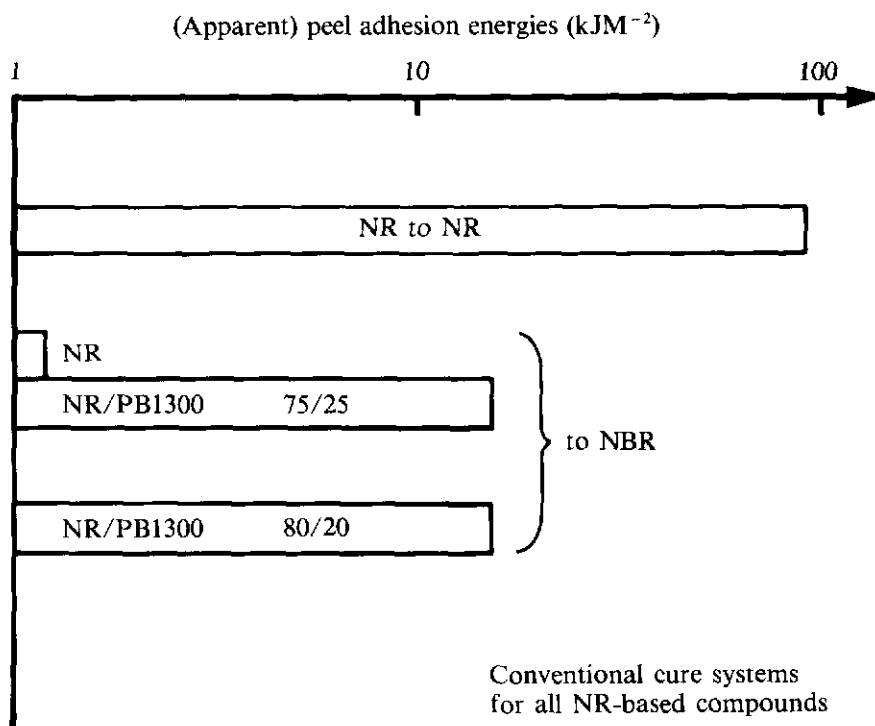


Figure 3. Apparent peel adhesion energies for NR compounds with conventional vulcanisation systems bonded to NR or NBR.

and EV systems are shown in Figure 7. Successful bonding occurred for all NR-NR testpieces irrespective of curing system. However, a clear loss in bond strength to NBR was observed as the curing system was changed from conventional through semi-EV to EV.

Mechanistic Aspects

Porter *et al.*¹⁷ have demonstrated that the lengths of crosslinks after vulcanisation, *i.e.* in mature networks, decrease as curing systems increase in efficiency. In the model proposed for bonding dissimilar rubbers shown schematically in Figure 1b, Stage 2 requires bonds similar to crosslinks to form across the interface. It is suggested that the possibilities of such bonds forming are greater if the crosslinks (bonds) are long: hence the decrease in adhesion level between NR/PB1300 and NBR as curing system changes from conventional to EV agrees broadly with this simple model. An

alternative suggestion is that bond formation arises from the maturation reactions of poly-sulphidic crosslinks near the interface and to their labile nature. These reactions, which continue throughout vulcanisation¹⁷, could also reasonably be involved in links across the surface. In either case, the independence of the NR-NR bond with regard to curing system would also be expected, as the diffusion of chain molecular portions from one interfacial surface into the other before cure means that crosslinking during vulcanisation will 'tie-in' diffused portions, whatever the detail of vulcanisation chemistry.

As already mentioned, successful bonding requires a fast vulcanisation system for the NBR compound. This system might also be involved in the bond development stage, *e.g.* by forming active species which could migrate across the interface and diffuse into the NR/PB compound. This suggestion is not supported by

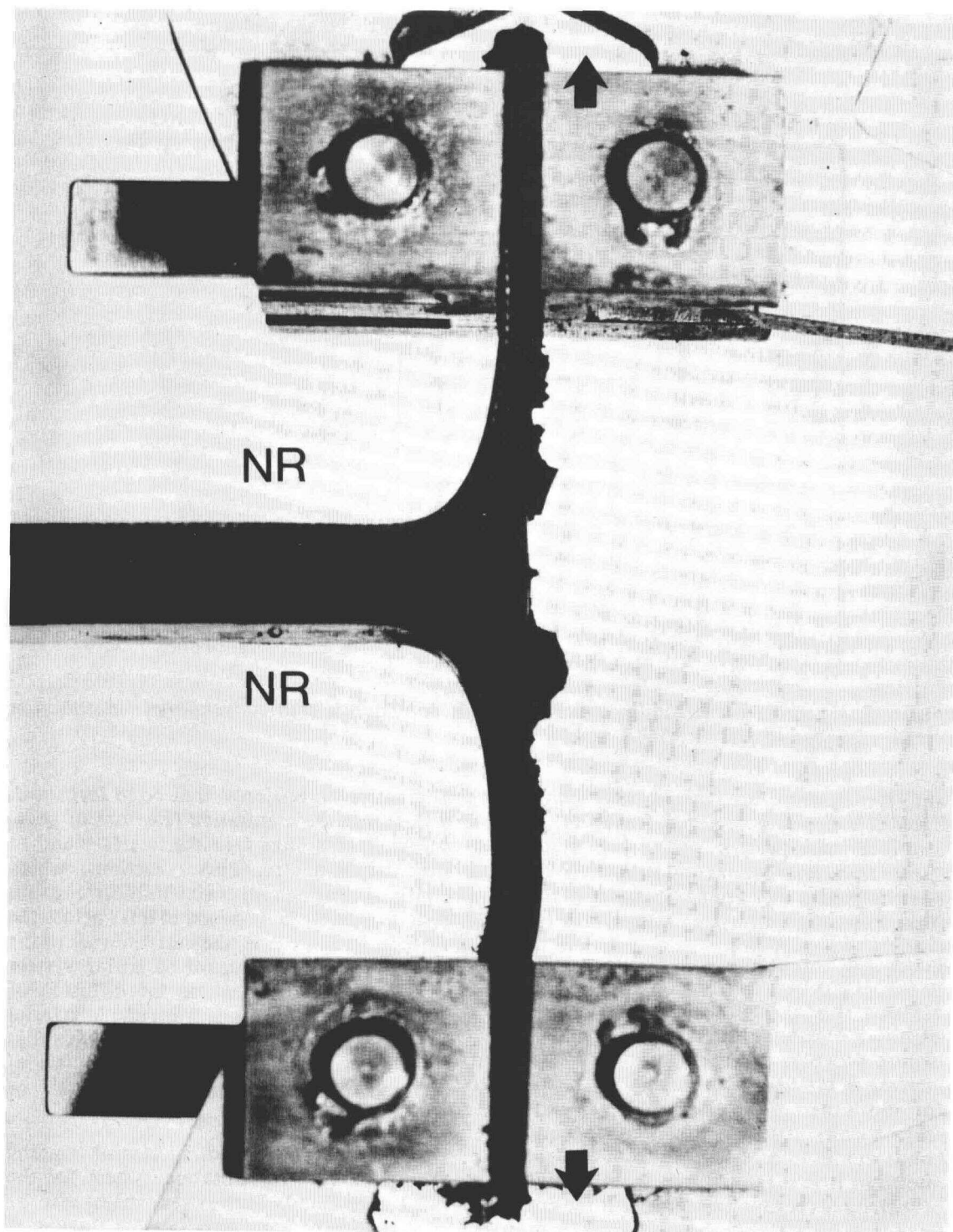


Figure 4. Peeled testpiece showing cohesive failure of NR-NR bond.

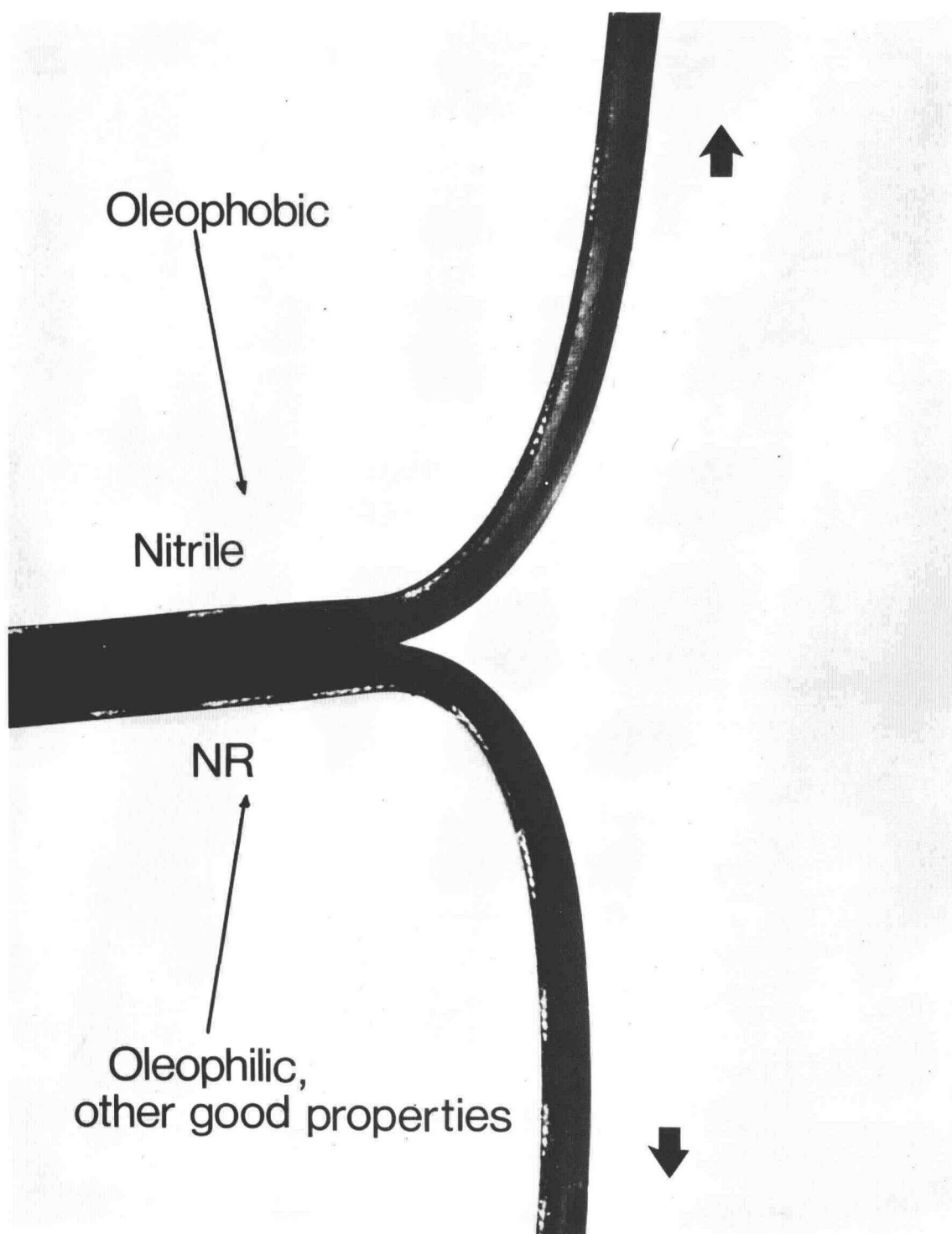


Figure 5. Peeled testpiece showing adhesive failure of NR-NBR bond.

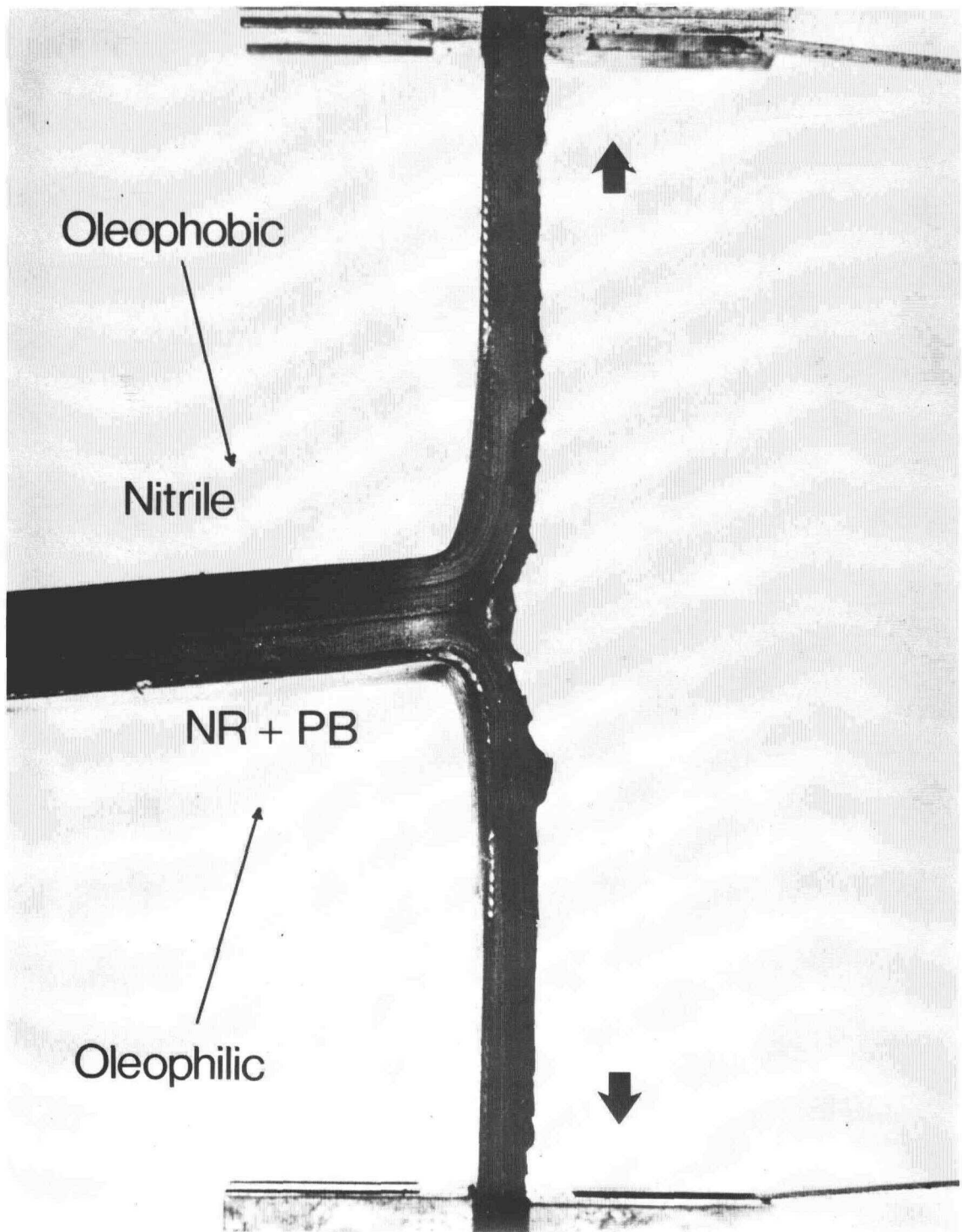


Figure 6. Peeled testpiece showing cohesive failure of NR/PB-NBR bond.

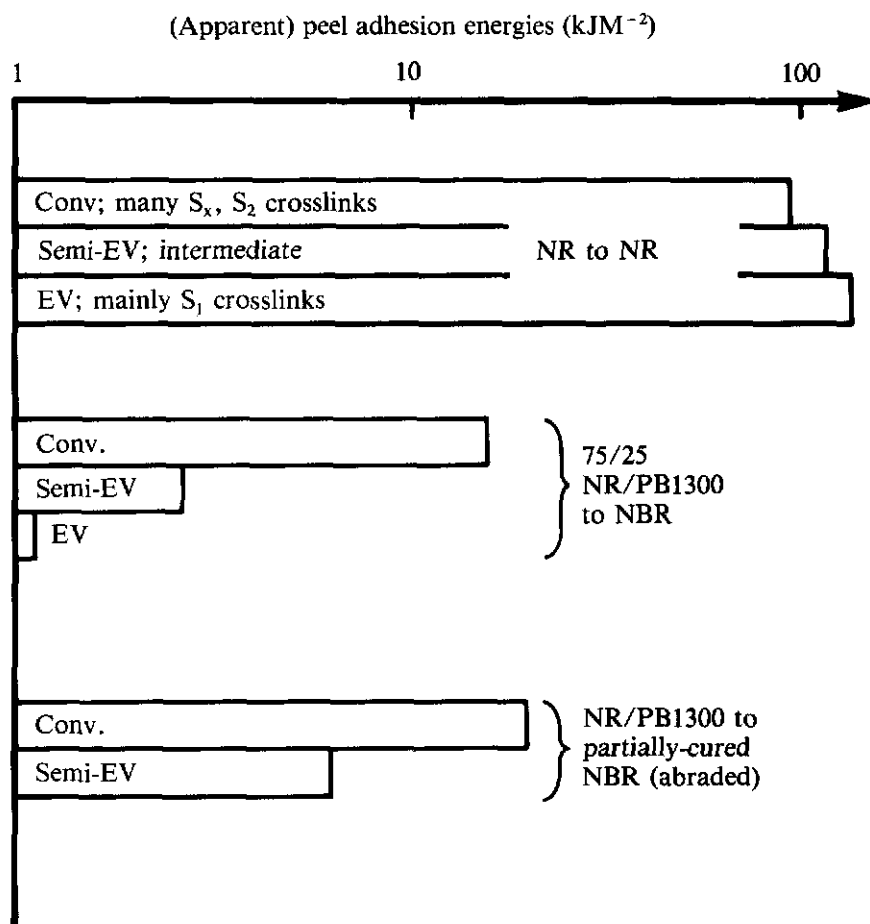


Figure 7. Apparent peel adhesion energies for NR compounds with varying cure systems bonded to NR or NBR.

the data in Figure 7 for two pressed slabs of NBR pre-cured for 20 min at 150°C (long enough for all active species to be used up in the early stages of crosslinking¹⁸), surface-abraded and then bonded to NR/PB1300 by the normal procedure. In one case the NR/PB1300 curing system was conventional, in the second case the semi-EV system was used. Results were at least as good as the two corresponding results for bonding to uncured NBR. This suggests that active species formed during early stages of NBR vulcanisation do not become involved in bond formation.

A more rigorous study of the interfacial region could reveal other aspects of wetting and

crosslinking relevant to successful bonding between NR/PB1300 and NBR; for instance, PB may conglomerate at the surface and extra sulphur may be involved locally in the bonding.

Durability and Fatigue

The bond strengths of samples immersed in water or oil for thirty days before testing are compared with untreated samples in Figure 8 as percentage loss of adhesion. Immersion in sea water caused very little change in the NR-NR bond strengths. As the peel failure was still cohesive, little deterioration in bulk strength had occurred. Oil caused swelling and excessive loss in bulk strength, giving completely

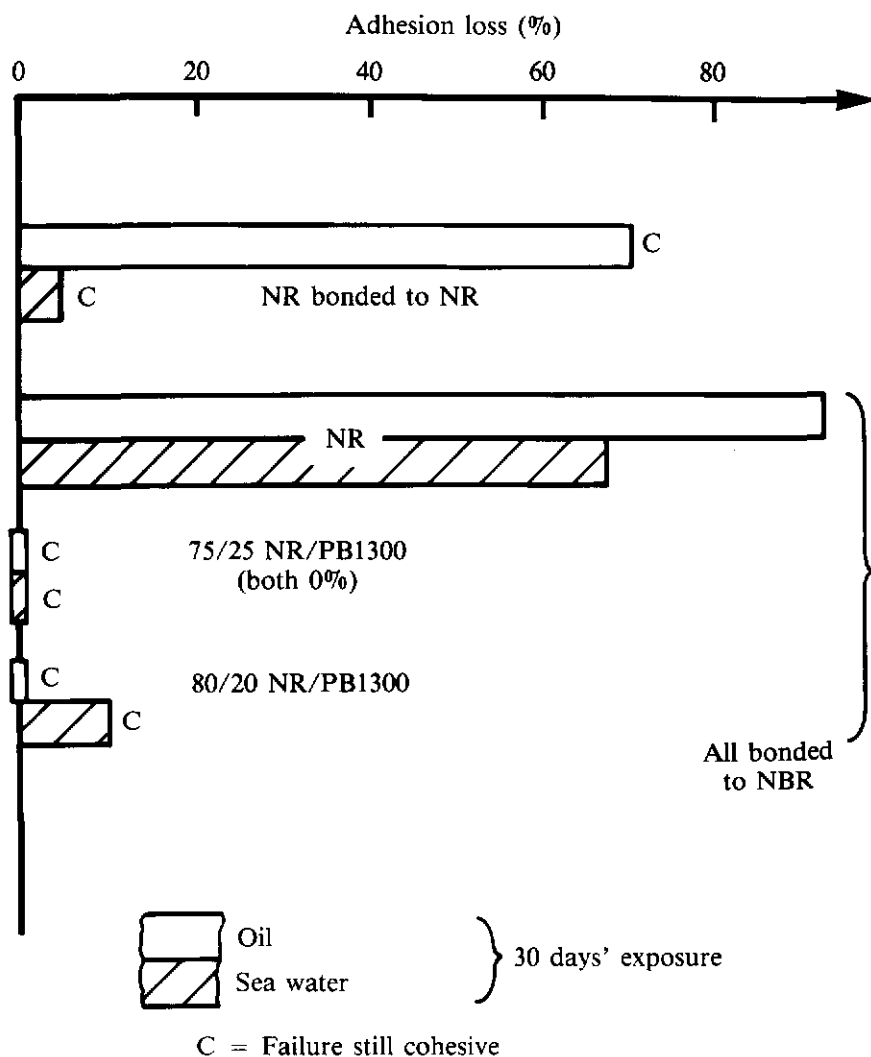


Figure 8. Effect of exposure to oil or sea water on bond strengths.

cohesive failure: the NR-NR bond was still intact.

The NR/PB1300-NBR testpieces gave <10% (and sometimes zero) adhesion loss at both NR/PB ratios, failure again being cohesive. The bond between the two rubbers remained intact in both oil and sea water and, perhaps surprisingly, swelling was restricted within the NR component so that its cohesive strength was never less than that of the NBR. The restricted swelling was presumably due to the influence

of the well-bonded NBR which itself was only slightly swollen.

In contrast, the poorly-bonded NR/NBR testpieces immersed in these liquids essentially lost any adhesion which the system originally possessed. The exercise as a whole suggests that the greater the initial bond strength, the greater the chance of retaining the bond when immersed in oil or sea water.

Although not detailed here, data have been obtained¹⁹ from cut growth fatigue

measurements which led to the tearing energy for most of the compounds discussed in this paper. Briefly, whereas at any tearing energy crack growth rate in the NBR compound was up to ten times faster than in NR, the rate in the 75/25 NR/PB1300 compound was the same as in NR. In addition, the critical tearing energy was 40 kJm^{-2} for both NR and NR/PB1300 whilst that for NBR was only 10 kJm^{-2} . Hence the presence of 33% of PB1300 in NR does not weaken the rubber in fracture energy terms. The main effects on general physical properties are losses in tensile strength and modulus and in hardness of about 10%.

ACKNOWLEDGEMENT

The author thanks the Board of the Malaysian Rubber Producers' Research Association for permission to publish this paper, Drs A. Stevenson and M. Porter for helpful discussions, and a referee for suggested refinements, especially concerning mechanistic aspects.

REFERENCES

1. HILDEBRAND, J.H., PRAUSNITZ, J.M. AND SCOTT, R.L. (1970) *Regular and Related Solutions*. New York: Van Nostrand Reinhold Co.
2. GEE, G. (1943) Interaction between Rubber and Liquids. *Trans Inst. Rubb. Ind.*, **18**(6), 266.
3. BURRELL, H. (1975) Solubility Parameter Values. *Polymer Handbook* (Brandrup, J. and Immergut, E.H. ed), 2nd ed, Chap. 3. IV-337. New York: John Wiley and Sons Inc.
4. BRYDSON, J.A. (1961) Selection of Compounding Ingredients. *Plastics*, 107.
5. VOYUTSKII, S.S. (1963) *Autohesion and Adhesion of High Polymers* (Transl Kaganoff, S.). New York: Interscience.
6. VASENIN, R.M. (1961) The Sticking Pressure in the Diffusion Theory of Adhesion of Polymers. *Vys. Soed.*, **3**, 679. RAPRA translation 1010.
7. SKEWIS, J.D. (1966) Self-diffusion Coefficients and Tack of Some Rubbery Polymers. *Rubb. Chem. Technol.*, **39**, 217.
8. CAMPION, R.P. (1975) The Influence of Structure on Autohesion (Self-tack) and Other Forms of Diffusion into Polymers. *J. Adhesion*, **7**, 1; also (1977) Microstructure and Autohesive Tack. *Adhesion I* (Allen, K.W., ed), Chap. 5. London: Applied Science Publishers Ltd.
9. HALE, P.T. (1981) Solubility Parameter Spectroscopy *Int. Rubb. Conf.* (Poster Session) Harrogate; also private communication.
10. CAMPION, R.P. AND STEVENSON, A. To be published.
11. AMERICAN CHEMICAL SOCIETY (1964) *Commemorative Volume on the Work of W.A. Zisman*, Advances in Chemistry series No. 43, Washington DC.
12. WAKE, W.C. (1976) *Adhesion and the Formulation of Adhesives*. London: Applied Science Publishers Ltd.
13. GARDON, J.L. (1976) Cohesive Energy Density and Adhesion. *Proc. Chem. Inst. Can. Symp. Polym. Interfaces: Focus Adhes. Montreal*, 33.
14. LEE, L.H. (1967) Wettability of Elastomers. *J. Polym. Sci. A-2*, **5**, 1103; (1968) Relationships between Surface Wettability and T_g of High Polymers, *J. Appl. Polym. Sci.*, **12**, 719.
15. LINDLEY, P.B. (1971) Ozone Attack at a Rubber-Metal Bond. *J. Inst. Rubb. Ind.*, **5**, 243.
16. STEVENSON, A. (1984) *Rubber in Offshore Engineering* (Stevenson, ed), p. 23. Bristol: Adam Hilger Ltd.
17. BATEMAN, L., MOORE, C.G., PORTER, M. AND SAVILLE, B. (1963) Chemistry of Vulcanisation. *The Chemistry and Physics of Rubber-like Substances* (Bateman, ed), Chap. 15. London: Maclaren & Sons Ltd.
18. PORTER, M. Private communication.
19. CAMPION, R.P. AND STEVENSON, A. (1985) The Role of Liquid Polybutenes in Enhancing the Adhesion of NR to NBR and Improving Durability. *Polym. Phys. Group Meet. Univ. of Reading*; abstract only.

APPENDIX A

THE (INTERFACIAL) MIXING OF TWO SIMILAR RUBBERS

The thermodynamic requirement for the mixing of two components is that the Gibbs free energy of mixing, ΔG , must be negative. The relation is:

$$\Delta G_m = \Delta H_m - T\Delta S_m \quad \dots 3$$

From regular solution theory¹, the molar entropy of mixing molecules of unequal size is given by:

$$\Delta S_m = -R (x_1 \ln \phi_1 + x_2 \ln \phi_2) \quad \dots 4$$

where x_1 , x_2 and ϕ_1 , ϕ_2 are the mole fractions and volume fractions of the two components. Applying Equation 4 to an interface of polymers of molecular mass 10^5 and density 0.95 g/cm^3 we can estimate the requirements for achieving a 50/50 mixture as follows:

$$\begin{aligned} \Delta S_m &= -(1.9872 \text{ cal/mole/deg}) [2 (0.5 \ln 0.5)] \\ &= -1.9872 (\ln 0.5)/(10^5/0.95) \text{ cal/cm}^3/\text{deg.} \\ &= 1.309 \times 10^{-5} \text{ cal/cm}^3/\text{deg.} \end{aligned}$$

Therefore at moulding temperature (383°K)

$$T\Delta S_m = 0.005 \text{ cal/cm}^3$$

$$\begin{aligned} \text{Also } \Delta H_m &= (\delta_1 - \delta_2)^2 \phi_1 \phi_2 \text{ cal/cm}^3 \\ &= 0.25(\delta_1 - \delta_2)^2 \text{ cal/cm}^3 \end{aligned} \quad \dots 5$$

Therefore from Equation 3, for ΔG_m to be negative,

$$\begin{aligned} 0.25(\delta_1 - \delta_2)^2 &< 0.005 \\ \text{or } \delta_1 - \delta_2 &< 0.14 \text{ cal}^{1/2} \text{cm}^{-3/2} \end{aligned} \quad \dots 6$$

However, if we assume that the mixing of as little as 0.1 mole % of one polymer into the surface layer of the other is sufficient to maintain contact, then the solubility parameter difference which can be tolerated (estimated as above) is given by

$$\delta_1 - \delta_2 < 0.24 \text{ cal}^{1/2} \text{cm}^{-3/2} \quad \dots 7$$

NB. For rubber compounds, Equations 6 and 7 might be underestimates for various reasons — the presence of low molecular mass rubber at the surface — local concentration variations — (for copolymers) favourable chain segment co-alignment.

APPENDIX B

THE MIXING OF NR AND LOW MOLECULAR WEIGHT PB

From *Equation 4*, the blend proportions affect the estimate. Taking the 75/25 proportion often employed, for NR (molecular mass 10^5) and PB1300 (molecular mass 1300):

$$\begin{aligned} x_1, \text{ the mole fraction of NR,} &= \frac{0.75/10^5}{0.75/10^5 + 0.25/(1.3 \times 10^3)} \\ &= 0.038 \end{aligned}$$

$$\begin{aligned} \text{Similarly } x_2 \text{ (for PB1300)} &= 0.962 \\ \text{(for PB1300)} & \end{aligned}$$

Therefore, assuming a representative density of 0.9 g/cm^3 ,

$$\begin{aligned} \Delta S_m &= -1.9872 (0.038 \ln 0.75 + 0.962 \ln 0.25) \\ &= 2.672 \text{ cal/mole/deg.} \end{aligned}$$

Representative blend molecular mass

$$\begin{aligned} &= (0.038 \times 10^5 + 0.962 \times 1.3 \times 10^3) \\ &= 5051 \end{aligned}$$

$$\text{Therefore } \Delta S_m = 2.672/(5051/0.9) = 4.76 \times 10^{-4} \text{ cal/cm}^3/\text{deg.}$$

For the PB to remain compatible during storage, take $T = 273^\circ\text{K}$.

$$\text{Therefore } T\Delta S_m = 0.13 \text{ cal/cm}^3$$

$$\text{From Equation 5, } \Delta H_m = (0.75) (0.25) (\delta_1 - \delta_2)^2 = 0.1875 (\delta_1 - \delta_2)^2$$

Therefore from *Equation 3*, for ΔG_m to be negative,

$$0.1875 (\delta_1 - \delta_2)^2 < 0.13$$

$$\text{or } \delta_1 - \delta_2 < 0.83 \text{ cal}^{1/2}/\text{cm}^{3/2} \quad \dots 8$$

NB. *Equation 8* might be an underestimate for the reasons in *Appendix A* and because of tortuosity effects of fillers.