

Factors Affecting the Adhesion between Unvulcanised Elastomers

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The self- and mutual-adhesion of various elastomers were investigated as a function of contact time and temperature by means of peel tests. Peel energies were measured for a peel angle of 90° at ambient temperature (ca 23°C) at a constant rate. The self-adhesion of unfilled polyisoprene elastomers, both natural and synthetic, with molecular weights less than 5×10^5 was found to attain its full-strength after a contact time of less than 2 min (the shortest investigated). For synthetic polyisoprenes (IR) of molecular weight 7×10^5 and above, the self-adhesion was observed to increase until contact times of 100 h or more were reached. For the IR elastomers studied, the contact time needed for the adhesion to reach the plateau level did not appear to correlate well with predictions based on interdiffusion of the long-chain molecules as the rate-determining process. Compared with the polyisoprenes, the self-adhesion of the unfilled styrene-butadiene polymer (SBR) studied, despite its having a much lower molecular weight, developed more slowly, behaviour consistent with the influence of SBR's higher glass transition temperature on its flow and diffusion behaviour. The mutual adhesion of natural rubber (NR) with epoxidised natural rubber (ENR) or to SBR, and the mutual adhesion of IR with ENR improved noticeably with time; the locus of failure moved from the interface into the weaker adherend provided sufficient contact time was permitted. As the polymer pairs are all immiscible, having significantly different solubility parameters, and the possibility of significant interactions between polar groups is absent, the development of such strong levels of mutual adhesion is surprising. The present results unexpectedly suggest a substantial difference between the time dependence of the adhesion of IR or NR to ENR, with the synthetic polyisoprene showing a stronger adhesion particularly at shorter contact times, the difference is apparent despite the comparison being made for IR and NR of similar molecular weight. The presence of carbon black filler had little effect on the self-adhesion of SBR. The mutual-adhesion between SBR and NR was increased by the addition of black, though it developed to its plateau level more slowly. The results reported here suggest, somewhat surprisingly, that the influence of carbon black on the self-adhesion of NR, unlike that of SBR, appears to depend upon the type of black.

Adhesion or tack is an important property of unvulcanised elastomeric materials. It is the

ability of two rubber surfaces to resist separation after their surfaces are brought into contact.

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There are two types of adhesion: auto- or self-adhesion, and mutual-adhesion, in which the two contacting bodies differ chemically or structurally. The mutual-adhesion of polymers is of great practical importance for the manufacture of such products as tyres.

The self-adhesion of unvulcanised elastomers has been extensively studied¹. One interesting feature that emerges is that the strength of the adhesion increases as a function of contact time until the cohesive strength of the unvulcanised elastomer is reached²⁻⁴. The attainment of good adhesion implies intimate molecular contact between the surfaces and the interdiffusion of polymer chains across the interface^{3,5}. The former must obviously be attained before the latter can begin, but the question arises as to which process controls the increase of the strength of adhesion with time. Voyutskii³ and Wool⁶ have proposed interdiffusion whereas Hamed^{1,7} has suggested the attainment of either intimate contact or interdiffusion may be the controlling factor depending upon the detailed circumstances. From their experiments, Gent and Kim⁸ have argued that the strength and extent of intimate contact is the governing factor at shorter contact times with interdiffusion playing a role only at the later stages of contact. Others⁹ observed that self-diffusion in solid polymers is strongly influenced by temperature and molecular weight, variables capable of affecting both flow and diffusion.

Fewer studies have been concerned with the mutual-adhesion between dissimilar elastomers. It has been suggested that interdiffusion also contributes to the development of mutual-adhesion with time, since it appears to be related to the degree of mutual solubility^{3,4}. Voyutskii and Vakula¹⁰ studied the role of diffusion phenomena in the development of adhesion between dissimilar polymers and found increases in adhesion with contact

temperature, time and molecular weight. Other investigations^{11,12} of the mutual-adhesion of various elastomers showed, in some cases, a marked increase with time up to quite high levels despite large differences in the solubility parameters of the materials used. The observation of Gent and Kim⁸ that an increase of adhesion could occur between dissimilar unvulcanised polymers led them to believe that the development of intimate contact and the strength of interactions between surfaces must be important in both self- and mutual-adhesion as they thought that interdiffusion between immiscible polymers unlikely to contribute significantly to the rise of adhesion.

This paper reports further work carried out on the self- and mutual-adhesion of various rubber pairs. The influence of molecular weight and carbon black filler on the development of tack with contact time are also investigated.

Theory

The possible role of interdiffusion in the development of the self- and mutual-adhesion of polymers will be assessed in the discussion. For this, it is useful to introduce some basic equations governing diffusion and miscibility. According to Einstein's equation, in time, t , after establishment of intimate contact at an interface, a diffusant will penetrate a distance, d , from the interface which is of the order:

$$t = \frac{d^2}{2D} \quad \dots 1$$

where D is the diffusion coefficient of the diffusing substance; for elastomer long chain molecules, D is found to vary approximately as the reciprocal of the square of the molecular weight, and to depend quite strongly on temperature⁵. Interdiffusion over a distance approaching the root-mean-square end-to-end

length of a molecule, L , may reasonably be assumed necessary for the self-adhesion to approach the cohesive strength of the polymer L , is given by¹³

$$L = \ell/N \quad 2$$

where ℓ is the length of the equivalent statistical link for the polymer chain (the link of an idealised freely jointed chain having the same end-to-end distance as the real chain), and N is the total number of links

For dissimilar materials in intimate contact, it has been suggested that limited interdiffusion may occur to produce a narrow interphase region Helfand and Tagami¹⁴ have suggested that the thickness of the interphase region, d_1 , is given by

$$d_1 = \frac{2\ell}{(6\chi)^{1/2}} \quad 3$$

where χ , the interaction parameter, is determined from the respective solubility parameters, δ_1 and δ_2 , by the relationship

$$\chi = \frac{(\delta_1 - \delta_2)^2}{\rho_0 kT} \quad 4$$

in which ρ_0 is the number of chain segments per unit volume, k is Boltzmann's constant, and T is the absolute temperature The parameters ρ_0 and ℓ are assumed to be similar for the polymers, if they are not, it is suggested¹⁴ the geometric mean be used The extent of interdiffusion at the interface is thus predicted to depend upon the difference between the solubility parameters of the two polymers

In order for two polymers to be miscible, the Gibbs free energy change on mixing¹⁵ given by Equation 5 must be negative

$$\Delta G_m = \Delta H_m - T\Delta S_m \quad 5$$

ΔH_m , the enthalpy change, is essentially independent of molecular weight and is a measure of the intermolecular interactions, ΔS_m is the entropy associated with the change in molecular arrangements ΔH_m is the parameter determining the miscibility of high molecular-weight polymers, as ΔS_m , essentially an inverse function of the molecular weight of the polymers being mixed, is likely to be small For two non-polar polymers with solubility parameters δ_1 and δ_2 , ΔH_m can be expressed¹⁵ as

$$\Delta H_m \propto (\delta_1 - \delta_2)^2 \quad 6$$

Hence miscibility on a molecular scale requires the difference in the solubility parameters of two elastomers be very small ΔH_m is often greater than $T\Delta S_m$, and hence non-polar polymer pairs are generally unable to satisfy the conditions for miscibility In the case of polymers containing polar groups or those possessing other groups which allow specific interactions, such as hydrogen bonding, to occur, ΔH_m may be negative so that mixing may be favourable

EXPERIMENTAL

Materials and Testpieces

The elastomers used (Table 1) were

- Natural rubber (NR SMRL)
- 50% epoxidised natural rubber (ENR), in which 50% of the double bonds are replaced by epoxide groups, thus raising the glass transition temperature, T_g , from -70°C to about -20°C
- Synthetic polyisoprene [IR Cariflex IR 305® (Shell) or Natsyn 2200® (Goodyear)] and
- Styrene-butadiene (styrene 23.5 wt %) [SBR Intol 1502® (Enichem)]

Except for some of the synthetic polyisoprenes, the unfilled elastomers were masticated to produce materials with Mooney viscosities [ML (1+4)] of approximately 40 units. The molecular weight, solubility parameter, T_g and ML are listed for each elastomer in Table 1. The filled materials were compounded with carbon black, the grade being either N330 or N990.

After mastication, the rubber was moulded under pressure into sheets between aluminium foil and 0.13 mm thick shim steel. Bonding agent

(Chemlok 205®/Chemlok 220®) was applied to the latter. The moulding temperature was 140°C or 150°C for 40 min or 60 min. Two procedures — degassing the rubber after mastication or cooling the mould under pressure — were tried in an attempt to reduce the formation of bubbles in the moulded sheets. They were only partially successful, bubbles tending to remain particularly with ENR and IR.

Pairs of strips 100 mm long and either 25 mm or 20 mm wide were cut before removing the

TABLE 1. PROPERTIES OF ELASTOMERS

| Elastomer | Molecular weight ^a $\bar{M}_w \times 10^{-3}$ | Solubility parameter ^b $\delta(\text{MPa})^{1/2}$ | Glass transition ^d T_g (°C) | Mooney viscosity ML (1 + 4) |
|--|---|---|---|--------------------------------|
| Synthetic polyisoprene (IR 305) | 1000 | 16.6 | -70 | 67 |
| | 690 | 16.6 | -70 | 58 |
| | 480 | 16.6 | -70 | 36 |
| | 440 | 16.6 | -70 | 23 |
| Synthetic polyisoprene (Natsyn 2200®) | 420 | 16.6 | -70 | 36 |
| Unfilled natural rubber | 470 | 16.6 | -72 | 39 |
| | 520 | 16.6 | -72 | 37.5 |
| Natural rubber with 50 p.p.h.r. of HAF black | 480 | 16.6 | -72 | 86 |
| Unfilled styrene-butadiene polymer | 270 | 17.0 | -60 | 40 |
| Styrene-butadiene polymer with 50 p.p.h.r. of HAF black | 190 | 17.0 | -60 | 86 |
| Epoxidised natural rubber 50 | 340 | 18.2 ^c | -19 | 36 |

^aMeasured by gel permeation chromatography

^bFrom Reference No. 15

^cFrom Reference No. 16

^dMeasured by differential scanning calorimetry.

aluminium foil. After removing the foil, the two strips of different width were brought into contact under a controlled pressure of 3 ± 0.5 bar. The different widths were used to prevent keying at the edges. A piston device (*Figure 1*) driven by compressed air was used to provide the pressure which was maintained throughout the contact time until the peel test was carried out. While the strips were under pressure, flow tended to occur. For long contact times, where substantial and uneven flow could occur, thicker strips of rubber were used. At the end of the contact period the edges of the strips were cut to give a width of 20 mm. The steel, hot-bonded to the elastomer testpieces, minimised extension of the peeled legs during a test.

The peel measurements were all made at about 23°C. The surfaces were brought into contact at that temperature unless otherwise stated.

Test Procedure

The rubber strips were peeled from each other by using the T-peel geometry, shown schematically in *Figure 1*, in an Instron testing machine at a constant crosshead speed of 200 mm min⁻¹ (equivalent to a peel rate of 100 mm min⁻¹). The peel force was recorded on a chart recorder (*Figure 2*), and an average of all the peaks estimated. The peel energy, P , was calculated from the average peel force, F , using the relation:

$$P = \frac{2F}{w} \quad \dots 7$$

where w is the width of the strip. The relation assumes the peeled legs of the strips are made inextensible by the steel backing. No account was taken of energy losses in the peel bend¹⁷.

These were thought to be negligible given the relatively large peel energies observed in

the present work. The minimum practicable time of contact before peeling was about 2 min; this was the time needed to remove the pressure from a testpiece and begin the peel test. The time taken to peel the strips completely was about 0.5 min.

RESULTS

Results for the dependence of peel energy upon contact time for NR and two synthetic polyisoprene elastomers of similar molecular weight are presented in *Figure 3*. The self-adhesion of the NR and IR (Cariflex 305[®]) reached its maximum value (3.5 kJm^{-2} – 5.5 kJm^{-2}) before the first contact time investigated (~ 3 min); the IR (Natsyn 2200[®]) took a little longer (~ 10 minutes). It is interesting that the locus of failure for the NR deviated randomly away from the interface into the bulk of the strips, whereas the locus remained in the vicinity of the interface in the case of the synthetic polyisoprene elastomers (though the peeled surfaces appeared uneven). Data for the self-adhesion of synthetic polyisoprene elastomers (IR305) of different molecular weights are shown in *Figure 4*. Whereas the self-adhesion for the two lower molecular weight materials attains its maximum value (about 3.5 kJm^{-2} – 5.5 kJm^{-2}) after the shortest contact time investigated, it is evident that the self-adhesion of IR with molecular weight 6.9×10^5 or 1.0×10^6 shows a steady increase with contact time. A possible plateau level at about 13 kJm^{-2} after about 60 h is reached by the former IR rubber. It is noteworthy that the degree of self-adhesion of the highest molecular weight IR is much lower at short times.

Figure 5 compares the development of the self-adhesion of SBR, both unfilled and filled with 50 p.p.h.r. of N330 carbon black, with

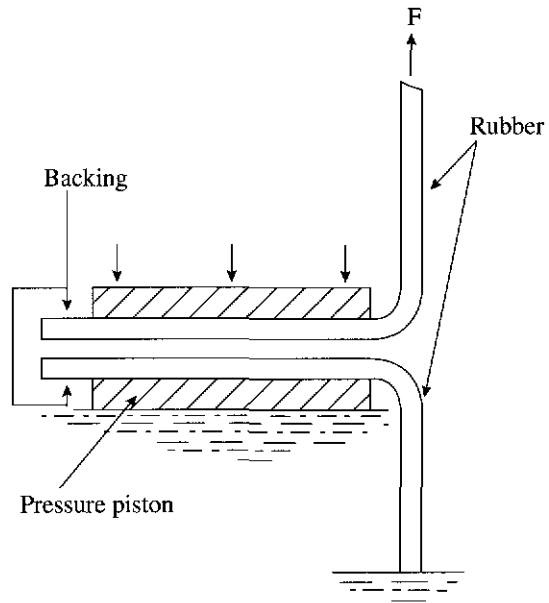


Figure 1. Schematic diagram showing test apparatus and peel geometry.

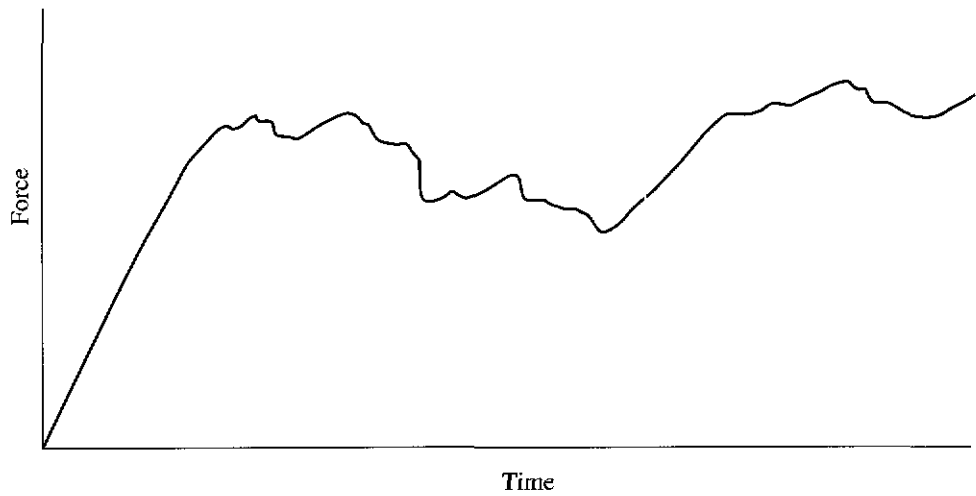


Figure 2. Typical record of peel force as a function of time.

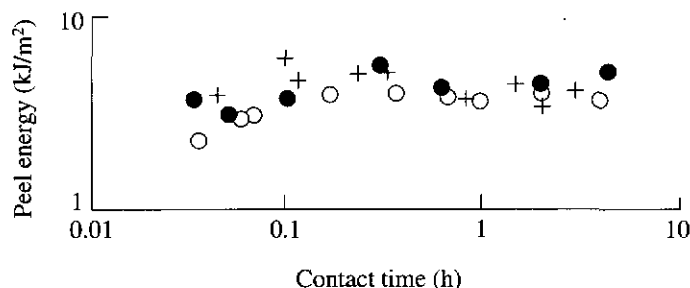


Figure 3. Variation of self-adhesion for unfilled NR and IR with time of contact. NR, $\bar{M}_w \sim 4.8 \times 10^5$ (●); IR (Cariflex 305®), $\bar{M}_w \sim 4.8 \times 10^5$ (+); IR (Natsyn 2200®), $\bar{M}_w \sim 5.1 \times 10^5$ (○).

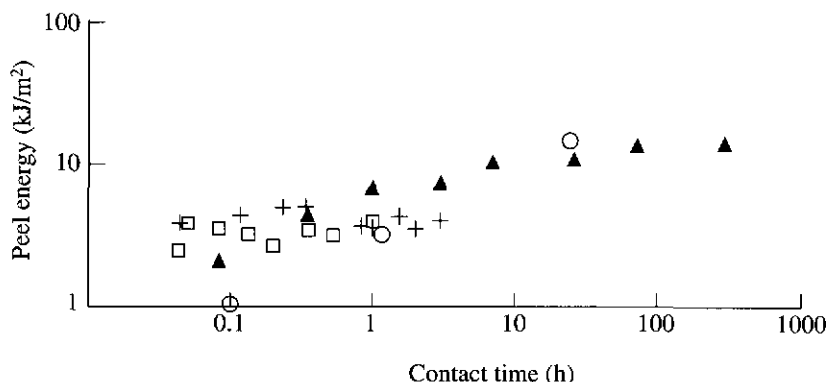


Figure 4. Variation of self-adhesion for IR (Cariflex 305®) of different molecular weights with time of contact. \bar{M}_w : 4.4×10^5 (□), 4.8×10^5 (+), 6.9×10^5 (▲), 1.0×10^6 (○).

contact time at room temperature. For the unfilled polymer, the results suggest a plateau level of around 8 kJm^{-2} for the self-adhesion has been reached after about 20 h contact. Comparison of this data with that for NR in Figure 3 confirms that NR reaches a high level of self-adhesion much more quickly than SBR. This is true in the present tests despite the SBR having a molecular weight half that of the NR, 1.9×10^5 compared with 4.8×10^5 . Interestingly, the self-adhesion of the SBR reaches a plateau level with respect to contact

time that is greater than the level seen in Figure 3 for the IRs and NR studied. The data for the filled SBR are similar to those for the unfilled at short contact times. At longer contact times (over 1000 h), there are indications that the self-adhesion may still be increasing. This suggestion is further supported by the data in Figure 6, which show the effect of a higher temperature during contact on the self-adhesion of the filled SBR. For contact at 60°C , the adhesion reaches a near-plateau level of 20 kJm^{-2} after some 30 h contact. The temperature during

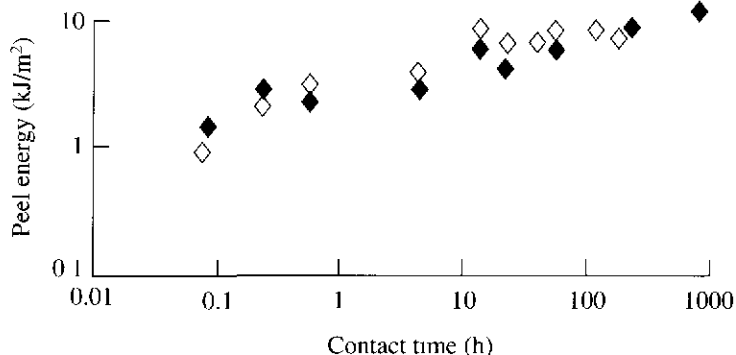


Figure 5 Variation of self-adhesion with time of contact for unfilled styrene-butadiene rubber (SBR) (\diamond) and 50 p.p.h.r. N330 black-filled SBR (\blacklozenge)

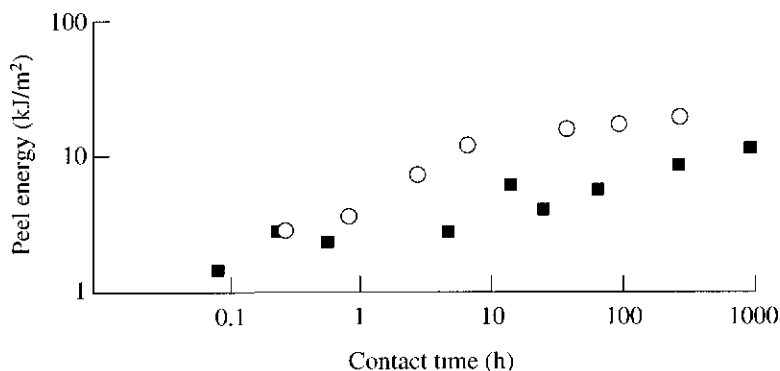


Figure 6 Effect of contact temperature on development of self-adhesion for 50 p.p.h.r. N330 black-filled SBR Contact temperature 23°C (\blacksquare); Contact temperature 60°C (\circ)

contact may be expected only to influence the kinetics of the development of the adhesion and not to affect the level of the plateau (since the peeling is carried out at 23°C). The behaviour of SBR filled with 50 p.p.h.r. of N990 black was broadly similar to that filled with N330. Considering the results in Figures 5 and 6 together, the presence of carbon black filler clearly does not prevent the development of substantial self-adhesion, but rather can raise somewhat the level attainable. A rise in the

maximum level would be expected from the observation¹⁸ that the inclusion of carbon black increases the green strength of unvulcanised SBR.

The effect of carbon black on the self-adhesion of NR and the influence of temperature during contact on the self-adhesion of filled NR are presented in Figure 7. With this batch of NR, a plateau level of about 6 kJm⁻² has been reached after the shortest

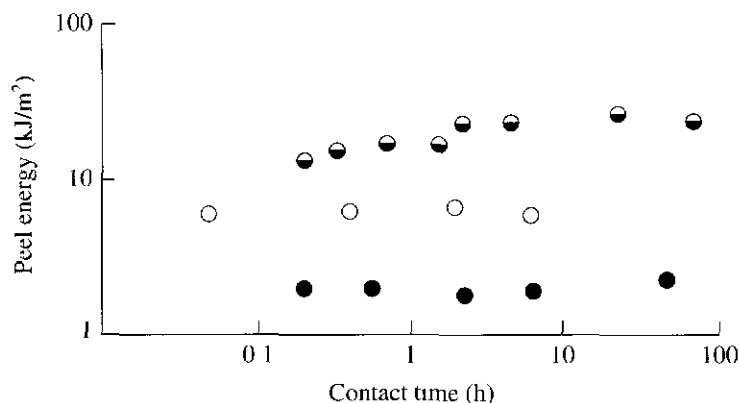


Figure 7 Effect of carbon black filler on development of self-adhesion of NR at room temperature and the influence of contact temperature on the self-adhesion of filled NR
 Unfilled NR ($\bar{M}_n \sim 5.2 \times 10^5$) contact temperature 23°C (○) 50 p p h r N330
 black-filled NR Contact temperature 23°C (●) Contact temperature 60°C (◐)

contact time investigated for the unfilled material, behaviour similar to that seen in Figure 3, as before the locus of failure did not follow the interface. Unlike the SBR, the addition of carbon black (N330) to the NR reduces the adhesion. For contact at room temperature (23°C) there is no sign of an increase of the adhesion with time and the failure locus followed the interface in all the tests. Despite this observation of no time dependence on the adhesion for filled NR surfaces brought into contact at 23°C, those brought into contact at 60°C (and subsequently peeled at 23°C) showed a much higher adhesion. The peel energies increased slightly with contact time, a plateau level of about 25 kJm⁻² being attained. The locus of failure moved from the interface to the bulk of the material after intermediate contact times. Surprisingly, the self-adhesion of NR filled with 50 p p h r of N990 black showed a different behaviour from the N330 filled rubber. The plateau adhesion was increased to about 10 kJm⁻², and the adhesion rose during the first 20 h contact.

Results for the unfilled, dissimilar polymer pairs IR/ENR and NR/ENR are shown in Figure 8. The IR/ENR pair developed the plateau level of mutual-adhesion (about 3 kJm⁻²) before the first contact time for which a peel measurement was made. The locus of failure at longer contact times (greater than 1 h) moved into the IR — the weaker adherend. The IR/ENR pair investigated previously¹² produced a much lower level of mutual adhesion (about 0.7 kJm⁻²) and the results indicated a slight increase of the adhesion with contact time. Though the ENR in each case had a similar molecular weight, the IR in the two studies differed in type (Natsyn 2200[®] for the present experiments and Cariflex 305[®] previously) and the molecular weight of the Natsyn was approximately half that of the Cariflex. For the NR/ENR pair the adhesion increased from about 0.3 kJm⁻² to 1 kJm⁻² over contact times from 0.1 h to 100 h. There was no indication of a plateau being reached. The locus of failure remained at the interface up to the longest contact time. Compared with previous data for these polymers¹², the level of mutual adhesion

was about three times greater for 0.1 h in the present tests but similar for 100 h contact. Thus, the development of the adhesion observed previously was much more pronounced.

The time over which the mutual-adhesion between NR and SBR develops is increased by the presence of carbon black (N330) (Figure 9). For the filled materials, after a contact time of over 100 h, the mutual-adhesion still appears to be rising, whereas in the case of the unfilled

elastomers the data available suggest that a plateau is reached after only about 0.5 h. The locus of failure for both filled and unfilled polymer pairs moves away from the interface and just into the SBR. The plateau level of the mutual adhesion of the unfilled SBR/NR pair was slightly less than that for the self-adhesion of the SBR. The mutual adhesion of the filled SBR/NR pair was similar to the self-adhesion of the filled SBR for all the contact times investigated.

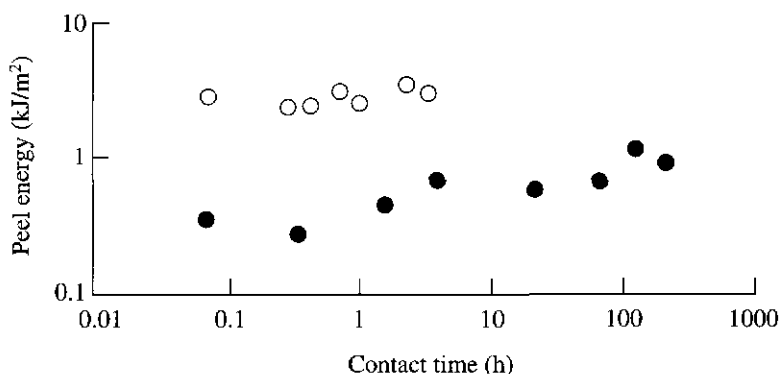


Figure 8. Variation of mutual-adhesion with time of contact for IR (Natsyn 2200[®]) ($\bar{M}_w \sim 4.2 \times 10^5$) and ENR (○); NR ($\bar{M}_w \sim 4.7 \times 10^5$) and ENR (●).

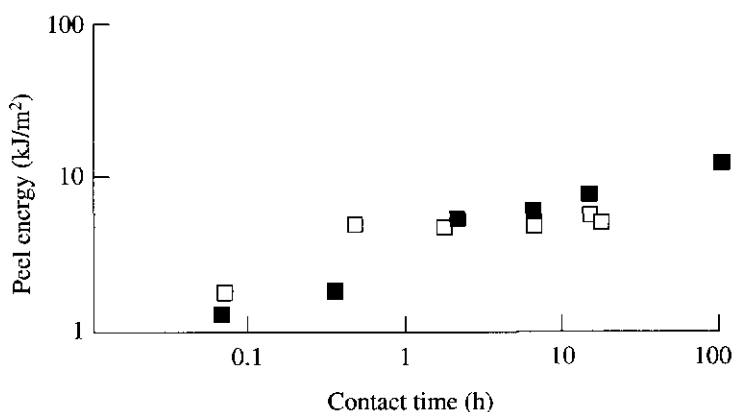


Figure 9. Variation of mutual-adhesion with time of contact for styrene-butadiene polymer (SBR) and natural rubber (NR) ($\bar{M}_w \sim 5.2 \times 10^5$) – each unfilled (□), and SBR and NR each filled with 50 p.p.h.r. N330 carbon black (■).

DISCUSSION

The rate at which adhesion increases after bringing two elastomer surfaces together is controlled by the improvement in the extent of intimate (molecular scale) stress-free contact or by chain interdiffusion at the interface. As Hamed¹⁷ suggests, the controlling mechanism is likely to depend upon the elastomers involved and the conditions of test. Factors such as T_g , molecular weight and contact temperature influence both mechanisms, but quantitative comparison of their observed effects with prediction may help to clarify their role in particular cases.

The present experiments on synthetic polyisoprene confirm that an increase of \bar{M}_w retards the development of self-adhesion but can raise the plateau level attained. Comparison of the self-adhesion data for SBR with that of IR or NR, suggests that the higher T_g of the SBR delays the development of self-adhesion. Despite the SBR investigated having a much lower molecular weight than the NR or IR, a slower rate for the development

of its self-adhesion was still clearly apparent. Raising the temperature speeds up the development of self-adhesion for both unfilled and filled materials.

The self-adhesion experiments performed on polyisoprenes of various molecular weights enable the observed time-scales over which the adhesion develops to be compared with estimates calculated on the basis that interdiffusion is the rate-determining factor. The depth of interdiffusion, d , required for the full development of self-adhesion may be of the order of the root-mean-square end-to-end distance L of a molecule (given by Equation 2). Values of L are calculated for NR and IR of different molecular weights (see Table 2). The figures are calculated taking the length of the isoprene unit and the number of units per statistical link to be 0.46 nm and 1.63 nm, respectively¹³. The values of the self-diffusion coefficients for polyisoprene elastomers can be estimated following Skewis⁵. Hence, the time for interdiffusion over the distance, d , for each rubber can be approximated using Equation 1. Comparing the values obtained with the times to reach the plateau level

TABLE 2. COMPARISON OF CALCULATED TIME FOR POLYMER CHAIN TO INTERDIFFUSE A DISTANCE EQUAL TO END-TO-END LENGTH WITH TIME TO DEVELOP PLATEAU LEVEL OF SELF-ADHESION

| Molecular weight (\bar{M}_w) ^a | Diffusion coefficient D ^b (m ² /s) | End-to-end length, L (nm) ^c | Calculated interdiffusion time, t^d (Minutes) | Time to plateau self-adhesion (Minutes) |
|---|---|---|---|---|
| 1 000 000 | 4.5×10^{-19} | 70 | 90 | >>1500 |
| 690 000 | 8×10^{-19} | 60 | 38 | 1000 |
| 480 000 | 1.4×10^{-18} | 50 | 15 | <5 |

^aMeasured by gel permeation chromatography

^bFrom Reference No. 5

^cCalculated using Equation 2

^dEstimated using Equation 1

of self-adhesion *Table 2* shows that the latter depend much more strongly on molecular weight than expected for a process controlled only by interdiffusion.

Like the polymer pairs investigated previously^{11,12}, the materials used in the mutual adhesion tests here are all incompatible. Hence any interdiffusion at the common interface would be expected to be limited to short chain segments. All the elastomer pairs investigated here (IR/ENR, NR/ENR and NR/SBR) show significant levels of mutual adhesion which in each case increases with time. For the IR/ENR and NR/SBR, the adhesion developed with time sufficiently for failure after the longer contact times to move away from the interface into the weaker adherend. The unfilled SBR/NR combination shows the shortest time to reach the plateau level of mutual-adhesion. According to *Equations 3 and 4*, the equilibrium thickness of the interphase region, d_i , is dependent on the solubility parameter difference and the length of the statistical link. Since data giving the length of the statistical link is only available for polyisoprene, d_i cannot be estimated for any of the polymer pairs. The relatively small value of the solubility parameter difference for the SBR/NR combination (see *Table 1*) may mean that for this pair it is easier for sufficient interdiffusion to take place for effective entanglements¹² to form in the interphase zone between the two polymers. In the absence of strong intermolecular forces at the interface, significant mutual adhesion may be expected to require chain ends to diffuse across the interface, form entanglements and re-enter their own material sufficiently to entangle further there. It is surprising that in spite of the similar behaviour of natural rubber and synthetic polyisoprene in the self-adhesion experiments, the mutual adhesion between these elastomers and ENR is distinctly different (*Figure 8*). The cause of such a difference is not clear.

The presence of filler increases the level of self-adhesion attainable in SBR, though the time-scale required to reach maximum adhesion is prolonged. The black has a similar influence on the mutual adhesion between SBR and NR. The influence of black on the self-adhesion of NR surprisingly appears to depend upon the type of black. From the experiments performed here, it is not clear why the behaviour of NR in this respect differs from that of SBR.

CONCLUSIONS

The time-scales over which the self-adhesion of high molecular weight synthetic polyisoprenes develop do not correlate well with predictions based on an interdiffusion process as the rate-determining process. Despite chemical incompatibility, elastomer pairs (SBR/NR, IR/ENR and NR/ENR) can show a time-dependent development of mutual adhesion. For the first two pairs the adhesion reached a level sufficient for failure to occur in the weaker elastomer.

According to most of the results reported here the presence of carbon black in NR or SBR does not prevent the development of strong levels of self- or mutual-adhesion; indeed, the addition of black raised the level of adhesion attainable after long contact times. The one exception found was the self-adhesion of N330 filled NR; the significance of this last observation needs to be established in a more detailed study.

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