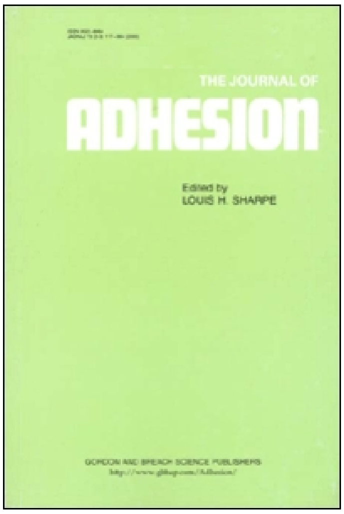

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Adhesion of Styrene-Butadiene and Silicone Elastomers to Rigid Substrates at Quasi-Equilibrium

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Adhesion threshold values for elastomers (SBR or silicone) in contact with rigid substrates (glass or polycarbonate) are obtained from the Johnson, Kendall and Roberts' test. The energy W_F involved in the formation of the contact at quasi-equilibrium shows no significant effect of the molecular weight of the elastomer. Moreover, W_F is of the same order of magnitude as the reversible energy of adhesion W_0. On the contrary, the energy W_R at quasi-equilibrium after forced contact depends on the molecular weight between crosslinks. However, the dependence is not universal for the different elastomers considered. It has not yet been possible to find the characteristics of the network which are responsible for the observed behaviours

KEY WORDS adhesion; elastomers; degree of crosslinking; formation; rupture; interface.

INTRODUCTION

Adhesion measurements between a viscoelastic material and a rigid substrate involve an important amount of energy dissipated viscoelastically. By performing the usual tests, such as peel tests, in the swollen state, at high temperature or very low peel rates, it is possible to reduce drastically the measured energy. The experimental value, however, stays higher than the reversible energy of adhesion calculated from the surface energies of the contacting materials. Moreover, it has been shown that the threshold value depends on the degree of crosslinking of the elastomer. In order to account for this effect, a factor related to the molecular dissipation[1] and proportional to the molecular weight between crosslinks was introduced in the Gent and Schultz' relationship.[2]

The formation and the rupture of the interface between a rubber and a rigid substrate in conditions close to equilibrium have been followed in a Johnson, Kendall and Roberts' test.[3] Preliminary results have been obtained for a styrene-

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butadiene elastomer in contact with glass or poly(methyl-methacrylate).[4] The energy involved in the formation of the contact, W_F, is independent of the degree of crosslinking and roughly equal to the reversible energy of adhesion. On the contrary, the energy at quasi-equilibrium after forced contact, W_R, depends on the molecular weight between crosslinks. The generalization of the experimental results obtained previously[4] to other systems has been looked for. Therefore, experiments have been performed with other random styrene-butadiene copolymers (SBR) of different molecular weights and distribution of molecular weights as well as with silicone rubber, the rigid substrates being glass and polycarbonate (PC).

2 EXPERIMENTAL

2.1 Johnson, Kendall and Roberts' Test

The so-called Johnson, Kendall and Roberts' test uses the contact between a rubber hemisphere and a flat, rigid substrate. In the absence of adhesion, the relation proposed by Hertz[5] gives the contact radius as a function of the elastic deformation under a normal load. However, the contact area is higher than expected by the Hertz approach due to the interfacial forces. The contribution of the surface energy to the total energy of the system has been taken into account by Johnson, Kendall and Roberts.[3] The condition of minimization of the total energy can be written as follows:

$$W = \frac{3}{32\pi E a^3}\left[\frac{16Ea^3}{9R} - P\right]^2 \qquad [1]$$

where: a = radius of the contact area
R = radius of the hemisphere.
E = Young's modulus of the elastomer
P = applied load

In the first experiment, the substrate is deposited very carefully on the top of the hemisphere and the contact area evolves under the sole weight of the substrate (about 0.1g). The evolution of the contact area is followed as a function of time up to quasi-equilibrium, which means that the contact radius stays constant.

Once this equilibrium is reached, the contact is forced by an additional weight (50g) superimposed during 5 minutes; the contact area increases under this extra load. After the weight removal, the contact area decreases spontaneously and the evolution of the contact is observed again up to quasi-equilibrium.

The radius of the contact area is followed in both experiments as a function of time as shown in Figure 1: curve F (= formation) corresponds to the formation of the contact under the sole weight of the substrate whereas curve R (= rupture) corresponds to the evolution after forced contact as described previously.

In this study, we only will consider the radius at quasi-equilibrium and calculate the corresponding energies of adhesion according to equation [1]. The energies involved in the formation of the contact and in the rupture after forced contact will be called W_F and W_R, respectively.

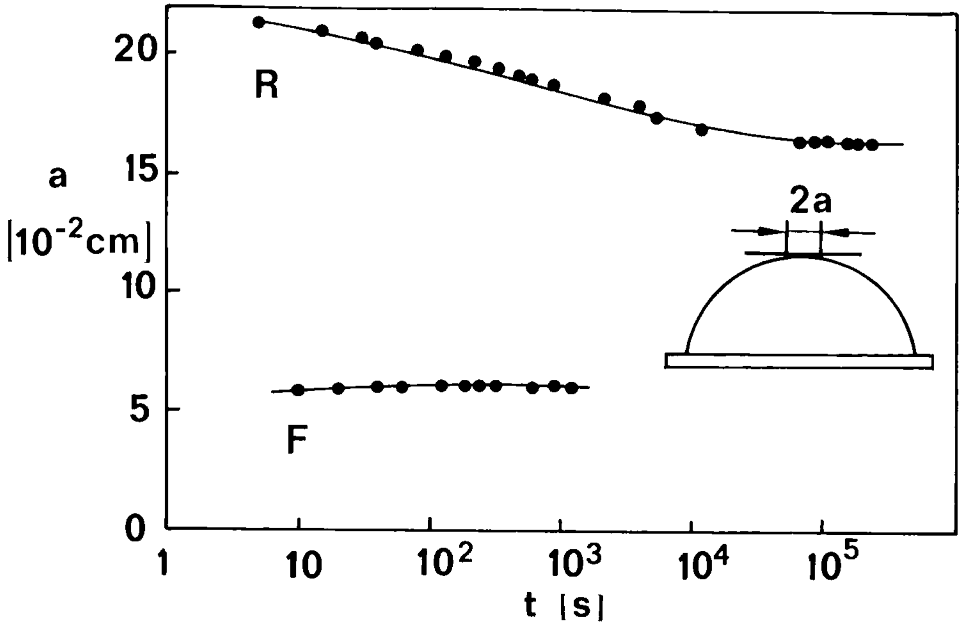

FIGURE 1 Evolution of the radius of the contact area during the formation of the contact (curve F) and during the propagation of the rupture after forced contact (curve R) as a function of time.

2.2 Elastomers

The earlier experiments (4) were performed with a styrene-butadiene rubber containing 40% of styrene. The results presented here are obtained, on the one hand, with three SBRs prepared in solution containing about 27% of styrene with different average molecular weights and distribution of molecular weights and, on the other hand, with endlinked polydimethylsiloxanes. Tables I and II show some basic characteristics of the initial polymers.

2.2.1 Sample Preparation

a) Styrene-butadiene networks

The mixing of rubber and dicumyl peroxide (DCP) was performed in an internal mixer at temperatures lower than 60°C;[6] 0.05 to 5% of peroxide was added to obtain samples presenting different degrees of crosslinking.

TABLE I
Characteristics of the SBR elastomers

	$M_w \times 10^{-4}$ (g/mole)	M_w/M_n
SBR 1	20.0	1.11
SBR 2	19.1	1.69
SBR 3	5.2	1.05

TABLE II
Characteristics of the polydimethylsiloxanes

Nominal viscosity $(mm^2/s)^a$	Nominal molecular weight $(kg/mole)^a$	M_n $(kg/mole)^b$	M_w $(kg/mole)^b$	M_w/M_n
80	3.2	2.9	5.7	1.94
750	18.0	12.5	26.3	2.11
2000	36.0	23.2	45.5	1.96
18 000	77.0	46.6	80.2	1.72

[a] data given by Petrarch Systems, Inc.
[b] data obtained by GPC analysis—personal communication by Rhône Poulenc

After mixing, the rubber hemisphere was moulded in a chromium-plated steel mould 37 mm in diameter. The following sequence of operations was applied:

—5 min at 90°C without pressure
—10 min at 90°C and 0.2 MPa
—release of the pressure
—5 min at 90°C and 0.2 MPa
—75 min at 150°C and 0.2 MPa
—cooling of the press platens by cold water circulation under pressure.

This procedure allowed us to obtain rubber hemispheres practically free of surface defects.

b) PDMS networks

Silanol-terminated polydimethylsiloxanes supplied by Petrarch Systems Inc. were used. These PDMSs were crosslinked with tetraethoxysilane (TEOS) (Aldrich Chemical Co) as a crosslinking agent and stannous 2-ethyl hexanoate (Aldrich Chemical Co) as a catalyst. The endlinking reaction was performed at room temperature using a technique proposed by Mark and Sullivan.[7] Both stoichiometric and excessive quantities of the crosslinking agent were used.

Some details of the sample preparation are discussed in a separate paper.[8] The casting and crosslinking were performed, under vacuum for 48 hours, in the chromium-plated steel mould used for the SBR hemispheres.

2.2.2 Network Characterization

Two characteristics of the networks are necessary: Young's modulus E and molecular weight between crosslinks M_c.

The Young's modulus was obtained by the same JKR test. When placing a heavy plate (P>45g) on top of the rubber hemisphere, the contribution of the adhesive forces to the contact area can be considered as constant. The modulus is then deduced from equation [1] applied to the contact areas a_1 and a_2 corresponding to two plates of, respectively, P_1 and P_2 weight. The difference between the energies involved, W_1 and W_2, is equal to zero and it is therefore possible to calculate the Young's modulus E.

$$E = \frac{9R}{16}\left[\frac{a_2^{3/2}P_1 - a_1^{3/2}P_2}{a_1^{3/2}a_2^{3/2}(a_1^{3/2} - a_2^{3/2})}\right]$$

Using this procedure, it is possible to measure independently both mechanical and adhesion characteristics with the same hemispheric sample.

The molecular weight, M_c, between crosslinks was determined by using swelling measurements at equilibrium in toluene at room temperature and the Flory-Rehner equation. The following relationship was used for calculation of the polymer-solvent interaction parameter χ:

$$\chi = \chi_0 + \beta V_2$$

where χ_0 and β are two constants and V_2 is the volume fraction of the polymer in the equilibrium swollen network.

The constants for the SBR/toluene system have not been found in the literature. Therefore, considering that the swelling behaviour of SBR in toluene is very similar to that in benzene,[9] the molecular weight M_c is calculated with V_2 values obtained by swelling SBR in toluene along with the constants for the SBR/benzene system. χ_0 and β values are, respectively, equal to 0.37 and 0.27.[10]

For PDMS networks, the values $\chi_0 = 0.44$ and $\beta = 0.36$ were used.[11]

In Figure 2, the moduli as determined in the JKR geometry are plotted as a function of the molecular weights between crosslinks calculated from swelling measurements for the SBR and PDMS networks. A good agreement with rubber elasticity theory is observed showing that the determination of the Young's modulus of the elastomers by the JKR technique is reliable. Moreover, a single curve is obtained for the three SBRs.

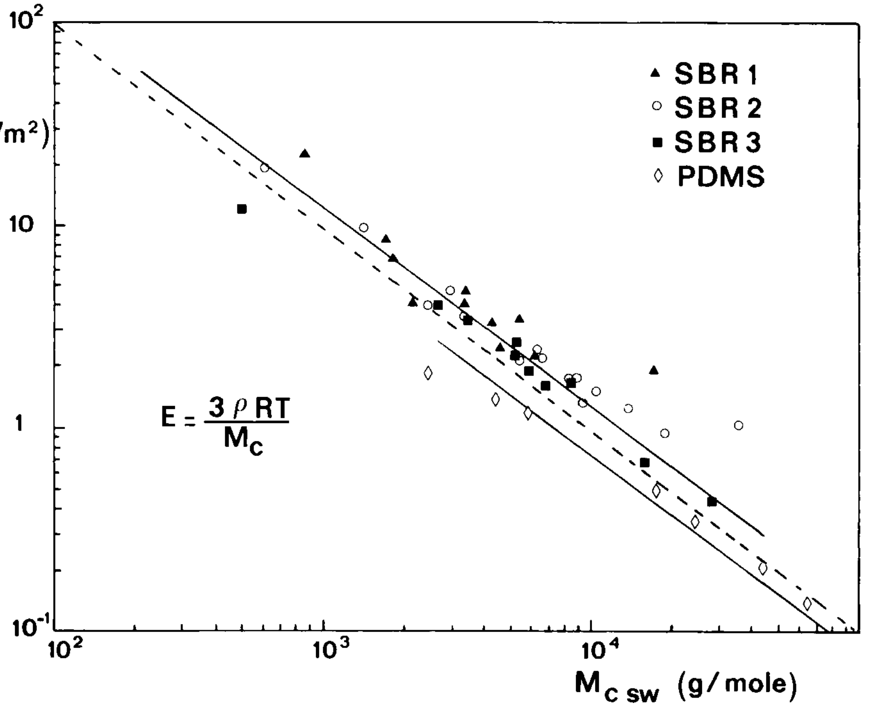

FIGURE 2 Young's moduli E of the SBR and PDMS networks as a function of molecular weight, M_c, between crosslinks from swelling measurements ($M_{c\,sw}$).

2.2 Surface Energy and Reversible Energy of Adhesion

The reversible energy of adhesion W_0 was calculated from the surface energy of the contacting materials using the classical (although questionable) relationship:

$$W_0 = 2\left(\gamma_1{}^D\gamma_2{}^D\right)^{1/2} + 2\left(\gamma_1{}^P\gamma_2{}^P\right)^{1/2}$$

where γ^D and γ^P are the dispersive and non-dispersive components of the surface energy of the two materials.

The values of the surface energy components were obtained by wettability measurements using the one-liquid phase method for both SBR and PDMS networks. It was shown again that the surface energy of the elastomers is not affected by the degree of crosslinking.

Glass has been considered as being spontaneously covered by several monolayers of water[12] so that W_0 was calculated with the components of the surface energy of water. The values considered for polycarbonate are those given by Cherry.[13] All the surface energies are reported in Table III whereas the calculated reversible energies of adhesion are given in Table IV for the different systems.

3 RESULTS AND DISCUSSION

Let us first consider the energy at quasi-equilibrium in the formation of the interface. Table V shows the average values of W_F obtained with various samples having different M_c in the range of 10^3–10^5 g/mole. No significant effect of the molecular weight has been observed. The results, in agreement with the previous paper,[4] show that W_F is roughly of the same order of magnitude as W_0 (Table IV). A slight difference can, however, be observed between the results for the three different SBRs.

TABLE III
Surface energies of the elastomers and the substrates

	γ^D (mJ/m^2)	γ^P (mJ/m^2)
SBR	40	1.3
Silicone	25	0.2
Glass (water)	21	51.6
Polycarbonate	33.5	5.8

TABLE IV
Calculated reversible energies of adhesion

	W_0 (mJ/m^2)
Glass/SBR	75
PC/SBR	78
Glass/Silicone	52
PC/Silicone	60

TABLE V
Apparent energy of adhesion in the formation of the interface

	W_F (mJ/m^2)
Glass/SBR 1	86 ± 15
SBR 2	64 ± 14
SBR 3	60 ± 10
PC/SBR 1	80 ± 19
SBR 2	67 ± 15
SBR 3	57 ± 8
Glass/Silicone	62 ± 14
PC/Silicone	49 ± 19

The energy at quasi-equilibrium after forced contact, W_R, varies drastically with the degree of crosslinking as shown in Figure 3. The results corresponding to the SBR/PC system are of the same order of magnitude as that obtained for SBR/glass assemblies and, for the purpose of clarity, are not given in Figure 3. Two different types of behaviour can be distinguished in this figure. On the one hand, the results for the high-molecular-weight SBRs (SBR 1 and SBR 2) can be expressed as follows:

$$W_R \propto M_c$$

On the other hand, the relationship for the silicone rubber in contact with glass or PC can be written as:

$$W_R \propto M_c^{0.5}$$

Previously, it was proposed[4] that both possible mechanisms, molecular dissipation[1] and molecular "extraction",[14] would lead to a linear relationship between W_R and the molecular weight. The behaviours of SBR 1 and SBR 2 are in agreement with this assumption. However, the behaviour observed for the lower-molecular-weight SBR (SBR 3) is rather close to the silicone rubber one although the scatter is larger.

In the case of a cohesive failure, Lake and Thomas[15] have shown that the threshold energy of fracture is proportional to $M_c^{0.5}$. Fuller and Lake[16] considered the differences between the interfacial failure between a vulcanized rubber and a rigid substrate and the cohesive failure. Because the chain configurations near an interface are different from those in the bulk and because the bond strength is considerably less for Van der Waals' bonds than for covalent bonds, they show that the threshold energy of adhesion in interfacial failure should be in between $M_c^{0.5}$ and M_c.

Although the interactions should be stronger between the silicone and the glass substrate than between the silicone and the PC, the established relationship is identical, only the ordinate is modified. The difference in behaviour should then find its origin in the network structure features, *i.e.* the physical entanglements or dangling ends.

It should also be noticed that the relationships are valid only in a limited range of degree of crosslinking (7×10^2 to 10^5 g/mole). Indeed, for very highly crosslinked

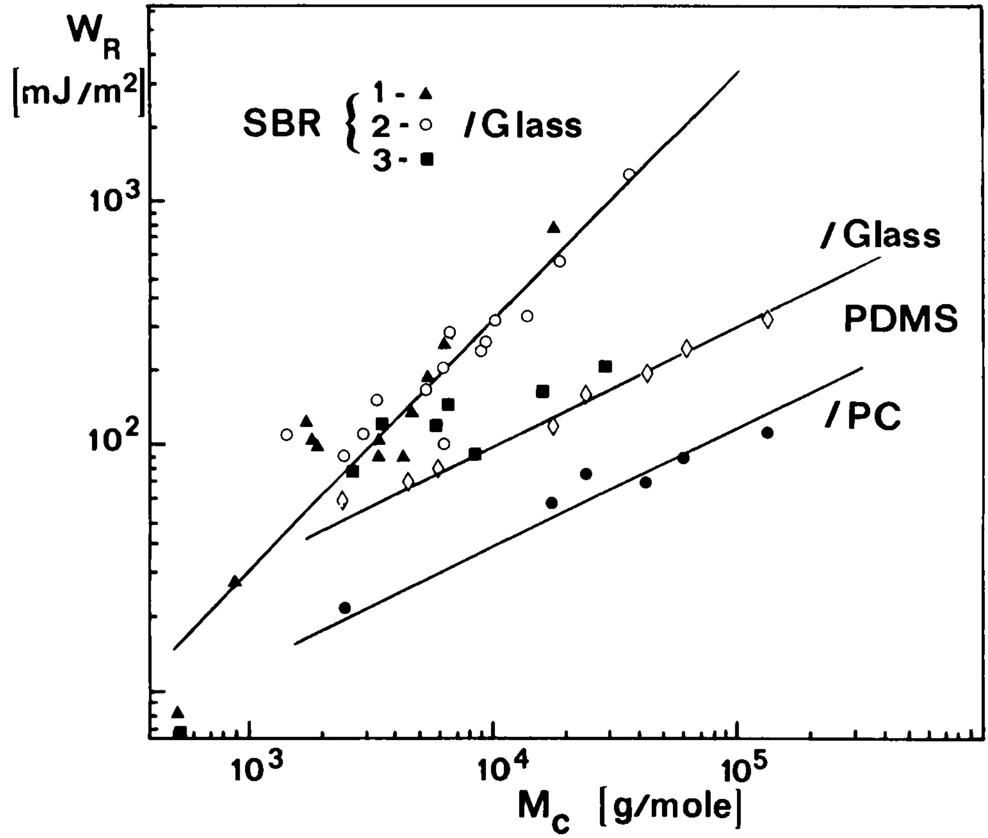

FIGURE 3 Energy of adhesion at quasi-equilibrium after forced contact as a function of molecular weight between crosslinks $M_c(= M_{c\,sw})$.

elastomers (M_c values lower than a few hundred), no contact area can be measured in the formation of the contact. After forced contact, the points corresponding to M_c values between 300 to 800 g/mole are below the curve for the SBR/glass interface in Figure 3. In this area, the polymer subjected to small deformations at room temperatures behaves as an elastic solid. For M_c values higher than about 10^5, it is unfortunately impossible to get homogeneous mixing of the peroxide due to the very small amounts involved. Moreover, the demoulding process does not lead to a good rubber surface.

Fractionation of the SBR2 has been performed by Dr. L. J. Fetters (Exxon Research and Eng. Co, Annandale, USA). It essentially eliminates a low molecular weight fraction. It has been checked[17] by H-NMR that fractionation causes virtually no change in either the polystyrene/polybutadiene composition nor in the polybutadiene microstructure. The results obtained with a fractionated crosslinked sample are in agreement with the general behaviour of SBR2. Therefore, no effect of the chains of low molecular weight which can be present at the hemisphere surface is detected.

4 CONCLUSION

Adhesion threshold values obtained either through the formation of the contact between an elastomer and a rigid substrate, or through the rupture of the interface after forced contact, show different dependences on the degree of crosslinking of the elastomer. Indeed, no influence of M_c on W_F is observed for both silicone and SBR, whereas the relationship between M_c and W_R is not universal. It has not yet been possible to find the characteristics of the network responsible for the different behaviour.

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