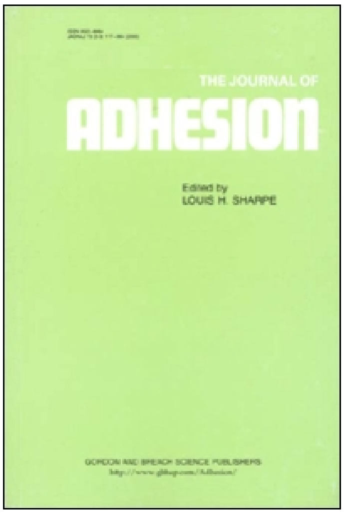

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ADHESION OF ELASTOMER LAYERS TO AN INTERPOSED LAYER OF FILLER PARTICLES

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Adhesion of elastomers to filler particles was studied by interposing a single layer of particles between two layers of a crosslinked elastomer and peeling the sandwich apart. Carbon black particles increased the peel strength by up to 100% compared with autohesion of the elastomer layers. Silica particles also increased the adhesion, but by a smaller factor, and there were significant differences using different elastomers. Also, the strength of adhesion depended on the degree of crosslinking of the elastomer layers: at higher levels of crosslinking, both self-adhesion and adhesion to particles were reduced. Nevertheless, this simple experiment gives an indication of the relative strength of adhesion for different combinations of elastomer and reinforcing filler.

Keywords: Adhesion; Elastomers; Fillers; Peeling; Reinforcement; Rubber; Strength

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INTRODUCTION

Elastomers are thought to adhere to certain filler particles quite strongly. Indeed, this is an important aspect of reinforcement by particulate fillers such as carbon black and silica. However, there is no convenient method for comparing the intrinsic adhesion of a specific elastomer to a specific filler. We have examined the strengths of adhesion of three common elastomers to particles of carbon black and silica, widely used as reinforcing fillers, by peeling a lightly-crosslinked sheet of the elastomer away from a single layer of particles. Although the results are somewhat scattered, they show that significant differences exist between various combinations of elastomer and filler.

EXPERIMENTAL

Measurements of adhesion were made using three common elastomers: a styrene-butadiene copolymer, denoted SBR (23.5 styrene/76.5 butadiene, SBR 1502); a high-cis polybutadiene, denoted BR (98% cis, Budene 1207, Goodyear Chemical Company, Akron, Ohio, USA); and natural rubber, NR (100% cis-polyisoprene). Lightly crosslinked sheets, about 1.5 mm thick, were prepared by adding to each elastomer various amounts of dicumyl peroxide (DCP) and pressing the mixtures between sheets of Mylar® film in a heated press. The fractional weights of DCP added to SBR were 0.1, 0.2, and 0.3%; to BR 0.15, 0.3, and 0.5%; and to NR 0.3, 0.5, 1, and 2%. Crosslinking was effected by heating for 60 min at 150°C.

To study adhesion between the crosslinked sheets, strips about 15 mm wide were cut from them, the protective Mylar films were removed, and the strips were pressed together for 10 min under a light pressure (about 1 MPa) at room temperature before peeling them apart.

In order to study adhesion to fillers, a thin layer of particles of either carbon black (N330) or precipitated silica (Hi-Sil 230, PPG Company, Pittsburgh, PA, USA), was interposed between two elastomer sheets. The filler was deposited on a Mylar sheet and spread over the surface with a blunt spreader blade until the layer of particles reached a uniform pale color. The carbon black layer, for example, became a light gray color. At this point the layer was assumed to be about one particle thick. One of the elastomer strips was then pressed against the filler-coated surface, picking up a layer of particles by a transfer process and leaving the surface of the Mylar film relatively clean. A second elastomer strip was then pressed into contact with the coated strip, sandwiching the layer of filler particles between them. In other experiments, two particle-coated strips were pressed together, sandwiching two layers of filler particles between them. A similar use of filler particles to bond sheets of rubber together has been described by Corish [1].

The strength of adhesion was assessed by peeling adhering strips apart (Figure 1) at room temperature and at a speed of 170 μm/s. The strength is characterized by the peel fracture energy **G,** given by **2F**/**w**, where **F** is the average peel force and **w** is the width of

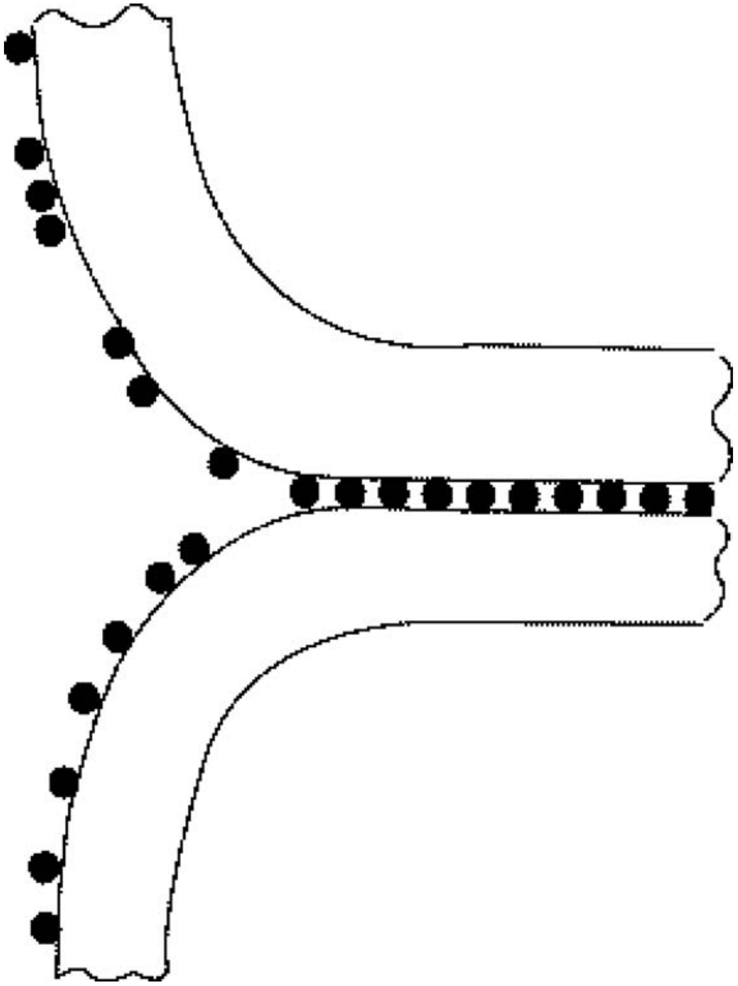

FIGURE 1 Sketch of rubber strips bonded together by a single layer of filler particles and peeled apart.

TABLE 1 Adhesion (J/m^2) of Elastomers Crosslinked With Dicumyl Peroxide (DCP)

Amount of DCP (%)	S	C	C–C	Si	Si–Si
NR					
0.3	105	131	131	118	102
0.5	49	63	46	46	39
1	19	31	18	21	19
3	15	16	<10	16	<10
SBR					
0.1	41	118	91	65	20
0.2	30	36	21	35	18
0.3	27	30	23	30	20
0.5	16	20	16	17	13
BR					
0.1	55	85	55	72	25
0.15	25	60	27	41	27
0.3	29	28	16	24	20
0.5	21	21	20	23	15

S, self-adhesion; C, with an interposed layer of carbon black particles; C–C, with an interposed double layer; Si, with an interposed layer of silica particles; Si–Si, with an interposed double layer.

TABLE 2 Adhesion (J/m^2) of Dissimilar Elastomers Layers with an Interposed Layer of Carbon Black Particles

Sandwich*	Strength of adhesion
NR-C-NR	31
(NR-C)-SBR	29
(SBR-C)-NR	23
SBR-C-SBR	118
NR-C-NR	31
(NR-C)-BR	32
(BR-C)-NR	23
BR-C-BR	84
SBR-C-SBR	118
(SBR-C)-BR	59
(BR-C)-SBR	56
BR-C-BR	85

*(NR-C), (SBR-C), (BR-C) denote strips of NR, SBR, and BR coated with a single layer of carbon black particles before pressing them onto a clean strip of the other elastomer.

NR crosslinked using 1% DCP; SBR, using 0.1%; BR, using 0.1%.

the adhering strips. Values of **G** are given in Tables 1 and 2. Repeat measurements showed reproducibility within about ±8%.

EXPERIMENTAL RESULTS

Self-adhesion was markedly higher for softer, less-crosslinked strips. This may be ascribed to better contact and a greater degree of molecular interdiffusion. When a layer of rigid particles is interposed, the strength of adhesion between elastomer strips would be expected to fall because contact between the strips would be lessened, if not entirely eliminated. However, the adhesion was found to be of the same order as before and even higher, up to twice as high. These observations suggest that there is relatively strong adhesion between elastomer and filler, comparable with that between layers of the elastomer itself. On the other hand, when two layers of filler particles were interposed (Table 1 and Figure 2) the adhesion was reduced, often becoming less than that for clean elastomer strips, showing that the particles adhered relatively weakly to themselves. (Adhesion with one layer of particles is denoted by R-C-R and with two layers of particles by R-C-C-R.)

The strength of adhesion was also measured for strips with a layer of silica particles interposed, denoted R-Si-R and R-Si-Si-R in Table 1, but the changes were smaller and the results were generally comparable with the adhesion shown by clean elastomer strips (Figure 3). But, again, two layers of particles gave lower adhesion than one layer, confirming that adhesion of elastomer to filler particles was greater than the strength with which particles adhered together.

For both carbon black and silica, the level of adhesion to fillers was significantly different with the three elastomers, being greater with lightly-crosslinked SBR than for NR and BR. The latter two elastomers showed generally similar levels of relative adhesion to carbon black and silica (Table 1). These relative rankings are in accord with other studies [2].

At higher degrees of crosslinking the strength of adhesion was reduced in all cases (Table 1). (In comparing different elastomers it should be noted that the degree of crosslinking, judged from measurements of elastic modulus, was about the same when the amount of DCP employed was 0.5% for NR, 0.1% for SBR, and 0.15% for BR.)

A direct comparison of adhesion between the elastomers and carbon black was obtained by measuring adhesion with a layer of filler particles sandwiched between two different elastomer strips.* Results are

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*This experiment was suggested by M. Brendel of the C.N.R.S. Institut de Chimie des Surfaces et Interfaces, Mulhouse, France.

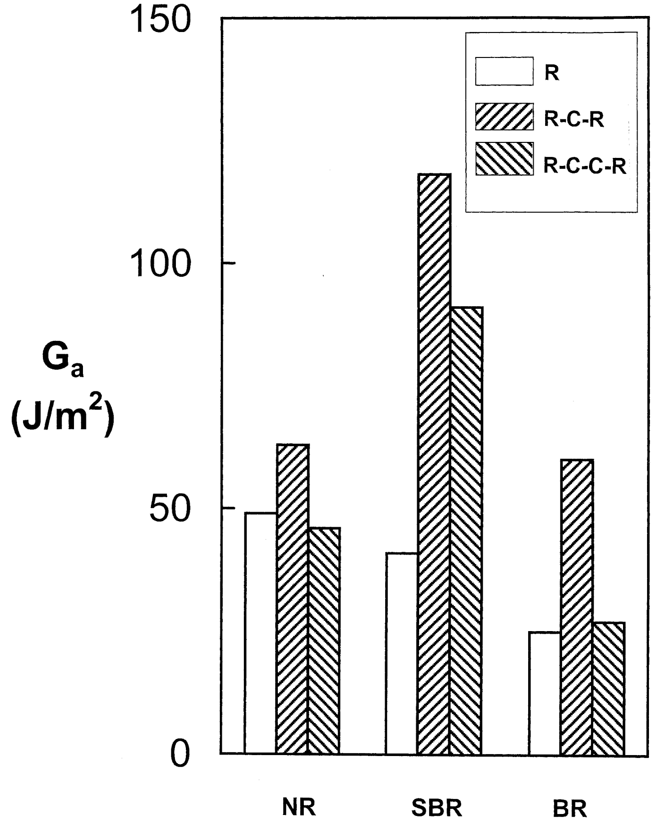

FIGURE 2 Peel strength, $\mathbf{G_a}$, for NR crosslinked with 0.5% DCP, SBR (0.1% DCP), and BR (0.15% DCP), with a layer of carbon black particles interposed, denoted R–C–R, or with two layers interposed, denoted R–C–C–R. Self-adhesion of the rubber strips is denoted R.

given in Table 2. Considering NR/SBR sandwiches first, the strength of adhesion was low whether the carbon black particles were originally applied to the NR or to the SBR strip, and about the same as for adhesion with two NR strips. Thus, it appears that adhesion of carbon black is lower to NR than to SBR. Consistent with this conclusion, the carbon black particles were found to be transferred to, or retained by, the SBR surface almost completely, indicated by the clean appearance of the NR surface after peeling the strips apart. Similar observations were made with NR/BR sandwiches, leading to the conclusion that carbon black adheres somewhat more strongly to BR than to NR. Measurements with sandwiches of SBR and BR suggested better

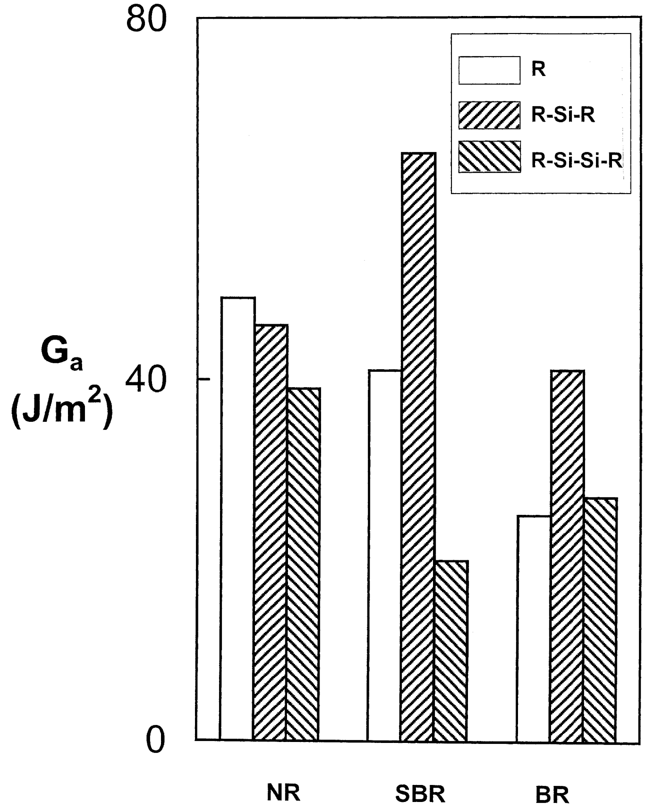

FIGURE 3 Peel strength, $\mathbf{G_a}$, for NR crosslinked with 0.5% DCP, SBR (0.1% DCP), and BR (0.15% DCP), with a layer of silica particles interposed, denoted R-Si-R, or with two layers interposed, denoted R-Si-Si-R. Self-adhesion of the rubber strips is denoted R.

adhesion to SBR than to BR. In every case the results were the same whichever strip had been coated with particles before being pressed against the other strip: the measured strength for an unsymmetrical sandwich using different elastomers was about the same as that for a symmetrical sandwich using two strips of the elastomer with weaker adhesion to carbon black. Thus, this experiment appears to be able to discriminate between adhesion with various combinations of elastomer and filler.

Care must be taken in such comparisons to use similar degrees of crosslinking, because at higher levels of crosslinking the self-adhesion of elastomers, as well as their adhesion to fillers, was much reduced.

However, provided that similar test conditions are used, the technique appears to afford a simple means of studying adhesion of elastomers to filler particles.

THEORETICAL CONSIDERATIONS

The force, **f**, required to pull a rigid spherical particle of radius **r** away from the surface of an elastic material is given by [3]

$$f = (3\pi/2)rG_o, \tag{1}$$

where $\mathbf{G_o}$ is the adhesive fracture energy per unit area. For a perfectly elastic substrate, $\mathbf{G_o}$ is expected to be of the order of van der Waals wetting energies, about 50 mJ/m^2. Assuming that the elastomer surface is covered with closely packed particles, the number, **n**, per unit area will be about $\mathbf{1/4r^2}$, and the total force, $\mathbf{F_m}$, required to detach unit area, or detachment stress, will be:

$$F_m = nf = (3\pi/8)G_o/r. \tag{2}$$

In peeling an elastic strip from a layer of particles, peel energy, **G**, is expended in stretching the elastic material by a force, **F**, until it reaches the detachment stress, $\mathbf{F_m}$, at the peel front. Thus [4],

$$G = t\int_o^{Fm} F.de, \tag{3}$$

where **t** is the thickness of the elastic strip and **e** is the tensile strain in the region of detachment. For simplicity, we assume that the material is linearly elastic, with a tensile modulus **E.** Equations (2) and (3) then yield

$$G = tF_m{}^2/2E = (9\pi^2/128)tG_o^2/Er^2 = 0.69\,tG_o^2/Er^2. \tag{4}$$

Values of **E** for lightly-crosslinked elastomers are typically about 1 MPa and the radius, **r**, of filler particle aggregates is about 0.25 μm. Assuming a van der Waals value for adhesion strength, $\mathbf{G_o}$, of about 50 mJ/m^2, and a strip thickness, **t**, of 1.5 mm, Equation (4) yields a value for **G** of about 40 J/m^2. This result is of the same order of magnitude as the measured adhesion fracture energies (Tables 1 and 2).

Equation (4) suggests that the measured strength will be strongly dependent on the radius of the particles, increasing in proportion to

$\mathbf{1/r^2}$, on the elastic modulus, increasing in proportion to $\mathbf{1/E}$, and on the interfacial adhesion strength, $\mathbf{G_o}$, increasing in proportion to $\mathbf{G_o^2}$. Experiments using layers of small glass beads with radii of 60, 100, and 400 μm gave adhesion strengths that were too low to measure, less than 1 J/m^2, and this is consistent with Equation (4). (For comparison, the strength of adhesion to a clean glass plate was about 50 J/m^2, much larger than values expected for $\mathbf{G_o}$ because of nonequilibrium effects.) Experiments using N110 and N990 carbon blacks showed about the same adhesion as with the N330 carbon black, even though the particle aggregate radii are reported to be rather different, about 0.1 and 0.4 μm, respectively, compared with 0.2 μm for N330. Thus, although the general level of adhesion to both carbon black particles and to the much larger glass beads is consistent with the above considerations based on JKR theory, there are discordant features that call for further examination.

REFERENCES

[1] Corish, P. J., Some aspects of rubber/rubber adhesion, *Prog. Rubber Plastics Technol.* **2**(1), 12–22 (1986).

[2] Hess, W. M., Herd, C. R., and Vegvari, P. C., Characterization of immiscible elastomer blends, *Rubber Chem. Technol.* **66**, 329–375 (1993).

[3] Johnson, K. L., Kendall, K., and Roberts, A. D., Surface energy and the contact of elastic solids, *Proc. Roy. Soc. London, Ser. A* **324**, 301–313 (1971).

[4] Gent, A. N., and Petrich, R. P., Adhesion of viscoelastic materials to rigid substrates, *Proc. Roy. Soc. London, Ser. A* **310**, 433–448 (1969).