

Bonding Elastomer Layers Together by a Surface Oxidation Reaction

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Synopsis

An experimental study has been carried out of the self-adhesion of thin layers of three crosslinked elastomers: *cis*-polyisoprene (natural rubber) and two polybutadienes. For the polybutadiene materials, the strength of self-adhesion was found to be strongly dependent upon the time of exposure of the two surfaces to air before they were brought into contact. The strength rose dramatically after the first hour or so of exposure so that in some instances the layers could not be forcibly separated later. When the surfaces were exposed to air for longer periods before joining them, the strength of self-adhesion fell to low levels again. This remarkable enhancement in self-adhesion, caused by prior exposure to air for short periods, did not take place on exposure to nitrogen or for samples of *cis*-polyisoprene, and it was reduced or delayed in samples containing antioxidant. It is therefore attributed to surface oxidation reactions that can lead to the formation of interfacial covalent bonds with polybutadiene but not with polyisoprene. Some possible reaction schemes are discussed.

INTRODUCTION

Little previous work has been published on the self-adhesion of crosslinked elastomers. The adhesion of a crosslinked elastomer to an inert rigid substrate is known to be dependent upon the speed and temperature of the test, due to viscoelastic effects.^{1,2} But at low rates of peeling and at high temperatures, when the contribution of viscoelastic energy losses is small, the work of separation appears to reach a limiting low value of the order of 1 J/m² of interfacial area.² Adhesion of crosslinked elastomers to each other appears to follow the same general pattern, and the work of separation is of the same order as for adhesion to inert rigid substrates.³

Recently, however, extremely strong adhesion has been observed between some crosslinked elastomer layers when they have been exposed to air for short periods at room temperature before being pressed together.⁴ In some cases the layers could not later be forcibly separated. Details of these observations and a tentative explanation of the phenomenon in terms of oxidative crosslinking reactions at the surfaces are given in the remainder of this paper. The effect could have direct application both to the practical problem of adhering elastomer layers together and also, if the proposed explanation is correct, as a means of studying surface oxidation reactions.

EXPERIMENTAL

Thin layers of each crosslinked elastomer were prepared by a molding process using mix formulations given in the Appendix. The molding times and temperatures used for bringing about crosslinking are also given there. Each ma-

terial was molded between a layer of thin cotton cloth, thickness 0.25 mm, backed by Mylar film, which adhered to one surface and a second layer of Mylar film, Type 300A (E. I. du Pont de Nemours and Co.) which adhered to the other surface. The elastomer layer itself was about 0.3 mm thick.

After preparation in this way, the samples were stored at room temperature for about 24 hr. The Mylar films were then removed from each of two sheets, exposing the elastomer surfaces to air. After a given period of time, two elastomer surfaces were brought into contact and pressed together under a light force for a further period, generally 24 hr, at room temperature. The strength of self-adhesion was then measured by peeling the adhering strips apart, as shown in Figure 1. During the peel experiment, the cloth backing served to prevent any significant extension of the peeled sections.

All peel tests were carried out at room temperature and at a rate of clamp separation of $83 \mu\text{m}/\text{sec}$. These conditions are not sufficiently gentle to eliminate viscoelastic contributions to the work of separation altogether. Only a qualitative interpretation of the experimental results is therefore attempted.

The work W_a required to peel apart a unit area of the interface was calculated from the peel force F per unit width of the test specimen^{1,2}:

$$W_a = 2F$$

RESULTS

The Bonding Phenomenon

As shown in Figures 2 through 4, the work required to separate two crosslinked strips of polybutadiene was found to depend strongly upon the period of exposure to air before they were brought into contact. Initially rather low, the strength of self-adhesion rose dramatically as the period of exposure to air increased, so that after exposure for 1–2 hr before the strips were pressed together they could not subsequently be separated without tearing the elastomer layers. For exposure periods greater than about 2 hr the subsequent adhesion became weaker, and it fell rapidly as the exposure time was increased still further. Eventually,

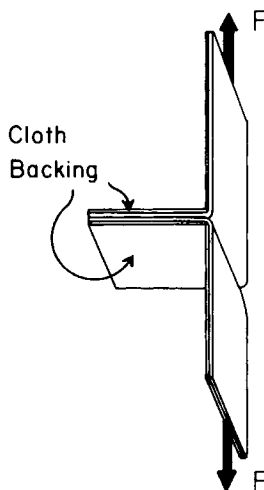


Fig. 1. Test method.

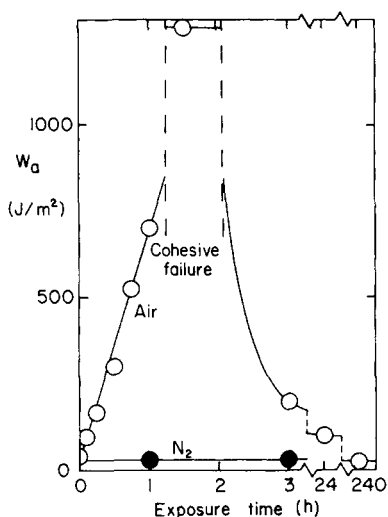


Fig. 2. Work W_a of separation vs. time of exposure to air or to nitrogen before bringing strips of Cis-4 polybutadiene into contact. Peroxide recipe (0.1% dicumyl peroxide).

after exposure periods of about 10 days, the self-adhesion of the elastomer layers was again quite small, comparable to the initial value.

If the protective Mylar films were removed from the elastomer layers in an atmosphere of nitrogen (in a glove box) and the two layers were then pressed together, the resulting strength of self-adhesion was found to be low and constant, independent of the period which elapsed between removing the Mylar films and joining the elastomer layers together, Figures 2 and 3. Thus, the striking increases, and later decreases, in self-adhesion shown in Figures 2 and 3 appear to be a result of reaction with atmospheric oxygen.

Similar effects were noted for peroxide cures, Figures 2 and 3, and for sulfur cures, Figure 4, so that the bonding reaction does not appear to be specific to the nature of the crosslink in the elastomer layers. In other experiments, carried

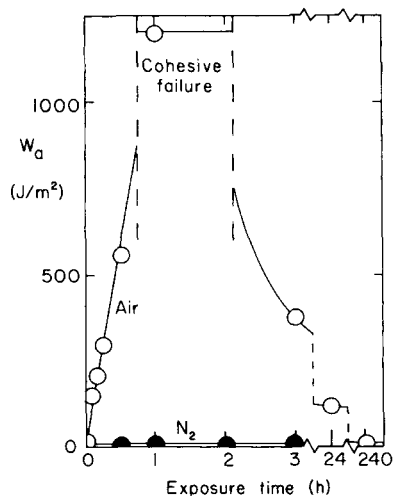


Fig. 3. Work W_a of separation vs. time of exposure to air or to nitrogen before bringing strips of Diene 35 NFA into contact. Peroxide recipe (0.05% dicumyl peroxide).

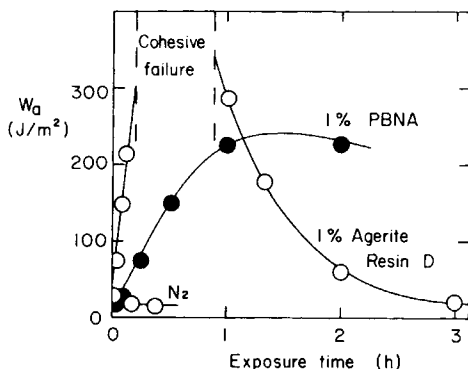


Fig. 4. Work W_a of separation vs. time of exposure to air or nitrogen before bringing strips of Diene 35 NFA into contact. EV sulfur recipe.

out in the dark and in a glove bag containing dry air, the development of self-adhesion took place equally rapidly so that the absence of light, humidity, and any ozone that might be present in the laboratory atmosphere does not impede the bonding reaction in any way. It is thus associated solely with exposure of polybutadiene layers to air before bringing them into contact.

When a more powerful antioxidant, phenyl- β -naphthylamine, was employed in place of Agerite Resin D in the mix formulation, the enhancement of self-adhesion required longer times of exposure to air to develop and did not reach the same high values, Figure 4. This result again suggests that an oxidation reaction is responsible for the remarkable degree of adhesion developed between crosslinked sheets of polybutadiene after exposure to air for relatively short periods at room temperature.

Further experiments were carried out to ascertain whether the actual process of peeling away the Mylar films induced an unusually rapid reaction of the elastomer with oxygen. The Mylar films were removed slowly in a nitrogen atmosphere, and then the elastomer strips were left undisturbed for about 3 hr. After this time, air was admitted to the glove bag. The subsequent adhesion of the elastomer strips was found to follow the same time dependence as before, upon the period of exposure to air before joining. Thus, transitory effects of the peeling process itself do not seem to be responsible for the observed interfacial bonding.

Experiments were also carried out with other protective films in place of Mylar: aluminum foil (Alcoa Wrap No. 5186, Aluminum Company of America) and Teflon-coated aluminum foil (Penfoil, Penetone Corporation). After removal of these foils from the elastomer surface, the subsequent strength of adhesion between two similar elastomer layers was found to vary with the period of exposure to air in substantially the same way as with Mylar. However, the strengths obtained for samples prepared with the Teflon-coated foil were appreciably lower, about one third, of those obtained with Mylar and aluminum foil. This may be due to some contamination of the elastomer surface by Teflon, or possibly to a less smooth surface finish. Nevertheless, all three foils yielded qualitatively similar results, indicating that the development of interfacial bonds as a result of air exposure is not due to a specific effect of Mylar film on the elastomer.

The fact that the adhesion developed at the interface between the elastomer

layers is extremely strong so that the layers cannot be pulled apart in some instances suggests that covalent chemical bonds are formed between them. When the adhering layers were immersed for several hours in reagents which can sever hydrogen bonds, for example, formic acid, acetic acid, and formamide, the layers remained firmly adhered together, suggesting that primary chemical bonds are indeed responsible for the strong adhesion.

In striking contrast to the strong self-adhesion developed in polybutadiene materials, no comparable effect was observed with natural or synthetic *cis*-polyisoprene. Indeed, the self-adhesion of crosslinked layers of natural rubber was found to be decreased somewhat by prior exposure to air. Now, it is well known that oxidative reactions lead to further crosslinking and hardening of polybutadiene vulcanizates, whereas, in contrast, they generally lead to softening of polyisoprene vulcanizates as a result of molecular scission.⁵⁻⁸ Thus, the observed adhesion phenomenon is wholly consistent with the development of interfacial bonding by means of oxidative processes in those polymers for which molecular interlinking is the principal result of oxidation. A possible reaction scheme is discussed later.

Samples of polybutadiene obtained at different times were found to respond quite differently to air exposure. It is thought that the antioxidants added to the material by the manufacturer may have been changed over a period of years. Even after extraction with hot acetone, however, the samples did not develop self-adhesion as rapidly, or to the same degree, as earlier samples. Either the added antioxidants are difficult to remove by this method or the new material is itself more resistant to oxidation. This aspect of oxidative interlinking needs further examination. It suggests that the process is strongly affected by minor changes in structure or composition.

Kinetics of Bonding

Initially, the strength of self-adhesion appeared to increase in direct proportion to the time t of prior exposure to air, Figures 2 through 4. The early stages of development of self-adhesion could therefore be described by two parameters—the intercept of these linear relationships at $t = 0$, representing the self-adhesion in the absence of any exposure to air, and the slope of the lines representing the rate of increase of self-adhesion with time of prior exposure. These values are listed in Table I.

The initial work of separation varied between about 10 and 100 J/m² for the various materials examined. (The same values were obtained in a nitrogen atmosphere.) They appeared to be inversely correlated with the degree of crosslinking so that the stiffer, more highly crosslinked materials exhibited generally lower values for the work W_a of separation at $t = 0$. This feature may be due in part to elastic stresses set up during contact, tending to separate the surfaces; in part to the effect of molecular network strand length on the adhesive strength under threshold conditions²; and in part to variations in mechanical hysteresis under the present experimental conditions. Although the range of initial self-adhesion values was relatively large and the subject clearly merits detailed study, it is not considered further in this investigation of oxidative effects.

As shown in Table I, the rates of increase in work of separation with the period of prior exposure to air were found to be surprisingly large in many cases. Easily

TABLE I
Initial Self-Adhesion and Initial Rate of Increase of Self-Adhesion with
Time t of Exposure to Air

Recipe (see Appendix)	W_a at $t = 0$, J/m ²	$\partial W_a / \partial t$ at $t = 0$, J/m ² -sec
Diene 35 NFA Polybutadiene		
Peroxide	8	0.3
EV Sulfur, 1% Agerite Resin D	28	0.6
EV Sulfur, 1% PBNA	18	0.06
Sulfur, no PBNA	35	0.5
Sulfur, 1% PBNA	90	0
Cis-4 Polybutadiene		
Peroxide	30	0.2
EV Sulfur, 1% Agerite Resin D	55	1.1
Natural Rubber		
Peroxide	27	-0.001
Natsyn 200 Polyisoprene		
Peroxide	15	0.001

measurable effects were observed after exposure times of only a few seconds at ambient temperature. Although the oxidation of unsaturated elastomers is known to be a facile reaction,⁵⁻⁸ the present materials do not undergo major changes in appearance or in bulk physical properties during several months of exposure to air at ambient temperature. The observed large effects of short periods of exposure to air on their self-adhesion are therefore quite unexpected.

It is noteworthy that similar effects are shown by both peroxide and sulfur recipes of both types of polybutadiene. Thus, neither a particular microstructure of the polybutadiene nor a particular type of crosslink is required for the development of interfacial bonds after prior exposure to air. There are some indications, however, that the process is more rapid with an EV sulfur recipe than with a peroxide recipe; and when the antioxidant phenyl- β -naphthylamine is employed, the crosslinking process takes place much more slowly, if at all.

As indicated in Table I, samples of *cis*-1,4-polyisoprene did not exhibit any comparable tendency to form interfacial bonds. Natural rubber samples tended to show a lower degree of self-adhesion after exposure to air, whereas synthetic *cis*-polyisoprene samples tended to show somewhat greater self-adhesion after exposure periods of a few hours. In both cases, however, the effects were much smaller than for the polybutadiene materials.

Some experiments were carried out to determine the rate at which interfacial bonding took place. As shown in Figure 5, the maximum degree of self-adhesion was attained relatively rapidly, within about 30 min after the elastomer layers were brought into contact, and it did not change significantly during several hours thereafter. As the bonding process is attributed to an oxidative reaction in the surface regions of the elastomer layers, any oxygen that has dissolved in these regions and is available to continue the reaction when the layers are brought into contact will be used up eventually and the bonding process will come to an end. Apparently the oxidative reaction only continues for about 30 min or so after the layers are joined together. This is comparable to the previous time of ex-

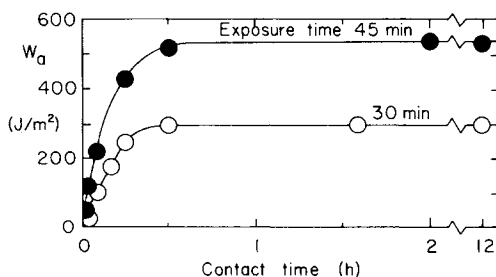


Fig. 5. Work W_a of separation vs. time of contact after exposure to air for 30 and 45 min. Cis-4 polybutadiene, crosslinked with 0.1% dicumyl peroxide.

posure to air. It indicates that the chemical reaction leading to interfacial bonding is a rather rapid one, even at ambient temperatures.

Contact Angle Measurements

In order to determine whether changes in the elastomer surface on exposure to air could be detected by other means, some measurements were made of the contact angles for small droplets of water placed upon the elastomer surface at various times after removing the Mylar cover sheet. The results are given in Table II. On exposure to air, significant decreases in the contact angle, by 4 to 7 degrees, took place within the first hour, followed by further small decreases during the next day. No comparable change was observed when the surfaces were exposed to a nitrogen atmosphere, indicating that the effect is again due solely to oxidation.

It is noteworthy, first, that this effect follows roughly the same time dependence as the development of self-adhesion discussed previously and, secondly, that it is readily observed in natural rubber (although somewhat smaller in magnitude), even though this material did not develop any self-adhesion after exposure to air. Thus, an oxidative reaction appears to take place readily in the surface regions of all the elastomers, as revealed by corresponding changes in the contact angle θ , but it only results in strong adhesion for the polybutadiene

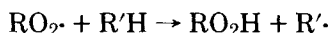
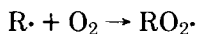
TABLE II
Changes in Water Contact Angle θ with Time t of Exposure to Air or to Nitrogen

t , hr	θ air, degrees	θ nitrogen, degrees
Diene 35 NFA Polybutadiene (Peroxide Recipe)		
0	88.9 ± 1.4	88.9 ± 1.4
1	82.5 ± 1.5	—
3	—	88.2 ± 2.0
24	80.6 ± 3.3	87.8 ± 1.8
120	80.8 ± 2.6	—
Cis-4 Polybutadiene (Peroxide Recipe)		
0	91.0 ± 2.0	—
1	83.8 ± 2.1	—
24	82.0 ± 2.5	—
Natural Rubber (Peroxide Recipe)		
0	89.2 ± 1.5	—
1	85.2 ± 2.7	—
24	84.2 ± 1.6	—

materials. This suggests that interfacial bonding is due to a particular feature of the oxidation of polybutadiene materials, not shown by polyisoprene. One particular mechanism is outlined below.

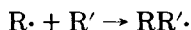
Proposed Interfacial Bonding Mechanism

Oxidation of polyolefins is reported to involve two main propagation steps⁵⁻⁸:



In the first, a polymer radical reacts with oxygen to form the peroxy radical which, in the second step, abstracts H from a nearby group to form a hydroperoxide and a second radical. Moreover, the hydroperoxide itself decomposes slowly, generating further radical species, so that the process is autocatalytic.

Now, this general reaction scheme does not account for hardening during oxidation. Another reaction must therefore be invoked—the addition of polymer radicals to other polymer molecules to form intermolecular bonds:



This reaction is known to occur in polybutadiene by addition to the C–C double bond but not to a significant degree in polyisoprene where the radicals appear to be less reactive. It can thus account for the interfacial bonding observed with polybutadiene but not with polyisoprene. Moreover, it will become of proportionately greater importance as the concentration of oxygen becomes lower, i.e., as oxidation continues in the interfacial region after the elastomer layers have been brought into contact. We therefore infer that the observed adhesion is due to the attack of polymer free radicals generated during oxidation upon molecules lying on the other side of the interface to bring about covalent interlinking.

CONCLUSIONS

The following general conclusions are obtained:

1. Exposure to air at ambient temperature causes a surprisingly rapid oxidation of the surface of polybutadiene and polyisoprene layers. This reaction causes a marked decrease in the contact angle of water within 1 hr.
2. When layers of polybutadiene are brought into contact during this oxidation reaction, interfacial bonds are formed and the layers become firmly adhered together. A significant increase in adhesion can be detected after exposure to air for only 1 min or less.
3. When the surface oxidation is substantially complete (after several hours in the samples studied here), the surfaces no longer adhere strongly together when they are brought into contact.
4. Samples of polyisoprene also undergo surface oxidation but do not adhere strongly together.
5. The bonding reaction in polybutadiene is attributed to macroradicals generated during oxidation which add to C–C double bonds in molecules lying across the interface and form covalent interfacial bonds.
6. The bonding reaction is highly sensitive to the presence of certain antiox-

idants. It was much slower and less pronounced when phenyl- β -naphthylamine was incorporated, for example.

APPENDIX

The following materials, mix recipes, and reaction conditions were employed for preparing test sheets.

Elastomers

The elastomers used were (a) polybutadiene, having *cis*-1,4, *trans*-1,4, and 1,2 contents of about 36, 54, and 10%, respectively (Diene 35 NFA, Firestone Tire and Rubber Company); (b) polybutadiene containing about 92% *cis*-1,4 units (Cis-4 1203, Phillips Petroleum Company); (c) *cis*-1,4-polyisoprene (Natural Rubber, Standard Malaysian Rubber 5); and (d) *cis*-1,4-polyisoprene (Natsyn type 200, Goodyear Tire and Rubber Company).

Peroxide Recipes

Dicumyl peroxide was added to each elastomer in the following amounts by weight: 0.05% with Diene 35 NFA, 0.1% with Cis-4 polybutadiene, and 1.0% with both types of *cis*-polyisoprene. Crosslinking was effected by heating for 2 hr at 150°C for the polybutadiene mixes and 1.5 hr at 150°C for the polyisoprene mixes.

Sulfur Recipes

Two recipes based on sulfur as the crosslinking agent were used.

1. EV (efficient vulcanization) sulfur recipe, parts by weight: elastomer, 100; zinc oxide, 5; zinc 2-ethylhexanoate, 2; 2-morpholiniothiobenzothiazole, 0.72; tetrabutylthiuram disulfide, 0.3; sulfur, 0.3; phenyl- β -naphthylamine or Agerite Resin D (R. T. Vanderbilt Company), 1. Crosslinking was effected by heating for 40–50 min at 140°C.
2. Regular sulfur recipe, parts by weight: elastomer, 100; zinc oxide, 5; stearic acid, 2; benzothiazyl disulfide, 1; tetramethylthiuram disulfide, 0.1; sulfur, 2.75; phenyl- β -naphthylamine, 1. Crosslinking was effected by heating for 80 min at 150°C.

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