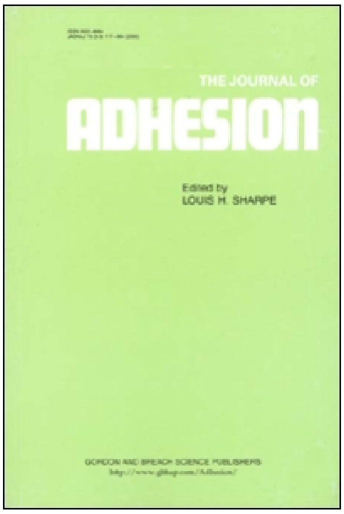

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Elastomer–Elastomer Interfaces: Mechanisms of Autohesion*

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Elastomer–elastomer joints are a special case of polymer bonding. Interfacial adsorption, molecular interdiffusion, and entanglements, as well as chemical bonding, are the different mechanisms which intervene in adhesion phenomena. Their relative contribution is not well known and depends on many parameters. If the formation of a thick, interdiffused interface may be important in order to get a strong interface, covalent bonding is often necessary and can occur even though no interdiffusion takes place. In this paper, we are interested in the **autohesion** mechanism of two elastomers (PI and SBR) for which the mobility and the reactivity have been reduced before assembly. The peel test in air and liquid medium helped us to understand the role of the different contributions.

KEY WORDS: autohesion; interdiffusion; chemical bonding; peeling; polyisoprene; styrene butadiene copolymer.

INTRODUCTION

Interfacial adsorption, molecular interdiffusion, and entanglements, as well as chemical reactions, are the different mechanisms which may intervene in elastomer autohesion. The precise contribution of each of these mechanisms depends on *many parameters such as*, for instance, molecular weight of the polymer and its microstructure, and the bonding conditions (time, temperature, pressure). When the elastomer sheets are not crosslinked before contact, the interface eventually disappears so that the strength of the interface finally reaches the cohesive strength of the bulk according to the diffusion theory proposed by Voyutskii[1] and completed by different authors[2–3].

Gent *et al.*[4–5] have shown that the threshold work of detachment is related linearly to the amount of interfacial bonding developed during covulcanization of the elastomer sheets. This relationship is valid over the entire range of interactions going from purely Van der Waals' attractions up to covalent bonds for different elastomer combinations, with the exception of a sulfur-cured EPDM system. The curing system does not seem to be the pertinent parameter according to the results obtained for polybutadiene crosslinked with sulfur. However, the effect of the curative formulation

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has been demonstrated by Zapp[6], who established that covulcanized networks are associated with a preponderance of monosulfide links formed during the initial stage of vulcanization. The rearrangement of the polysulfidic bonds during further heating does not lead to strong interfacial resistance if no monosulfide links are originally present.

Addition of reinforcing fillers to the polymer reduces the mobility of the macromolecules and, therefore, should reduce the interdiffusion of the chains through the interface. The amount, as well as the surface properties, of the carbon black fillers added can explain the different behaviors which have been observed[7-8]. In this study, the evolution of the **autohesion** of two carbon black filled elastomer systems, cured with sulfur, was controlled by the state of cure before bonding according to the procedure used by Gent *et al.*[4-5]. The interface strength obtained by a peel test in air and in liquid medium (non-swelling and nonreacting liquid) was measured in order to aid in the understanding of the interfacial mechanisms.

EXPERIMENTAL

The autohesion of the following systems was studied: a styrene-butadiene copolymer (SBR), obtained by a solution process and containing about 26% of styrene, on the one hand, and a polyisoprene rubber (PI) with a high amount of *cis* 1–4 units, on the other hand. Both elastomers contained carbon black and were crosslinked by sulfur according to the recipe given in Table I. Two temperatures of curing, 126 and 150 °C, were investigated.

Before bonding, the elastomer sheets were partially and separately crosslinked to various extents by changing the curing time in a heated press. In order to avoid extension of the peeled parts of the assembly, a synthetic backing consisting of polyamide and Kevlar® fibers was added to each sheet before crosslinking. On the other side of the sheet, the elastomer was protected by a thin poly(ethylene terephthalate) film. The samples were quenched in iced water in order to ensure a reproducible state of pre-crosslinking. Then, two sheets of the same elastomer and of the same degree of crosslinking were brought into contact very quickly after the pulling off the PET film. This assembly was placed in the heated press until completion of the reaction of vulcanization. The pressure during both pre-crosslinking and crosslinking stages is equal to 2MPa.

This procedure leads to symmetrical and homogeneous joints and the interfacial stresses are minimum. Moreover, the peel energies can be compared because the final

TABLE I
Formulation for vulcanizates

Elastomer	100
Carbon black N347	50
Stearic acid	1.5
Antioxidant (6-PPD)	1.5
Sulfur	1
Accelerator (CBS)	1
Zinc oxide	4

properties of the elastomer are identical whatever the degree of crosslinking before contact.

Due to the fact that filled elastomers are considered, the state of cure was estimated from swelling measurements in cyclohexane without calculating molecular weights between crosslinks. The degree of conversion of the vulcanization reaction, α, was defined as the swelling ratio after t min at the given temperature to the value corresponding to optimum curing.

A 180° peel test was used to evaluate the performance of the elastomer joints. The results presented here were obtained at room temperature and peel rates between 0.05 and 25 mm/min. The principle of the peel test in liquid medium[9-10] was applied. The variation of the peel strength occurring in the presence of a liquid which does not modify the bulk properties of the elastomer by swelling or reaction and does not change the locus of the failure is equal to the variation of the reversible energy of adhesion or cohesion. If one considers that:

$$\Delta\mathscr{W} = \mathscr{W}_L - \mathscr{W} \quad \text{and} \quad \Delta W = W_L - W$$

where the first equation corresponds to the variation of the reversible energies of adhesion in liquid ($\mathscr{W}_L$) and air ($\mathscr{W}$) and the second one to the measured energies of separation in liquid (W_L) and air (W).

According to the Gent and Schultz relationship between the measured energy and the reversible energy of adhesion[11], it is possible to write:

$$\frac{\Delta W}{W} = \frac{\Delta\mathscr{W}}{\mathscr{W}}$$

If this equation is verified, it can be assumed that only physical interactions are present at the interface. When the two ratios are different, it is possible to calculate a chemical contribution to the measured energy.

If one assumes that the chemical interactions are not affected by the liquid, the reversible energies of adhesion (in the case of autohesion) in air and liquid can be written as the sum of the physical and chemical contributions as follows:

$$\mathscr{W} = 2\gamma_s + \mathscr{W}_{\text{chem}} \quad \text{and} \quad \mathscr{W}_L = 2\gamma_{sL} + \mathscr{W}_{\text{chem}}$$

The chemical contribution is then calculated from:

$$\varphi_{\text{chem}} = 1 - \frac{2\gamma_s}{\mathscr{W}}$$

It is, however, not possible to distinguish between the failure of a covalent bond established during covulcanization of the two rubber sheets from the failure of an interdiffused and entangled chain which is not extracted. The influence of the peel rate, the temperature of the test or the presence of a swelling liquid have to be examined.

RESULTS AND DISCUSSION

As expected according to the viscoelastic properties of the materials, the energy of peeling increases with increasing rate of peeling for both systems. In Figure 1 are given

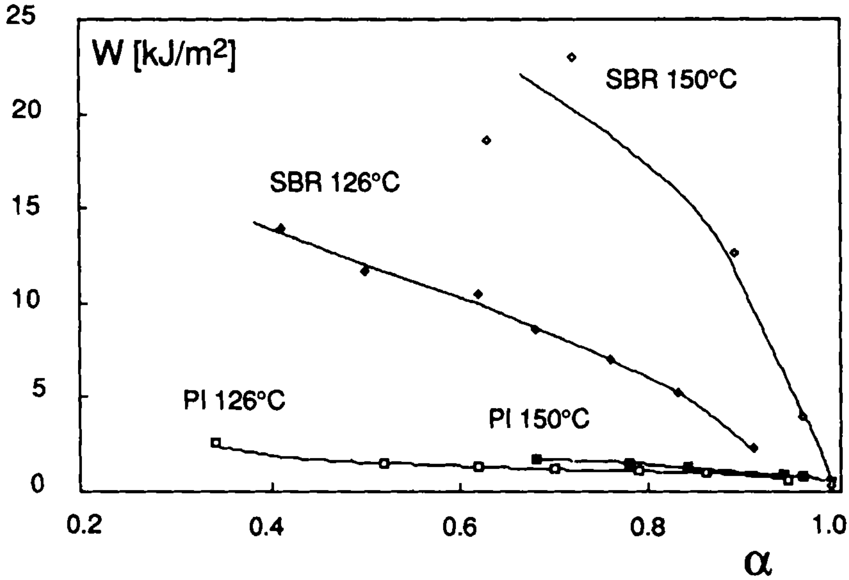

FIGURE 1 Peel energies at room temperature and at a peel rate of 5 mm/min for joints obtained at 126 and 150 °C.

the results of the peel test at room temperature and a separation rate equal to 5 mm/min as a function of the state of cure before bonding expressed by α. The maximum measured energy depends on the limited strength of the backing material. It was not possible to find any material strong enough and flexible enough to cover the whole range of degree of crosslinking for these filled polymers.

The overall higher peel values obtained for SBR can be related to the dissipation properties of this elastomer compared with PI. At room temperature, the loss modulus of SBR is about twice that of PI, whereas the elastic moduli are of the same order of magnitude. However, interesting differences can be observed. The effect of the temperature of crosslinking is very important for SBR. On the contrary, the dependence is very weak for PI. This effect cannot be explained by a difference in bulk properties due to the curing temperature. Indeed, the dynamic mechanical properties are about the same whether the samples are cured at 126 or 150 °C. It should, nevertheless, be noted that the lowest degrees of pre-crosslinking for which peeling at room temperature was made possible are affected by the curing temperature: about 0.4 when the vulcanization occurs at 126 °C compared with about 0.6 for a vulcanization temperature of 150 °C for both systems. This means that below these values the peel strength increases drastically.

If testing at higher temperatures helped to widen this range for SBR assemblies (α equal to 0.3 could be reached at 80 °C), this parameter was quite ineffective for PI. The peel energy drastically increased after a smooth variation with α. The peel forces are almost identical for peel temperatures equal to 0, 21 and 40 °C over the studied range of peel rates. This behavior may be related to strain-induced crystallization phenomena as already observed by different authors[12–13]. Moreover, it should be noted that the locus of failure for the PI joints is either interfacial (in this case, both peeled parts look smooth with a glossy aspect) or cohesive (the separation leads to a more or less rough surface) when W is higher than about 5 kJ/m^2. At room temperature, this was seen only for peel rates above 2.5 mm/min. A slip-stick type of failure is only observed for SBR joints when W is between about 7 and 15 kJ/m^2 which means that the peel force oscillates between a minimum and a maximum value; both aspects described for PI joints are observed alternately. Below 7 kJ/m^2, the failure was interfacial and above 15 kJ/m^2, it was cohesive.

In Figure 2, the separation energy is plotted as a function of peel rate at room temperature in air and in ethanol for two samples. For the higher peel rates ($V_p > 10$ mm/min), the curve corresponding to ethanol meets the one corresponding to

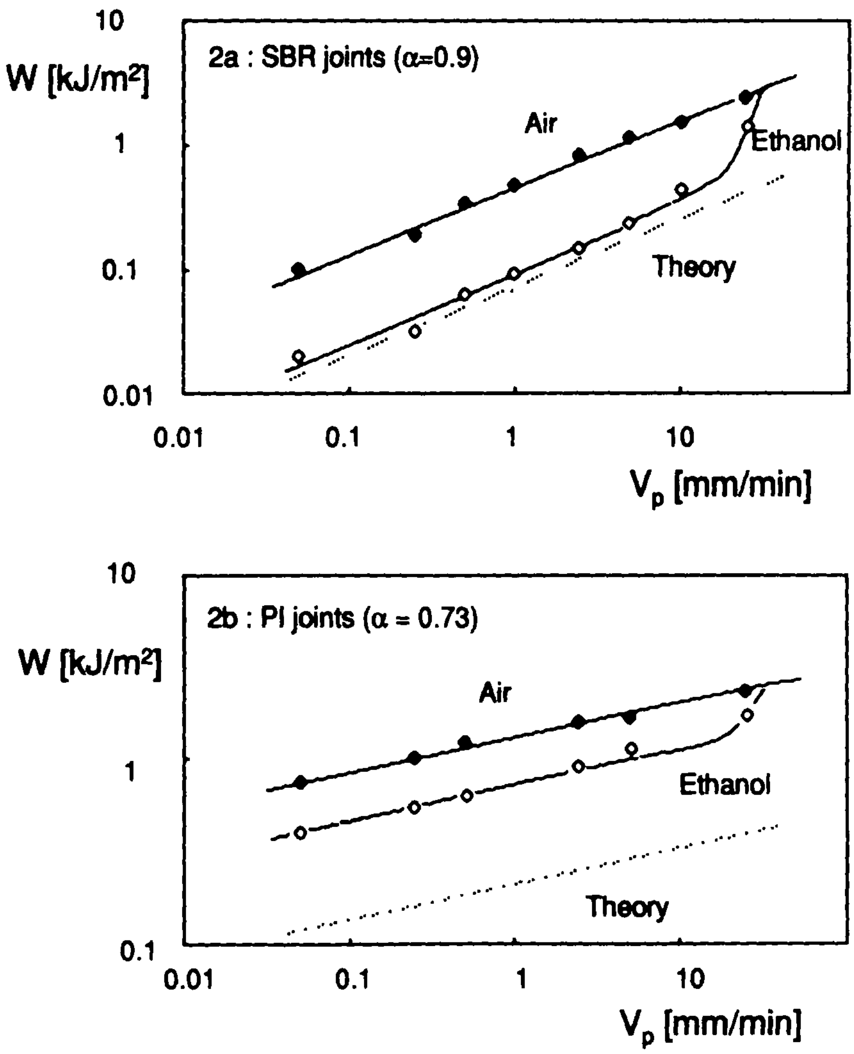

FIGURE 2 Peel energy as a function of peel rate, V_p, for two media: air and ethanol.

air due to the fact that the liquid is not present anymore at the peel front. But for lower peel rates, the decrease of the peel energy is in agreement with the decrease of the reversible energy of adhesion as shown in Figure 2a or smaller than it as in Figure 2b. From these variations the chemical contribution, φ_{chem}, can be calculated knowing the surface free energy, γ_s, of both elastomers. Wettability measurements with liquids of different polarities lead to the following values: for SBR, γ_s is equal to 31 mJ/m^2, whereas it is slightly higher for polyisoprene (34 mJ/m^2). No significant effect of the degree of cure or the temperature of cure was noted.

Figure 3 shows the chemical contribution, φ_{chem}, for PI and SBR joints as a function of the degree of crosslinking before assembly. Before analysing these results, it should be noted that similar results are obtained for other liquids such as isopropanol and silicone oil of low viscosity (1.7 cP). Distinct behaviors are observed for these assemblies. For SBR joints (Fig. 3b), when almost all crosslinking agent has reacted ($\alpha > 0.9$) before the two layers of elastomers are brought into contact, only physical interactions are responsible for the interfacial strength: φ_{chem} is equal to zero for both temperatures of reaction. For lower degrees of crosslinking ($\alpha < 0.9$) and a temperature of vulcanization of 150 °C, the chemical contribution increases progressively. For 126 °C, it is not possible to draw a conclusion because the presence of the liquid changes the locus of failure and the principle of the peel test in liquid medium no longer applies. Again, no significant influence of the temperature of reaction is observed for PI: similar chemical contributions are determined for both temperatures. The value is quite constant over a wide range of $\alpha (0.5 < \alpha < 0.9)$. However, even for degrees of crosslinking close to the optimum, this contribution is not negligible (about 10%). In these conditions ($\alpha > 0.9$), no free sulfur is left in the layers that are assembled. Therefore, only chain interdiffusion can be responsible for the observed phenomena. According to Zapp[6], the maturation of the polysulfidic links should not intervene.

Both mechanisms intervening in the formation of the interface, diffusion of the polymer chains and rate of co-crosslinking at the interface, are dependent on temperature. The distinction between the failure of interdiffused chains, the extraction of these chains and the rupture of a covalent bond formed during covulcanization is not possible at this point. However, an interesting complementary observation can be commented on. Sheets partially crosslinked to various extents at 150 °C were put into contact for 5 min at a pressure equal to 0.55 MPa without further heating. It was considered that this time was sufficient to establish intimate contact. The peel force was then measured for a peel rate equal to 2.5 mm/min in air and ethanol. The absolute values of peeling are not comparable because the bulk properties are not the same at different states of cure and, therefore, the dissipated energy is different. However, the ratios $\Delta W/W$ can be compared. Table II gives the results as a function of α for SBR and PI joints.

No chemical bonding can occur in these conditions. The variation of the peel strength can, therefore, only be attributed to interdiffusion phenomena. The theoretical variation of the reversible adhesion for both systems is of the order of 85%. For α values higher than 0.8, the interdiffusion process at room temperature and for the conditions of contact is negligible for PI, whereas it is significant for lower values. For α equal to about 0.8 and less, the behavior in liquid media shows that interdiffusion phenomena and probably chain entanglements occur at the interface in PI joints. The

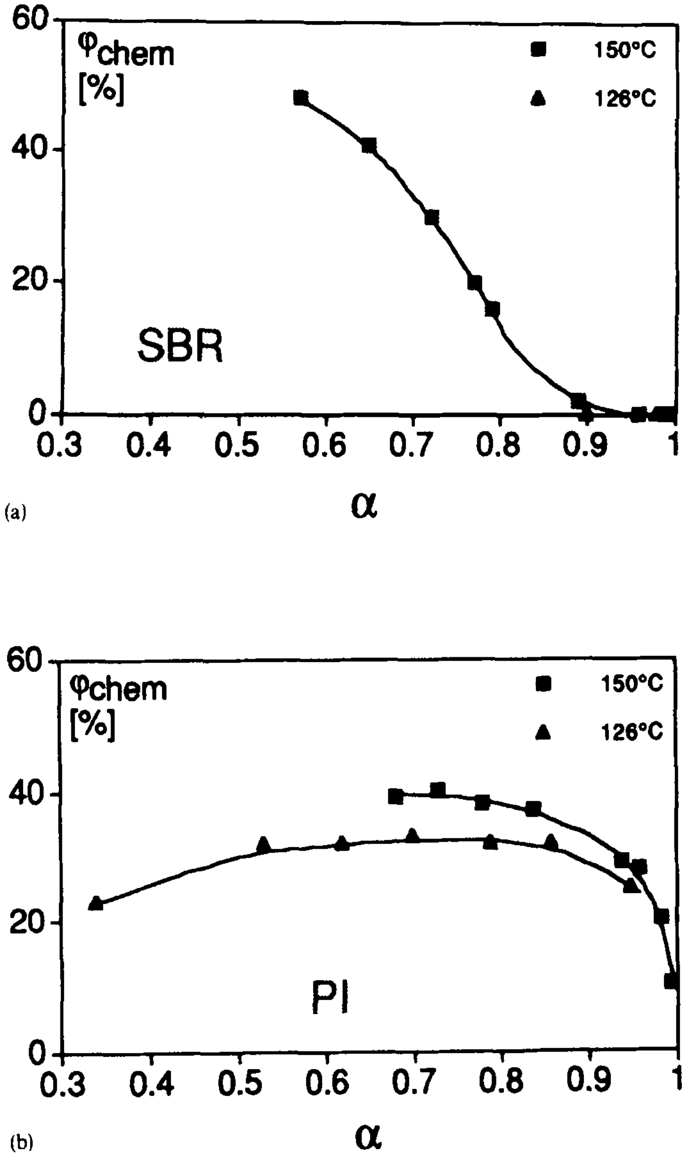

FIGURE 3 Chemical contributions to the adhesive strength for SBR (3a) and PI (3b) joints as a function of the conversion ratio of the crosslinking reaction before bonding.

variation observed for SBR joints corresponds to quasi-spontaneous delamination of the joint in the presence of the liquid. Therefore, contrary to what is observed for PI, only physical interactions are established in the whole range of α values studied for SBR. Nevertheless, for α equal to 0.3 and peel rates higher than 2.5 mm/min, the experimental variation of the peel energy is much lower than the expected 85%. It is then possible to assume that diffusion of chain ends or short chains may occur. These

TABLE II
Variation of the peel energy as a function of the degree of crosslinking for non-fully-cured elastomers

α	0.99	0.85	0.8	0.7	0.6	0.5	0.3
PI $\Delta W/W[\%]$	81	77	72	28	0		
SBR $\Delta W/W[\%]$	95	94	95	96	96	96	96

slightly interdiffused chains can be extracted at low peel rates but not at higher ones. The fundamentally different behaviors of these two elastomers is evidenced again. These results can be compared with those obtained by Skewis[14] and Hamed and Shich[15] showing that natural rubber has better tack than SBR.

CONCLUSION

The study of the interfacial strength of two elastomer sheets partially crosslinked before bonding has shown that adsorption phenomena and chemical bonding is occuring. The mobility of the SBR chains is lower and interdiffusion phenomena are quite limited in the range of degrees of crosslinking which could be studied. For PI, this contribution is much more important and is even possible for sheets of degrees of cure close to the optimum. It has been shown that peel tests in air and liquid media are able to contribute very useful information for the interpretation of the nature of the interactions at polymer interfaces, even in the difficult case of autohesion.

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References

1. S. S. Voyutskii, *Autohesion and Adhesion of High Polymers* (Interscience, NY, 1963).
2. P. G. de Gennes, *J. Chem. Phys.*, **55**, 572 (1971).
3. R. P. Wool, and K. M. O. Connor, *J. Appl. Phys.*, **52**, 5953 (1981).
4. R. J. Chang, and A. N. Gent, *J. Polymer Sci., Polymer Phys. Ed.*, **19**, 1619 (1981); **19**, 1635 (1981).
5. M. D. Ellul, and A. N. Gent, *J. Polymer Sci., Polymer Phys. Ed.*, **22**, 1953 (1984).
6. R. L. Zapp, *Rubber Chem. Technol.*, **46**(1), 251 (1973).
7. J. Kurian, G. B. Nando, P. P. De, A. K. Bhattacharya, and S. K. De, *J. Adhesion Sci. Technol.*, **2**(1), 21 (1988).
8. V. G. Raevsky, *Adv. Coll. Interf. Sci.*, **8**, 1 (1977).
9. A. Carré, and J. Schultz, *J. Adhesion*, **18**, 171 (1984).
10. M. F. Vallat, and M. Nardin, *J. Adhesion* (1995), in press.
11. J. Schultz, and A. N. Gent, *J. Chim. Phys.*, **70**(5), 708 (1973).
12. T. L. Smith, *J. Appl. Phys.*, **35**, 27 (1964).
13. R. G. Stracer, E. D. von Meerwall, and F. N. Kelley, *Rubber Chem. Technol.*, **58**, 913 (1985).
14. J. D. Skewis, *Rubber Chem. Technol.*, **39**, 217 (1966).
15. G. R. Hamed, C. H. Shich, *Rubber Chem. Technol.*, **59**, 883 (1986).