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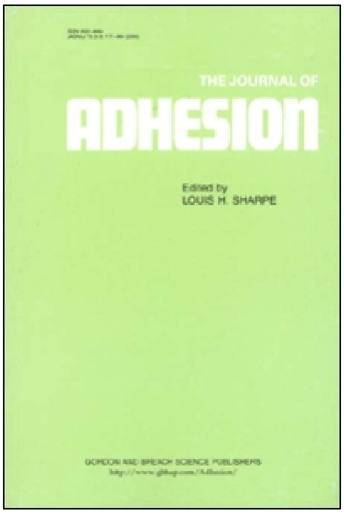

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Comparison of the Adhesion and Cohesion of Triblock and Random Copolymers of Styrene and Butadiene

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Comparison of the Adhesion and Cohesion of Triblock and Random Copolymers of Styrene and Butadiene

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A substantially greater detachment energy is required to strip a polyethylene terephthalate (Mylar) film from a styrene-butadiene-styrene (SBS) triblock copolymer compared to that for peeling from a random styrene-butadiene (SBR) copolymer. This is true even though the intrinsic interaction between the Mylar and each elastomer is expected to be similar because of their virtually identical chemical composition. It is proposed that this difference in peel strength (between the SBS and SBR) is a consequence of the much higher dissipative capacity of the former elastomer. Another manifestation of this is the higher cohesive tear strength of the SBS compared to the SBR. Extents of energy dissipation within each elastomer during detachment of the Mylar adherend are consistent with the hypothesis that the average maximum stress experience before detachment is some similar fraction of each elastomer's tensile strength.

INTRODUCTION

In a previous publication,[1] it was shown that the adhesion of an SBS triblock copolymer to a simple Mylar adherend was substantially greater than that of a lightly crosslinked random SBR to the same adherend. This was true even though the two copolymers had a similar proportion of styrene and butadiene. Because of their similar chemical composition, it is expected, for equilibrium bonding, that the interfacial interaction between each elastomer and the Mylar is alike. After all, in both cases, the interaction is due to van der Waals attractions between butadiene and styrene units of the elastomer and the polyethylene terephthalate surface. Certainly, it is not expected that the inherent interaction across the interface would differ by 1–2 orders of magnitude as does the work of adhesion to detach these elastomers from Mylar.[1] Why, then, does the SBS polymer require so much more energy for detachment from the Mylar compared to the SBR copolymer?

It is well-known that the strength of an adhesive joint depends not only on the intrinsic interaction across the interface, but also on the ability of the joint members to dissipate mechanical energy into heat.[2–10] If large amounts of mechanical energy are dissipated while stressing an adhesive joint, then this will be reflected by an enhancement in the energy that must be supplied to fracture the joint. Indeed, when peeling apart a joint consisting of flexible stripping members and a rubbery adhesive (at typical rates and room temperature), the peel force is a *direct* measure of the extent of energy dissipated during fracture.

The previous question may now be restated. Why, when stripping a Mylar film from an SBS copolymer, is substantially more energy dissipated than when the Mylar is stripped from an SBR copolymer (especially since the intrinsic interfacial interaction is apparently not that different)? It is the primary purpose of this paper to shed some light on this question.

MATERIALS AND EXPERIMENTAL

The elastomers used in this study were both styrene-butadiene copolymers containing about 35% styrene:

1) Kraton 1101—SBS triblock copolymer, supplied by Shell Chemical Company.

2) Ameripol 1513—random SBR copolymer, supplied by the B. F. Goodrich Company.

Each was used as received from the manufacturers. When desired, dicumyl peroxide (Dicup R, Hercules, Inc.) was added to a rubber on a laboratory 2-roll mill. All tests with the SBR copolymer were carried out on lightly crosslinked samples containing 1.0% dicumyl peroxide. The stripping member was Dupont Mylar A (polyethylene terephthalate) film with a thickness of 76 μm.

Testpiece preparation

Testpieces were prepared by applying heat (150°C) and pressure for 60 minutes to the set-up shown in Figure 1. The lower surface of the rubber layer was bonded to a steel plate with a Chemlock (Lord Corp.) adhesive in order to prevent failure at this interface during the later peel testing. The rubber layer thickness (0.5 mm) was controlled by a spacer plate.

After molding, 25 mm wide strips were cut for testing. An Instron test machine was used to measure bond strengths at various peeling rates. The test geometry used in this study is illustrated in Figure 2. The rubbery layer remained flat as the Mylar was peeled at 180°.

Tear strengths were determined using a simple trouser tear geometry[11] to fracture a strip 0.5 mm thick. Tensile properties were measured in accordance with ASTM D 412 at a strain rate of 20 min^{-1}.

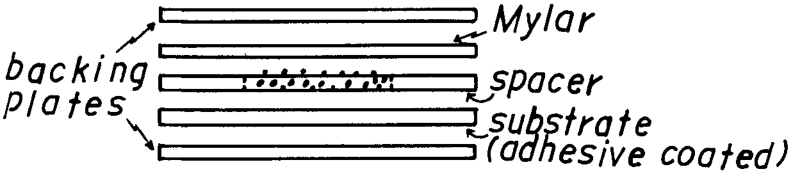

FIGURE 1 Molding arrangement for test piece preparation.

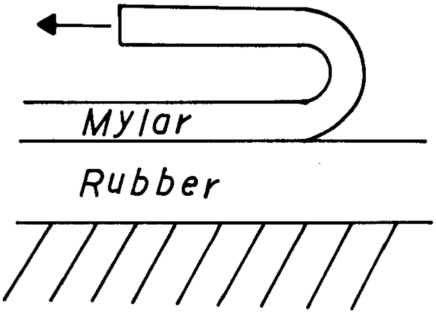

FIGURE 2 180° peel test geometry.

RESULTS AND DISCUSSION

Figure 3 shows the detachment energy as a function of peeling rate

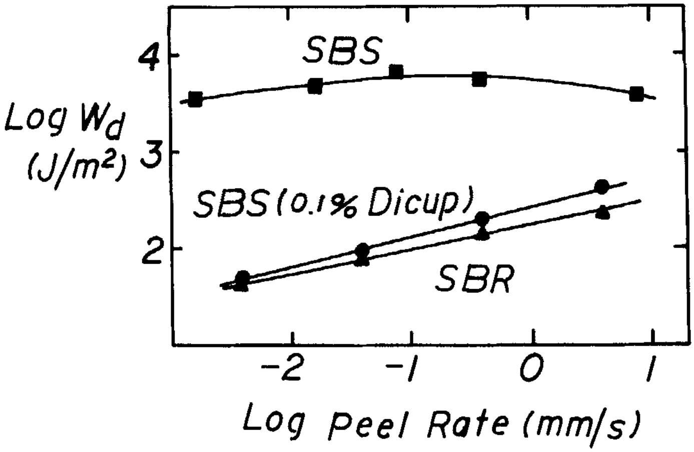

FIGURE 3 Comparison of the work of detachment of Mylar stripped from SBS, SBS (0.1% Dicup) and SBR.

needed to strip a Mylar film from either an SBS or SBR layer. In all cases, failure was interfacial between the rubber and Mylar. The detachment energy of the SBS is much greater than that of the SBR. As stated previously, it seems reasonable to assume that the intrinsic interaction across the interface is similar in the two cases. Certainly, it is not expected that the intrinsic interaction would differ by two orders of magnitude as does the work of detachment at lower rates. It is proposed that the higher detachment work is a consequence of the higher dissipative capacity of the triblock copolymer.

Consider the somewhat analogous problem of the tear strength of the SBS and the SBR copolymer. The intrinsic molecular interactions that existed across the fracture plane (before tearing) is likely similar in the two cases, consisting primarily of carbon-carbon covalent bonds (which are ruptured during fracture) in each case. However, the SBS copolymer has a much higher tear energy (Figure 4)—a consequence of its *supermolecular* structure. If interfacial bonding were sufficiently strong to cause cohesive failure of the rubbers upon peeling in both cases, then the triblock would obviously exhibit the greater peel force. Let's define γ_o as the critical level of interaction (between the rubbers and Mylar) just sufficient to result in rubber tear during peeling rather than clean interfacial separation from the Mylar. It is assumed that γ_o is similar for both elastomers. For a surface

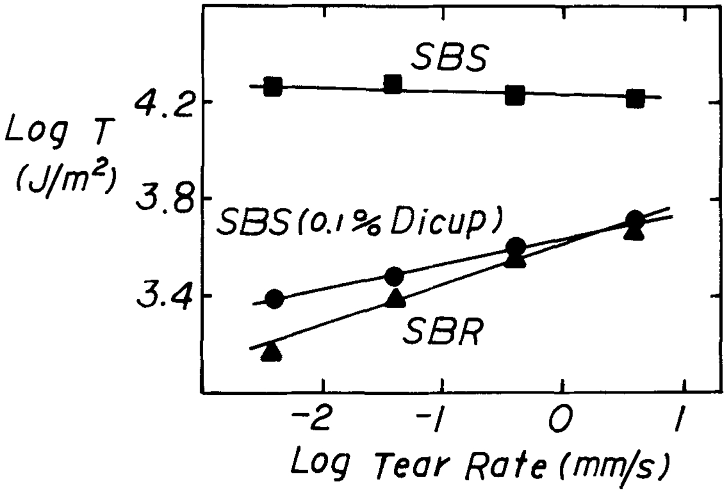

FIGURE 4 Comparison of the tearing energy of SBS, SBS (0.1% Dicup) and SBR.

interaction $\gamma < \gamma_o$, it appears that the block copolymer dissipates more energy when deformed, resulting in a higher peel force.

From hysteresis tests performed in tension, it is found that about 60% of the input energy is dissipated upon cyclic deformation of the SBS triblock, whereas only 32% is dissipated by the SBR copolymer. Therefore, qualitatively, the adhesive peel strengths and the cohesive tear strengths for the two rubbery layers have the same ranking as their fractional energy dissipated during cyclic deformation. Quantitatively, however, there is a much greater difference in the peel or tear energies of the two elastomers than can be accounted for just by differences in this fractional energy dissipation. Energy dissipated while peeling Mylar from SBS *must* be one to two orders of magnitude (depending on rate, Figure 3) greater than that when peeling Mylar from the SBR copolymer. In order for this to be possible, it is necessary that the maximum stress before detachment is greater for the SBS compared to the SBR (just as the tensile stress before rupture is greater for the SBS compared to the SBR, Figure 5). This is apparently true even though γ is expected to be similar in both cases.

At first, it may seem counter-intuitive that for the same interfacial interaction one material can sustain a greater stress before detachment compared to that of another material. However, it must be remembered

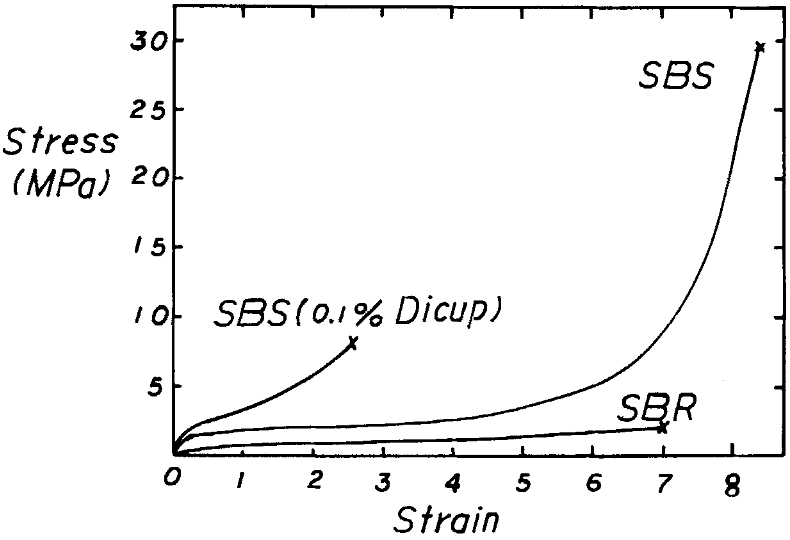

FIGURE 5 Stress–strain curves of SBS, SBS (0.1% Dicup) and SBR. Crosses denote breaking points.

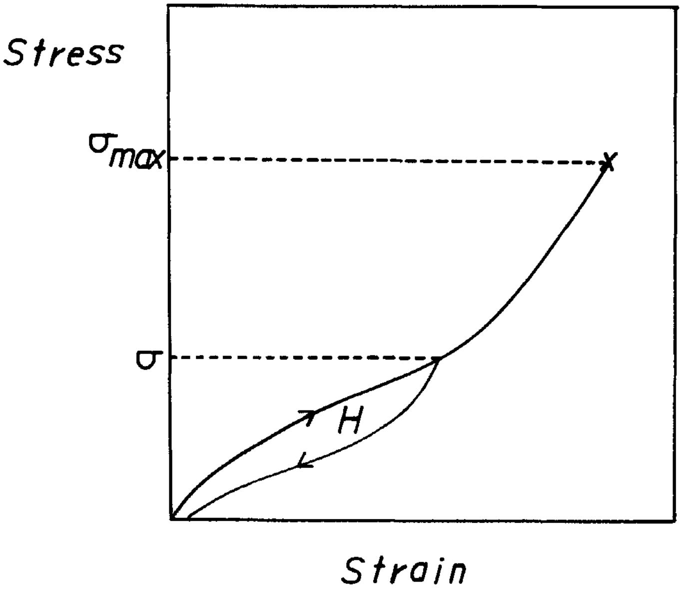

FIGURE 6 Schematic diagram illustrating hysteresis during a cyclic tensile test.

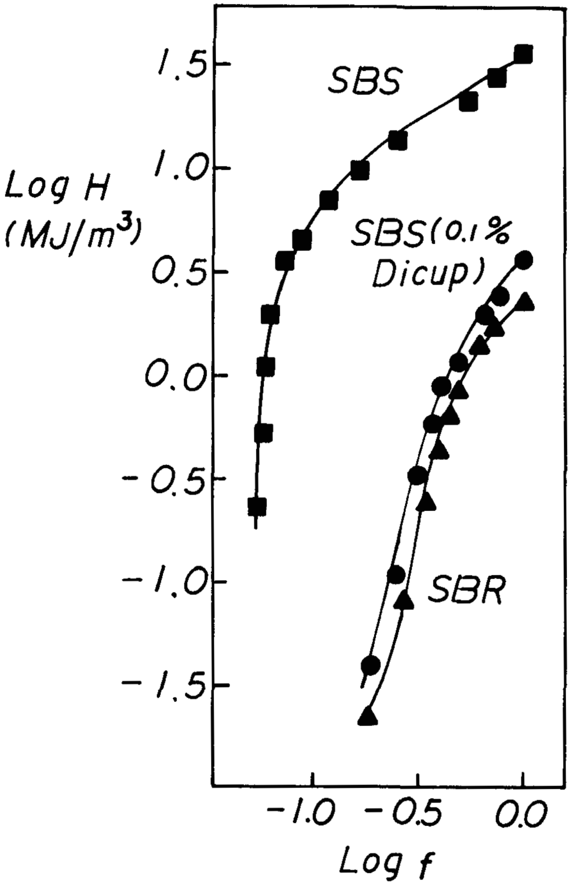

FIGURE 7 Hysteresis of SBS, SBS (0.1% Dicup) and SBR as a function of the fraction of the maximum tensile strength obtained (for each material) while cycling.

that the strength of an adhesive joint (or material) depends not only on the intrinsic interaction that existed across the failure plane (before fracture), but also the ability of the joint members to dissipative mechanical energy and thereby delay the onset of crack growth. It is this great difference in the dissipative capacity of materials that leads to major differences in joint strengths (in spite of interfacial energies differences that are relatively small).

Perhaps the average maximum stress in the rubber before adhesive detachment in each case is some similar fraction *f* of each elastomer's maximum stress σ_b before tensile rupture. *This hypothesis is only likely to be valid if the inherent interaction γ at the rubber–Mylar interface is similar for both types of elastomer*, as seems reasonable here. Other elastomers with a *different* chemical nature (such that they would interact to a greater or lesser extent with the Mylar surface) would not be expected to detach at the same f that it is suggested the SBR and SBS materials do.

The large differences in peel energies for the SBS and SBR copolymers can be explained by examining differences in the dissipative properties of each elastomer as a function of the maximum stress experienced during a cyclic deformation (*e.g.*, while peeling). Let's consider the amount of energy dissipated within each elastomer during cyclic deformations in tension to various stresses σ. This is shown schematically in Figure 6. The hysteresis values H are plotted as a function of f ($f = \sigma/\sigma_b$) in Figure 7 for both the SBR and the SBS. Note that the values of H for the various values of f of the SBS and SBR differ by a factor of 10 to 100. Significantly, the ratios of the SBS-Mylar bond strengths to the SBR-Mylar bond strengths are also in the range 10–100 (Figure 3). Thus differences in the energy dissipated during peeling for the two elastomers are quantitatively consistent with the assumption that each elastomer detaches from the Mylar at some similar fraction f of its maximum tensile strength.

This hypothesis is further confirmed by results obtained when the adhesion of Mylar to SBS crosslinked with a very small (0.1% Dicup) amount of peroxide is measured. This minute amount of Dicup addition is not expected to significantly change the intrinsic interaction between the SBS and the Mylar. The stress–strain response of the crosslinked SBS is also shown in Figure 5. Lightly crosslinking the SBS changes the shape of its stress–strain curve—removing the yield plateau, increasing modulus and substantially reducing stress and strain at break.

In addition, as shown in Figures 3 and 4, the adhesion of the SBS to Mylar and its cohesive tear strength are markedly reduced after light crosslinking. In fact, the modified SBS shows adhesive and cohesive strengths comparable to those of the SBR. This is true even though their stress–strain curves are quite different. However, the energy dissipative capacities of these two materials are quite similar as shown in Figure 7. That is, values of H *vs* f are about the same.

Thus, when the dissipative properties of the materials are similar, then their adhesive and cohesive strengths are also similar. Again, it is important to keep in mind for the adhesive failure case that this is expected to be true only for materials that have approximately the same intrinsic interaction with the adherend.

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References

1. A. N. Gent and G. R. Hamed, *Rubb. Chem. Technol.* **51**, 354 (1978).
2. A. N. Gent and R. Petrich, *proc. Roy. Soc.* **A310**, 433 (1969).
3. A. N. Gent and G. R. Hamed, *Polym. Engr. Sci.* **17**, 462 (1977).
4. A. N. Gent and G. R. Hamed, *J. Appl. Polym. Sci.* **21**, 2817 (1977).
5. A. N. Gent and G. R. Hamed, *Rubb. Chem. Technol.* **55**, 483 (1982).
6. T. Igarashi, *J. Appl. Polym. Sci.* **13**, 2129 (1975).
7. E. H. Andrews and A. J. Kinloch, *Proc. Roy. Soc.* **A332**, 385 (1973).
8. E. H. Andrews and A. J. Kinloch, *Proc. Roy. Soc.* **A332**, 401 (1973).
9. G. R. Hamed, *Rubb. Chem. Technol.* **54**, 403 (1981).
10. H. E. Blair, *et al.*, *J. Adhesion* **3**, 89 (1971).
11. R. S. Rivlin and A. G. Thomas, *J. Polym. Sci.* **10**, 291 (1953).