

ADHESION OF PSA BASED ON STYRENIC BLOCK COPOLYMERS

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INTRODUCTION

We studied the adhesion of blends of styrene-isoprene-styrene triblock copolymers (SIS), styrene-isoprene diblocks (SI) and a tackifying resin (miscible with the isoprene phase, high T_g). The proportion of SI in the polymeric blends SIS+SI varies from 0 to 54%.

The adhesive properties of these blends were evaluated through probe tests, during which a rigid and flat surface was brought into contact with an adhesive film and was then separated from it at a constant velocity. The parallel plates geometry provided by flat probe tests is optimal to study soft adhesives in the large deformation range: the adhesive layer is submitted to a uniform displacement field. As Figure 1 shows, a video system makes it possible to observe the mechanisms of deformation during separation. The mechanisms observed during the debonding call upon three phenomena: nucleation and growth of cavities, related to the linear viscoelasticity of the material and occurring under low strain in a still confined geometry; interfacial propagation, related to the surface properties of the adherent, and fibrillation, related to the elongational properties of the polymer backbone and leading to strain hardening.

We investigated two parameters: the effect of the diblock/triblock ratio and the effect of temperature. The tack properties were then compared to the shear properties at low strain and to the large-strain behavior in extension.

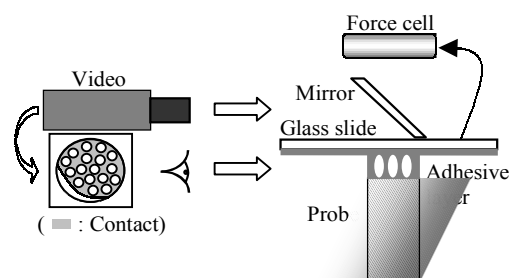


Figure 1: Data acquisition and observation of debonding mechanisms in probe tests.

EXPERIMENTAL

Materials and sample preparation

Four model formulations of styrenic block copolymer blends, the characteristics of which are given in the table below, were obtained from Exxon Mobil Chemical, Machelen, Belgium. All the adhesives formulations contained 60% (R60) of a hydrogenated resin (Escorez 5380).

	SIS (15% S)		SI (15% S)	
T2 (Vector 4100)	100%	$M_w=154k$	0%	
T2D19 (Vector 4113)	81%	$M_w=154k$	19%	$M_w=72k$
T2D42 (Vector 4114)	58%	$M_w=154k$	42%	$M_w=72k$
T3D54 (DPX 565)	45.7%	$M_w=176k$	54.3%	$M_w=83k$

The adhesive films (~120 μm -thick) were prepared by casting solutions of SIS-SI-resin blends in toluene on precleaned glass slides. The films were dried first at room temperature during 24 hrs, then 48 hrs under vacuum, at 45°C.

Small strain rheological properties

The shear properties of T2R60 and T3D54R60 in the linear viscoelastic regime were measured on a parallel plate rheometer RDA II.

At 20°C, differences in properties due to a change in the SI content occur in the $5 \cdot 10^{-3}$ - $5 \cdot 10^{-1}$ $\text{rad} \cdot \text{s}^{-1}$ range where an increase in the SI content leads to an decrease in the elastic modulus G' and to an increase in the loss modulus G'' (Figure 2). In this range, the blends are thus more dissipative if there is more SI.

For both materials a broadened glass transition is observed (frequencies > 1 Hz, not shown here), and a second relaxation process appears at low frequencies (high temperatures) while the SI content is increased (Figure 3).

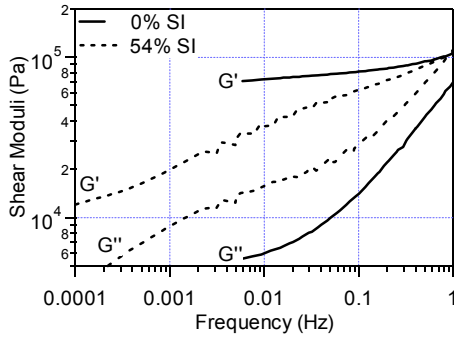


Figure 2: Shear moduli for T2R60 and T3D54R60 (master curves), $T_{ref} = 20^\circ\text{C}$.

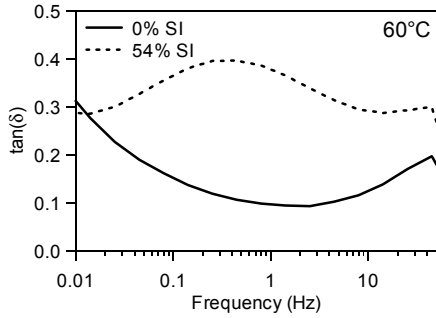


Figure 3: Loss tangent for T2R60 and T3D54R60, $T = 60^\circ\text{C}$.

Tensile tests

Tensile tests were performed on a standard tensile testing machine (JFC TC3), allowing large displacements of the crosshead (up to 400 mm) and low force measurements ($F_{max} = 10$ N, resolution: 0.5 mN). These tests were done on samples prepared by hot melt blending for practical reasons.

The crosshead velocities V_t were chosen in order to apply similar initial strain rates than the debonding velocities used in probe tests ($V_t = 5 \text{ mm.s}^{-1} \Leftrightarrow V_{DEB} = 1 \mu\text{m.s}^{-1}$).

Figure 4 shows that decreasing the SI content or increasing the crosshead velocity leads to a higher stress for all extensions and to a more pronounced strain hardening.

The deformation of the samples appeared to be quite homogeneous, at least in the direction of the tensile stress.

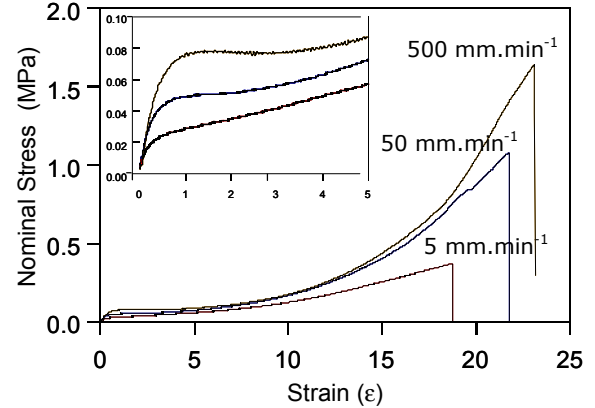
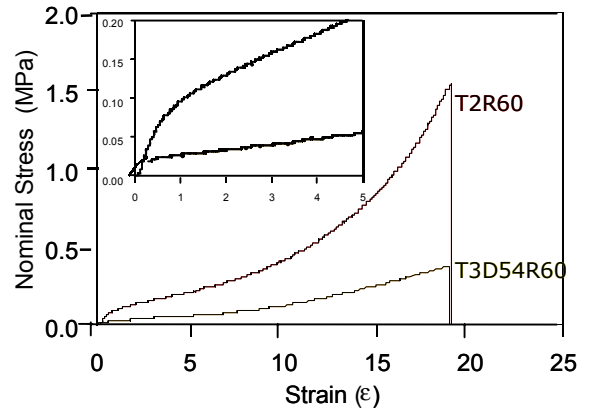


Figure 4: Up: at $V_t = 5 \text{ mm.s}^{-1}$. Down: T3D54R60.

The video probe experiment

We performed probe tests on our custom-designed apparatus using a MTS 810 hydraulic testing machine [1]. One test is divided into three parts. A flat stainless steel probe (diameter 10 mm) approaches the adhesive layer lying on a microscope glass slide at a constant velocity ($V_{APP} = 30 \mu\text{m.s}^{-1}$). When the contact pressure (P_C) reaches 1 MPa, the movement stops during a contact time (t_C) of 1s. The probe is then removed at a constant debonding rate (V_{DEB}) varying from 1 to 1000 $\mu\text{m.s}^{-1}$.

Force (F) vs. time (t) and displacement (d) vs. time curves are thus directly obtained. Nominal stress (σ) and strain (ϵ) curves are obtained using the values of the initial film thickness (h_0) and the initial contact area (A_{Co}): $\sigma = F(t)/A_{Co}$ and $\epsilon = (d(t) - h_0)/h_0$.

For each experimental condition, we carried out three to five probe tests. We show here representative (nominal) stress vs. strain curves

and average values of typical mechanical parameters such as the maximum stress σ_{\max} , the maximum extension ϵ_{\max} and the adhesion energy $W_{adh} = h_0 \cdot \int_0^{\epsilon_{\max}} \sigma(\epsilon) d\epsilon$.

RESULTS

The effect of the SI content

As the diblock used in this study has a molecular weight which is half that of the triblock and has the same styrene content, increasing the SI content is equivalent to replacing one triblock with two diblocks. This loss of connectivity causes a loss of elastic strands in the material which appears to have two consequences (Figure 5).

- The measured σ_{\max} in probe tests decreases as the amount of diblock increases.
- The strain hardening process, represented in stress-strain curves by the progressive increase in the nominal stress after σ_{\max} , leads to higher values of ϵ_{\max} under lower levels of nominal stress.

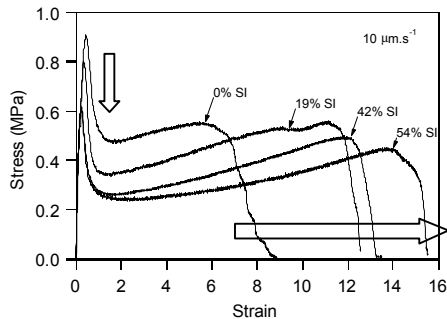


Figure 5: Stress-strain curves of the four adhesives, $T = 22^\circ\text{C}$, $V_{\text{DEB}} = 10\mu\text{m}\cdot\text{s}^{-1}$.

Since the adhesion energy is the integral under the stress-strain curve multiplied by h_0 , its variation with the proportion of diblock reflects both effects. Therefore as one would expect from the aspect of the stress-strain curves it is not very affected by the percentage of diblock and no clear trend can be observed. However the underlying reasons for the measured value of W_{adh} being different one expects a different behavior depending on the applications.

The effect of temperature

Increasing the temperature from 22°C to 60°C leads to lower σ_{\max} and ϵ_{\max} regardless of the percentage of diblock (Figure 6).

However, if the material has a large diblock content (54%), a pretty long fibrillation still takes place (although there is no apparent strain hardening at 40°C and 60°C). The detailed mechanisms show no discernible differences between the three temperatures.

On the other hand, when the adhesive contains only triblock, the shape of the curve at 40°C and 60°C differs markedly from the one at 22°C . This indicates a change in debonding mechanisms between 22°C and 40°C . Video images of the debonding show that at low temperature, the walls between cavities are able to support a tensile stress and produce a strain hardening whereas at high temperature, the interfacial crack propagation becomes easier and the debonding proceeds quickly by interfacial crack propagation. As shown on figure 3, the adhesive containing no SI shows a less dissipative behavior at 60°C than the adhesive with 54% SI. As a consequence the lateral growth of cavities on the surface appears to be favoured for the T2R60 and the adhesive debonds from the surface.

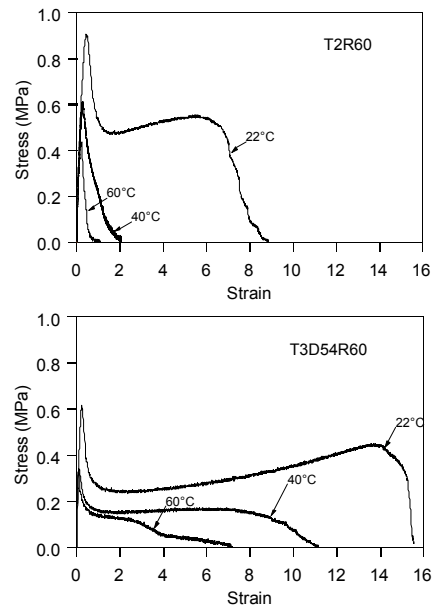


Figure 6: Stress-strain curves for T2R60 and T3D54R60, $T = 22^\circ\text{C}$, 40°C and 60°C , at $V_{\text{DEB}} = 10\mu\text{m}\cdot\text{s}^{-1}$.

DISCUSSION

If the measured value of σ_{\max} is directly connected with the cavitation process and the cavitation is the result of an elastic instability, one can propose that σ_{\max} should be controlled by the small-strain elastic properties of the adhesive layer.

Figure 7 shows σ_{\max} as a function of initial strain rate $\dot{\epsilon} = V_{DEB}/h_0$ in probe tests and G' as a function of the average strain rate in shear $\omega/2\pi$ at 40°C. There is a rather good correlation between σ_{\max} and G' : $\sigma_{\max} \approx 10 \times G'$ for all debonding velocities at 40°C and 60°C and for low debonding velocities at 20°C. The cavitation criterion of Gent [2] according to which the cavitation in elastic rubbers should occur when $\sigma \approx 3G'$ is thus qualitatively satisfied for SIS-SI-resin blends.

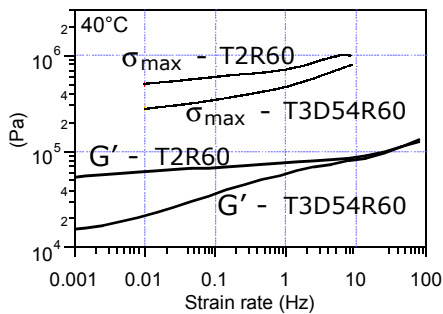


Figure 7: Maximal stress σ_{\max} and elastic modulus G' at 40°C.

The strain hardening observed in the fibrillation part of the probe tests curves can be qualitatively correlated to our tensile tests: in both case, the lower the SI content, the more pronounced the strain hardening. Indeed, the fibrillation part of a probe test situated can be considered as a series of parallel tensile tests. Quantitative comparisons cannot however be made here because the samples were not prepared in the same way.

CONCLUSION

Probe tests were undertaken on SIS-SI-resin blends and correlated to their rheological properties. Experimental results show that the

beginning of a probe test (where the cavitation process takes place) quantitatively corresponds to the small-strain shear properties of the adhesives while the end of the test (fibrillation, strain hardening) can be qualitatively - so far - related to the large-strain elongational properties.

REFERENCES

- [1] H. Lakrout, P. Sergot and C. Creton, J. Adhesion, **2001**, *69*, 307-359.
- [2] A.N. Gent, P.B. Lindley, Proc. Roy. Soc. A, **1958**, *249*, 195-205.