

## **Styrenic block copolymers as hot-melt PSA's: Role of molecular architecture on properties**

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### **Introduction**

Because of environmental concerns there has been a push, particularly in Europe, to develop solventless technology. In the area of pressure-sensitive-adhesives (PSA), two strategies have been used to achieve this goal: water-based acrylic emulsions and so called hot-melt PSA. This latter category relies on the microphase separation of block copolymers which form a solid-like nanostructure at low temperature, but become a low viscosity liquid at high temperature where this nanostructure is no longer thermodynamically stable. The block copolymers typically used for PSA applications have short blocks with a high glass transition temperature, and long blocks with a low glass transition temperature. The most classic example of this type of copolymer is the styrene-isoprene family. The main control parameter distinguishing the base polymers, is the ratio between triblock copolymers and diblock copolymers. In all cases, a so-called tackifying resin, only miscible with the isoprene phase, has to be added to the formulation, to lower the elastic modulus to a value which is low enough to be a good PSA. In the study reported here, we have investigated in detail the effect of changing the diblock/triblock ratio in the base polymer on the adhesive properties of the formulated PSA.

### **Experimental**

Although peel tests are widely used to characterize adhesion of soft adhesives, they are not well adapted to a detailed investigation of the failure mechanisms. We have developed an instrumented probe test as a powerful analytical tool to investigate the properties of pressure-sensitive-adhesives[1]. Probe test are typically carried out in the following way: a flat ended cylindrical probe is brought in contact with a thin PSA film, previously coated on a rigid transparent substrate, kept then in contact at a well defined compressive pressure for a certain time, and subsequently removed at a constant probe velocity[2]. The force displacement curve is recorded together with video images of the fracture mechanisms and a stress-strain curve is obtained by normalizing the force by the maximum contact area during the compression stage and the displacement by the initial thickness of the film. To complement the results of the probe tests, we have also performed rheological characterizations of the PSA with a parallel plate rheometer, as well as tensile tests in the large strain regime to assess the non-linear elastic properties of the PSA.

In this study[3] we have worked with a series of model PSA provided by ExxonMobil Chemical Europe. Four base polymers were used with varying amounts of diblock copolymer, and each formulation was prepared with 60wt% tackifying resin and 40wt% of base polymer. Details on molecular weights of the block copolymers and formulations are given on Table I.

Table I: Molecular characteristics of the base polymers model PSA.

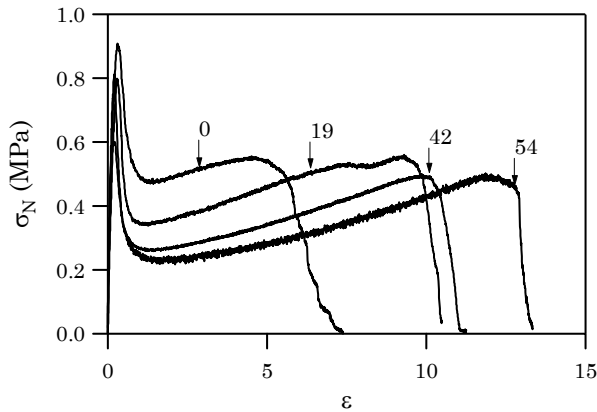
	wt.% SI	$M_w(\text{SIS})$	wt.% S in SIS	$M_w(\text{SD})$	wt.% S in SI
Pure triblock	0	154k	15.1	-	-
19% diblock	19	154k	15.1	72k	15
42% diblock	42	156k	15.1	72k	15
54% diblock	54	176k	16.1	72k	16

## Results and discussion

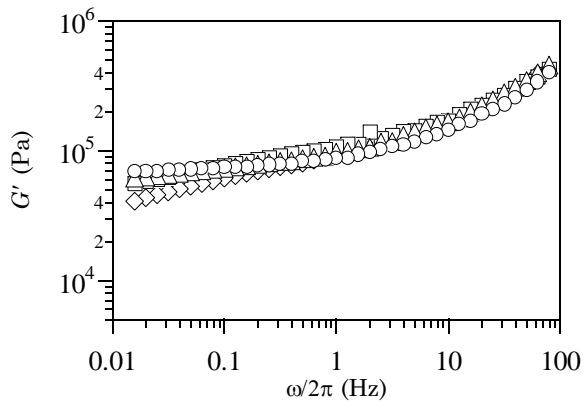
Typically, at room temperature and when the probe is a polished steel surface, all of our model PSA form a foam of highly extended fibrils when they are debonded from the probe. These fibrils eventually detach from the surface when they are sufficiently extended to strain harden. In this fibrillar regime, the practical work of adhesion is not really controlled by the interface but more by the nonlinear elastic properties of the adhesive and by the amount of elastic energy that can be stored in the fibrils before detachment[3]. 80% of the energy necessary to debond the PSA is due to the fibrillar structure. We focus therefore now on the effect of the diblock content on the fibril formation and detachment.

A series of probe tack curves typical of a this type of failure is shown on figure 1. Note in all cases, at high extension, the abrupt drop in stress characteristic of the elastic detachment of the fibrils.

This foam structure does not vary much with diblock content in the formulation. However the large strain part of the stress-strain curve is significantly affected by the ratio diblock/triblock as can be seen on figure 1. The PSA made with pure triblock has the highest plateau stress while, an increase in diblock content causes the fibril extension to occur at lower stresses but detach at higher extensions.



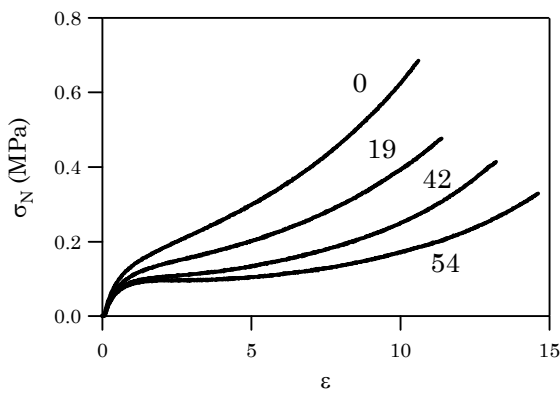
**Figure 1:** Probe tack curves of a series of block copolymer based adhesives. The probe velocity is the same ( $100 \mu\text{m/s}$  corresponding to an initial strain rate of  $1 \text{ s}^{-1}$ ) and the number refers to the proportion of diblock in the blend. Data from [3].



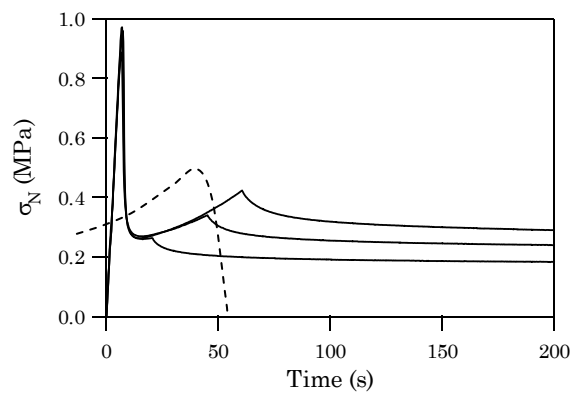
**Figure 2:** Elastic modulus  $G'$ , (b) loss modulus  $G''$  and as a function of frequency for various SI contents, at  $T = 22^\circ\text{C}$ ,  $\circ$  : 0 wt.% SI,  $\triangle$  : 19 wt.% SI,  $\square$  : 42 wt.% SI,  $\diamond$  : 54 wt.% SI.

Since it is well-known that PSA properties are controlled by their rheological properties, we measured the dynamic shear modulus  $G'$  of each PSA at a frequency approximately equivalent to

the initial strain rate applied to the layer. Results on figure 2 clearly show that at the strain rate of 1 Hz, all PSA are roughly equivalent in terms of shear modulus, failing therefore to account for the differences observed on figure 1. The reason for this failure is that in this regime, the response of the PSA is very dependent on the *non-linear elastic* properties of the adhesive. When the triblock in the formulation is replaced by two diblocks, the linear viscoelastic properties are not much affected (and only at low frequency) but the nonlinear elastic properties are very affected as shown on figure 3. This can be easily accounted for by a rubber elasticity model taking into account both entanglements (which dominate the behavior at low strains) and crosslinks (which dominate the behavior at high strains)[4]. Since for our PSA the density of entanglements is unusually large relative to the density of crosslinks, the effect of the crosslink density is only visible at high strains. A second important result of our experiments is that the fibrils formed by such adhesives are essentially elastic, so that they first store energy during extension to release it rapidly during the detachment of the foot of the fibril from the surface. The relaxation behavior of the four model adhesives after a 500% extension is shown on figure 4.

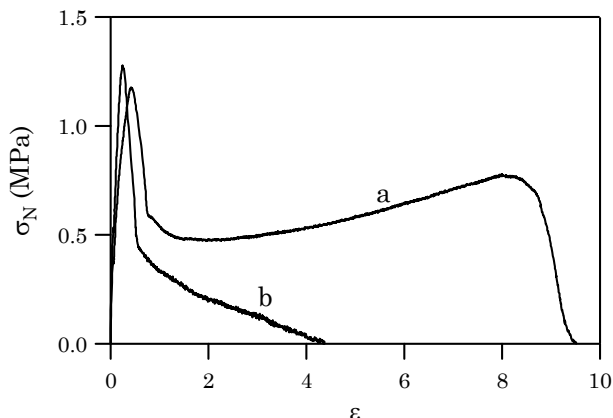


**Figure 3:** Stress-strain curves in uniaxial elongation of the same adhesives tested in probe tack on figure 1. Data from [3].

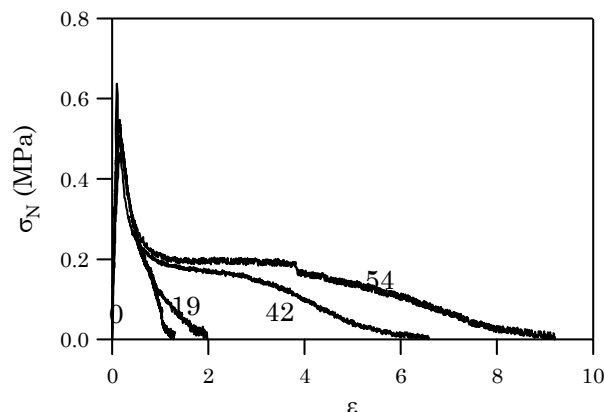


**Figure 4:** Nominal stress vs. time curves with displacement stops: 600 s stops at the beginning, the middle and the end of the fibrillation process, compared to a debonding curve without stop (----).

Now if the probe is no longer steel but is for example coated with a thin layer of an ethylene-propylene elastomer, the stress-strain curves obtained from probe tests become completely different as shown on figure 5 and 6 for the same series of adhesives. For the 19% diblock adhesive for example, the stress decreases continuously to zero after the peak and a shoulder is observed rather than a plateau. If a plateau is observed (for the high diblock PSA or at high debonding velocity), it is at much lower stresses and without signs of strain hardening. In this mixed regime, failure is controlled by a competition between interfacial crack propagation and fibril growth[5]. The rate at which the cracks caused by cavitation can propagate at the interface, controls the maximum elongation in the tensile direction and the practical work of adhesion  $W$ . In this regime, adhesion depends on the ratio  $G_c/E$  which has the dimension of a distance[6]. Within the framework of linear elasticity, it represents the characteristic distance at which the layer is pulled off from the adherent[7]. An example of a series of probe test curves for the PSA series is shown on figure 6. The increasing value of the detachment deformation and the progressive (rather than abrupt) drop in stress at the end of the detachment is typical of a mixed mode of failure where interfacial failure competes with fibril extension.

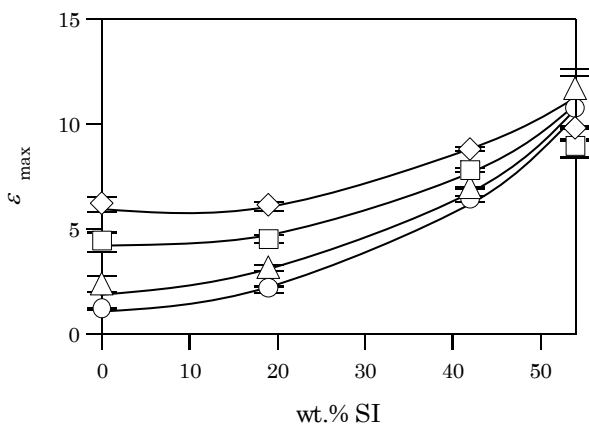


**Figure 5:** Nominal stress vs. strain curves for the blend with 19 wt.% SI on stainless steel (a) and on EP (b), at  $V_{deb} = 100 \mu m.s^{-1}$ .

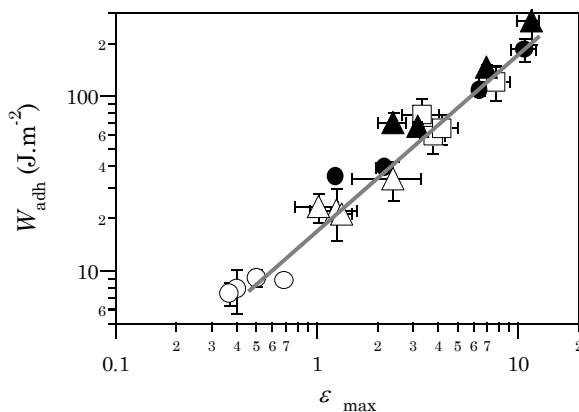


**Figure 6:** Nominal stress vs. strain curves on EP. Influence of the diblock content for a given debonding velocity  $V_{deb} = 1 \mu m.s^{-1}$ . Numbers indicate the diblock content.

This increased resistance to crack propagation which slows down the interfacial debonding and favors the formation of fibrils is directly correlated with the dissipative character of the adhesive. The 54% diblock PSA has the highest value of  $\tan \delta$  at small strains and the highest level of hysteresis in large strain tensile tests. This higher level of dissipation is apparent also in relaxation tests where the high diblock content PSA relax much more markedly than the PSA based on pure triblocks. In this mixed failure regime, an easy parameter to monitor the work of adhesion is the maximum extension of the fibrils. As shown on figure 7, the more diblock is added to the PSA and the larger is  $\epsilon_{max}$  which is itself directly correlated with  $W$  in this mixed regime as shown on figure 8.



**Figure 7:** Maximum elongation  $\epsilon_{max}$  as a function of diblock content for the four debonding velocity: 1 (○), 10 (△), 100 (□) and 1000  $m.s^{-1}$  (◇).



**Figure 8:**  $W_{adh}$  as a function of maximum elongation  $\epsilon_{max}$  in the mixed regime. ○ :  $V_{deb} = 1$ , △ : 10, □ : 100  $\mu m/s$

## Conclusion

We have shown that depending on which failure mechanism is active, very different material properties control the practical work of adhesion. If the adhesion is weak and the failure mechanism is mainly interfacial, the practical work of adhesion is mainly controlled by the dissipative properties of the adhesive. However if the adhesion is high and a fibrillar structure can be formed, the practical work of adhesion will be controlled by the amount of elastic energy that can be stored in the fibrillar structure.

Hence this implies that an adhesive which has been optimized for strong adhesion may be performing very poorly on a low adhesion surface where  $G_c$  is too low to allow the formation of a fully developed fibrillar structure.

Conversely a highly dissipative adhesive which will do well on a low adhesion surface may perform poorly on a high adhesion surface, because very little elastic energy can be stored in the fibrils before they detach. For our adhesives based on styrenic block copolymers, the presence of diblock in the formulation markedly decreases the large strain modulus of the PSA and increases the dissipation both in small strains and in large strains. Accordingly the PSA based on pure triblock resists to higher stresses on steel but performs poorly on EP surfaces, while the high diblock PSA perform much better on EP surfaces but, on steel, do not resist to stresses as high as the pure triblock PSA.

## References

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