

# HOW CAN TENSILE TESTS BE USEFUL TO DESIGN OPTIMIZED PSA ?

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## Introduction

The adhesive properties of PSA are typically characterized with standard mechanical tests where the PSA is first bonded then debonded from a solid surface in standardized conditions. Unless that surface is a release coating the debonding involves extensive deformation of the PSA layer with fibril formation and growth. Within these fibrils the PSA is deformed well into the regime where its modulus is no longer independent of deformation. Yet simple empirical models to predict PSA properties such as the viscoelastic window model<sup>1</sup> as well as more mechanistic models<sup>2</sup>, are restricted to the linear viscoelastic properties to predict PSA adhesive properties.

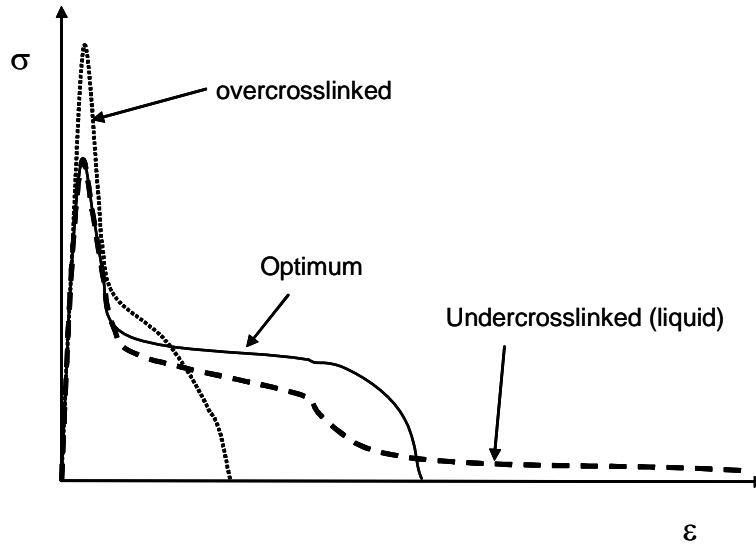
We propose here an alternative and complementary methodology which takes advantage of the sensitivity of the large strain tensile test to details of the structure of the PSA which are amenable to modifications by the synthetic chemist.

## Some theoretical concepts

The optimization of the properties of a PSA involves a fine balance between cohesion (to avoid creep and obtain an adequate shear resistance) and adhesive properties to dissipate energy upon peeling the PSA from a solid surface. This behaviour can typically be optimized by using viscoelastic lightly crosslinked polymer networks. In this case the synthetic chemist starts with a polymer with a very wide molecular weight distribution and adds a random crosslinking reaction. The initially wide molecular weight distribution gives a very viscoelastic material at all frequencies and the light crosslinking prevents creep.

Unfortunately this optimization is inherently limited by the fact that additional crosslinking will make the material less dissipative at increasingly higher frequencies and therefore the peel force will drop. As a result, increasing the cohesion of the PSA causes invariably a decrease in the peel force as every engineer working with PSA knows. For the adhesive performance on steel or glass this is not a very serious problem and simple crosslinked homogeneous materials can be optimized to give a good compromise between adhesion and cohesion. However when the PSA are used on difficult to bond surfaces such as polyolefins, this optimization of crosslinking significantly reduces performance. In other words it is difficult to obtain at the same time a high adhesion on polyethylene and a high shear resistance. This is where an optimization of the nonlinear properties can be useful.

A good tool to study the mechanisms of PSA debonding is the probe test<sup>2,3</sup>. In such a test where a stainless steel flat ended probe is brought in contact and then detached at a constant velocity from a PSA layer, the detailed shape of the force-displacement curve (which can be converted to a stress-strain curve by an appropriate normalization<sup>4</sup>) gives informations on the details of the mechanisms of debonding and can be much better correlated to the structure of the PSA. An example of interpretation for a simple network is given in figure 1.



**Figure 1:** Schematic of three types of stress-strain curves obtained by debonding a PSA layer.

The three tack curves shown on figure 1 are representative of three types of PSA. The dashed line shows the curve typically obtained with PSA showing insufficient cohesion, with a first plateau and a second plateau due to air penetration. The overcrosslinked curve shows a deformation at a high level of stress but an early detachment of the fibrils leading to a moderate level of peel force. This type of curve would be typically obtained with a PSA having excellent shear resistance but moderate peel force. Finally the optimized PSA, will show the characteristic peak followed by a plateau value and a significant value of detachment stress. Although the linear viscoelastic properties of these three PSA will be different, they will not allow a prediction of the tack curve.

### Non-linear elastic behaviour of polymer networks

When a polymer network is stretched at large strains, the stress-strain curve becomes non-linear. For a simple crosslinked network obeying rubber elasticity, the simple extension curve is given by:

$$\sigma_N = G\left(\lambda - \frac{1}{\lambda^2}\right) \quad (1)$$

However, this simple representation does not include the finite extensibility of the polymer chains, nor does it include any softening effect on the stress-strain curve which are typically observed for weakly crosslinked systems. Several models, both empirical and molecularly based exist in the literature but a more detailed review would be beyond the scope of this paper. However a simple equation in uniaxial extension for a network undergoing softening then hardening at very large extensions could be<sup>5,6</sup>:

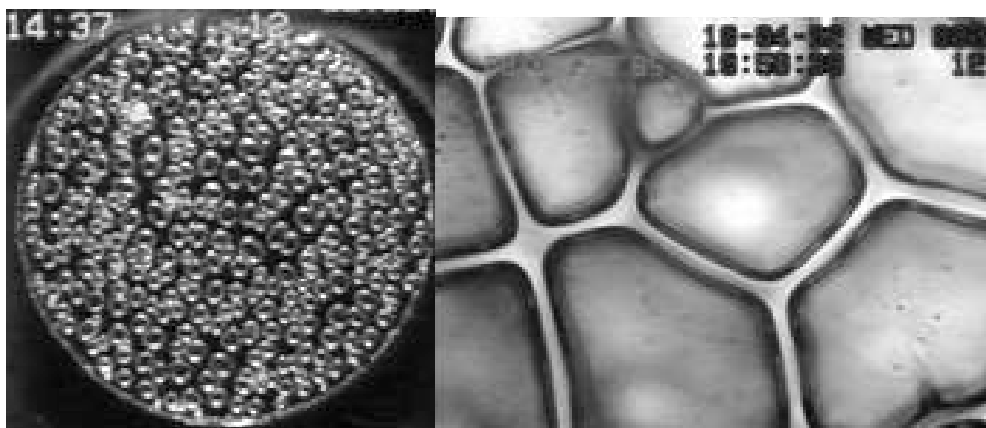
$$\sigma_N = 2\left(C_1 + \frac{C_2}{\lambda}\right)\left(\frac{1}{1 - J_1/J_m}\right)\left(\lambda - \frac{1}{\lambda^2}\right) \quad (2)$$

Where  $C_1$  and  $C_2$  are the Mooney-Rivlin parameters,  $J_1$  is the first strain invariant (equal to  $\lambda^2 + 2\lambda^{-1} - 3$ ) and  $J_m$  is the maximum value that  $J_1$  can take and represents the finite extensibility of the chains. It is

easy to show that Equation 2 predicts a low strain modulus equal to the Young's modulus, a softening at intermediate strains due to the first term and a hardening at high strains due to the second term.

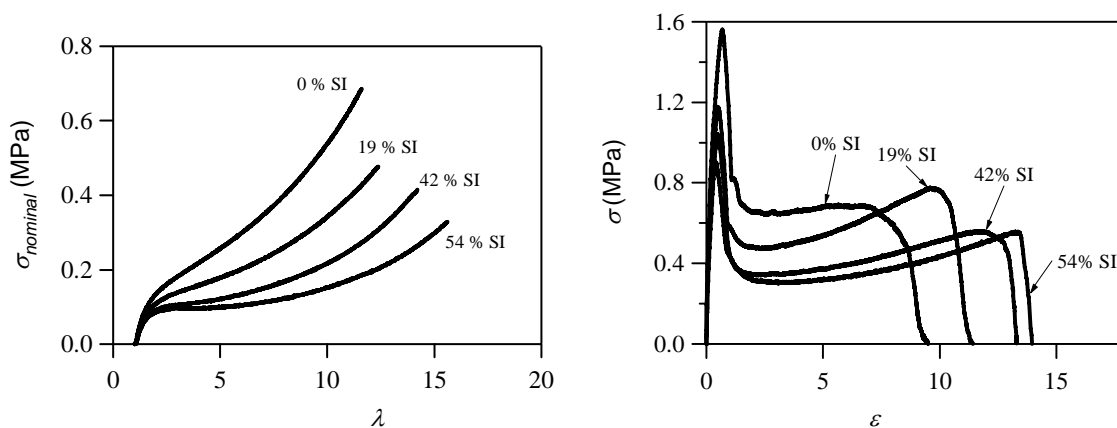
### Experimental results: hot-melt systems

Probe tests on PSA films show that fibrils form after cavities are initially nucleated in the layer if the resistance to interfacial crack propagation is sufficiently high to prevent cavities from coalescing<sup>7-9</sup>. The cavities that are formed during debonding are shown on Figure 2 for a hot-melt PSA at two different magnifications.



**Figure 2** : Typical images of the cavities forming in hot-melt PSA during debonding from a smooth steel surface. The diameter of the full probe (left) is 1 cm. The width of the image on the right represents about 500  $\mu\text{m}$ . the white areas are the walls between cavities

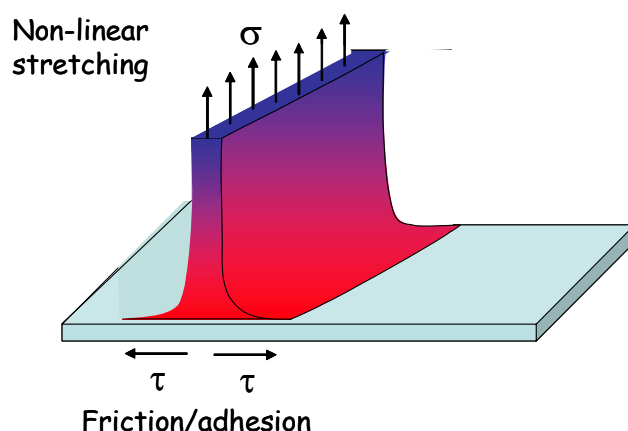
After they are formed however the cavities grow as cigars in the tensile direction until the wall between two adjacent cavities eventually detaches. The maximum deformation of the PSA layer before detachment occurs is mainly controlled by the non-linear viscoelastic properties of the PSA. Figure 3a compares a series of tensile tests for hot-melt PSA's based on styrene-isoprene-styrene block copolymers. The stress-strain curves show that all materials show a pronounced softening at intermediate strains, followed by a hardening at high strains. However depending on the details of the molecular composition (in this case the diblock/triblock ratio), the shape of the stress strain curve changes. On figure 3b, we show the corresponding probe tack tests on a steel surface at a debonding velocity imposing an equivalent initial strain rate: It is clear that, after the initial cavitation peak, the deformation of the layer becomes easier as the amount of diblock increases and the maximum deformation before failure increases<sup>10</sup>.



**Figure 3:** a) tensile tests and b) probe test for four different hot-melt PSA. The materials are ternary blends of styrene-isoprene-styrene triblock copolymers, styrene-isoprene diblock copolymers and a tackifying resin miscible with the polyisoprene domains<sup>11</sup>.

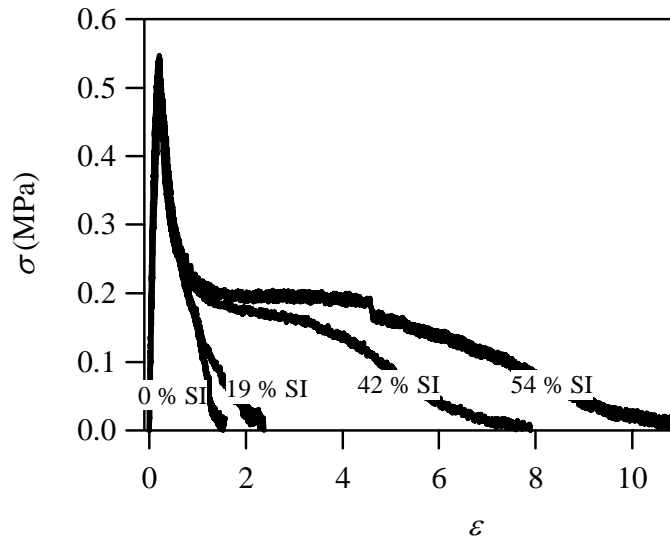
The integral of a probe test stress-strain curve is a relatively good predictor of the 20 minute peel force on an equivalent surface. As one can see from Figure 3b, the four PSA tested here will have roughly equivalent peel forces and this is confirmed by experiments. One can wonder therefore, what is the practical importance of controlling the nonlinear properties of the PSA. This non linear behavior has some important consequences on the performance of the PSA. Let us review them here in order. In terms of cohesion the classic test performed in industry is the shear test where a fixed weight is attached to a PSA layer bonded to a steel surface and the time to failure is recorded. In this experiment, and of course as a first approximation, it is the initial modulus at very low frequency which is important and controls the time to failure. The higher is the initial modulus and the better is the resistance to shear. However in a peel test or in a loop tack test, the PSA film is highly deformed before failure and typically forms a fibrillar structure. In this case it is the softening stress which is important to determine the deformation of the fibrils. Finally, when, at very large deformations, the polymer chains in the network approach their finite extensibility, the nominal stress increases again and causes the final detachment of the fibrils (which are in reality walls between cavities).

The importance of controlling the nonlinear properties is more apparent however when the PSA is detached from a low energy surface where extension of the fibril and fibril detachment compete. The detachment of a wall seen on Figure 2 (right) can be schematically described on Figure 4:



**Figure 4** : Schematic of the foot of a wall between cavities at rather large strain. This schematic represents in 3D the walls of Figure 2 (right hand-side picture).

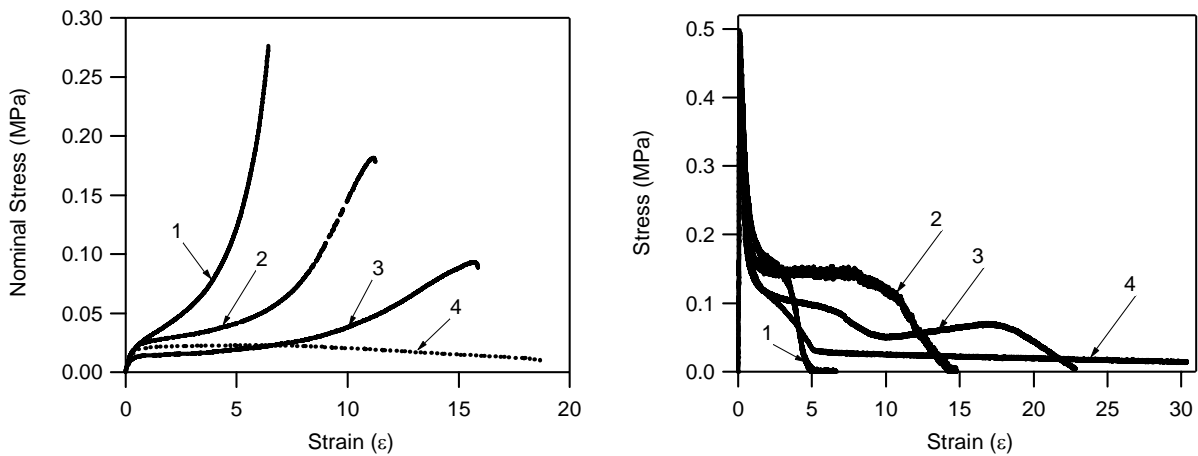
It is clear from the schematic that there will be a competition between the stress applied to the wall by the stretching of the wall, and the interfacial friction stress preventing the foot from detaching. Probe test curves on a low energy surface<sup>10</sup> are shown on figure 5 for the same series of PSA shown on figure 3.



**Figure 5** : Probe test curves at the same probe velocity as on figure 3 but on a low-energy surface (in this case a fluorinated surface)

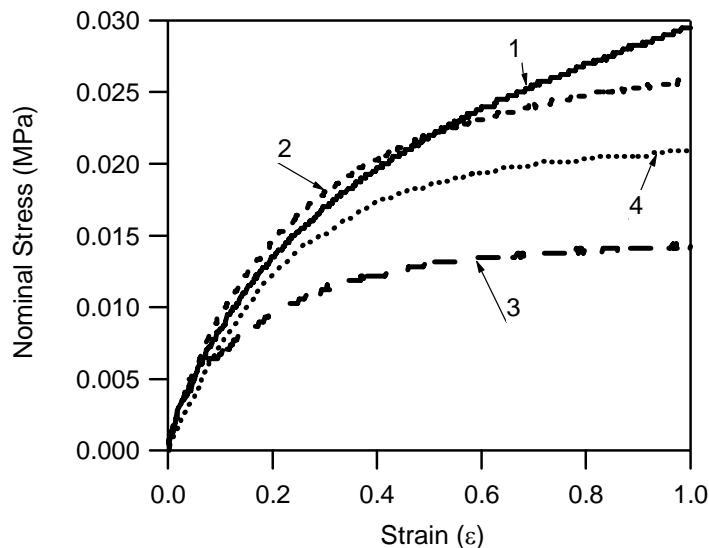
In this case the PSA which does not contain any diblock copolymer and has the highest softening stress, does not form fibrils at all (deformation at detachment is very low), while the PSA containing 54% of diblock in the polymer phase can still form quite extended fibrils. In other words the stiffer PSA impose a higher stress on the cavity wall which causes early detachment. Note however that following the schematic of figure 4, the introduction of diblock copolymer increases the softening process but also makes the PSA more dissipative at low frequencies which probably increases the interfacial friction force that the foot of the wall must overcome to detach.

Another interesting example of the role played by the nonlinear properties of PSA is given in Figure 6. Several typical tensile stress-strain curves for a series of waterborne acrylic PSA are shown on figure 6a. Curve 1 is the most typical of a crosslinked network although it still does display a significant softening. Curve 2 and 3 represent two different PSA with different types of softening and hardening behaviors and finally curve 4 does not display any hardening at large strain and behaves like a fluid. These differences in behaviour have been obtained chemically by modifying the structure of the polymer film made from colloidal particles and by modifying the overall degree of crosslinking of the structure. Note that the small strain modulus for all these PSA remains in the same range which would not have been the case for a homogeneously crosslinked material.



**Figure 6:** Tensile tests and probe tests for series of acrylic waterborne PSA.

It is clear from the probe tests that PSA 4 is too liquid since its probe test curve displays the characteristic double plateau<sup>12</sup> followed by a fibril extension and cohesive failure. The three other PSA fail adhesively but with important differences. PSA 1 does not deform much before the fibrils detach, a behaviour characteristic of a more crosslinked adhesive, while PSA 3 resembles PSA 4 but fails adhesively. PSA 2 has the most interesting behaviour with a well defined plateau stress after the peak at a value close to that of PSA1 but with a much more extensive deformation of the fibrils before detachment. These differences in probe tests are directly related to the shape of the tensile curves and would not be apparent in the linear regime as can be seen on Figure 7. Based on the initial part of the tensile curve, all four PSA's have a tensile modulus  $E$  close to 100 kPa. However their behaviour in large strain and their adhesive properties are greatly affected by the details of their structure.



**Figure 7:** Initial stages of the tensile tests shown on figure 6a for the same four waterborne PSA.

## Conclusions

The key concept behind the softening properties is that of a stiff but breakable structure interpenetrated with a soft but unbreakable one. In other words at low stress the stiff structure controls the small strain modulus and is resistant to creep, but as the applied stress increases the stiff structure is broken and the material now feels the elasticity of the second structure which is much softer but also much harder to break. Only when the second structure becomes highly extended, will the material harden again. This type of heterogeneous network structure has been reported for hydrogels<sup>13,14</sup> and has led to a high toughness, but it is the first time that it is clearly demonstrated for PSA. Because of the peculiar properties expected from polymer networks in PSA, such double networks hold great promise on low adhesion surfaces if the complex structure can be finely controlled by the synthesis procedure or by molecular self-assembly.

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## Acknowledgements

We acknowledge funding from the European Framework 6 project N° **505442-1** (N-SHAPE)