Macromol. Symp. **2004**, *214,* 147-156

Linear Viscoelasticity and Non-Linear Elasticity of Block Copolymer Blends Used as Soft Adhesives

*Alexandra Roos, Costantino Creton**

Laboratoire de Physico-Chimie Structurale et Macromoléculaire, E.S.P.C.I., 10 Rue Vauquelin, 75231 Paris Cédex 05, France
E-mail : costantino.creton@espci.fr

Summary: The debonding of pressure-sensitive-adhesives from a rigid surface often occurs with the formation of a fibrillar structure bridging the surface and the adhesive. This fibrillar structure is responsible for the large (of the order of 1 kJ/m^2) adhesion energy, which is measured, for this type of adhesive despite the very low level of applied stress. One way to account for this dissipated energy is viscous flow in the elongation process of the fibrils. However, for certain types of adhesives, the extension of the fibrils is essentially a quasi reversible elastic process and the energy is only dissipated rather rapidly when the fibrils are detached from the surface. It is therefore essential to characterize the elastic properties of theses adhesives not only in the linear viscoelastic regime but also in the large strain non-linear elastic domain. We have therefore performed tensile tests of model adhesive films based on block copolymers. The respective roles played by the linear viscoelasticity and non-linear elasticity in controlling the properties will be discussed.

Keywords: adhesion; elasticity; fibril; polymer; viscoelasticity

Introduction

When they are removed from a surface, soft adhesives readily form a foamy structure, highly oriented parallel to the tensile direction, which is very analogous to a fibrillar structure[1, 2]. These fibrils have been observed both in peeling experiments[3-5] and in tack experiments[6, 7]. The microscopic processes by which this foam develops have been the focus of many recent studies[8-11] but the actual mechanical properties of the adhesives themselves have only been investigated in the linear viscoelastic regime[12-15]. Yet it is well-known that elongational properties, involving the orientation of the polymer chain, cannot be readily predicted from the linear viscoelastic properties in shear, in particular for polymers with more complicated architectures and very

DOI: 10.1002/masy.200451011

pronounced elastic effects[16]. One such class of polymers is that of the diblock and triblock copolymers based on styrene and isoprene. For these copolymers, several detailed analyses of their tensile behaviour have been published[17, 18]. However none of theses studies have considered blends of triblock and diblock copolymers and, furthermore, most of these studies have focused on the change in the microphase separated structure which occurs upon deformation[18] and not necessarily on the stress-strain behaviour itself.

We have characterized a family of model pressure-sensitive-adhesives based on block copolymers, not only in the linear viscoelastic regime but also in the large strain regime where non-linear elasticity is dominant. In order to directly relate these results to the adhesive properties, we have performed adhesion experiments in the probe tack geometry as well as a relaxation experiment of the oriented fibrillar foam.

Experimental

The block copolymers were synthesized by anionic polymerization by ExxonMobil Chemical. They are styrene-isoprene-styrene triblock copolymers (SIS) and styrene-isoprene diblock copolymers (SI). Both copolymers contain 15 wt.-% styrene and the molecular weights are 156 kg/mol and 72 kg/mol, respectively. Hence, the diblock is essentially one half of the triblock. In order to obtain PSA properties the block copolymers must be blended with a low molecular weight resin, called a tackifying resin. We used a hydrogenated C-5 resin, commercially available under the trade name Escorez 5380, which was provided by ExxonMobil Chemical. The four model adhesives were prepared by varying the relative amounts of each component. The ratio resin/polymer was kept constant at 60% resin/40% polymer but the diblock/triblock ratio within the polymer phase was varied from 0% diblock to 54% diblock. From now on, the adhesives will be referred to by their diblock content.

All components were dissolved in toluene. The adhesive films (120 μm thick when dry) were obtained by depositing the toluene solution on a standard microscope glass slide and letting the solvent slowly evaporate, first at room temperature and then at 45 °C under vacuum for 24 hours.

Adhesion tests were performed with an instrumented probe tester, where a flat-ended steel cylinder with a polished surface comes in contact with the adhesive film under a controlled pressure and for a given contact time. The probe is then removed from the adhesive at a constant velocity and the force is measured as a function of distance. If the real contact area is known (from a video camera) the force displacement curve can then be transformed into a nominal stress, nominal strain curve, where the strain ε is defined as the displacement of the probe from the time where the force becomes positive (tensile), normalized by the initial thickness of the film. The maximum stress (σ_{max}), maximum strain at detachment (ε_{max}) and adhesion energy W_{adh} are typically extracted from the curves (see Figure 2).

The probe tack tests were performed on the custom made instruments developed in the laboratory[6, 19], with the following experimental parameters: contact pressure: 1 MPa, contact time: 1 s, debonding velocity V_{DEB} varying from 1 to 100 µm/s. The relaxation tests were performed by stopping the driving motor of the probe tack apparatus when the fibrillar foam structure was well formed and monitoring the relaxation of the force under constant displacement conditions.

The tensile tests were performed on a standard tensile tester. The rectangular samples were prepared in a similar way to those for the adhesive tests, but were 300 µm thick and 4 mm wide, and the initial distance between the grips was 15 mm. The crosshead speed was varied between 5 and 500 mm/min, corresponding to an initial strain rate varying between 0.005 and 0.5 s^{-1}. The rheological properties in oscillatory shear were measured on a RDA II Rheometrics parallel plates rheometer at 22 °C. These samples were 2 mm thick and 25 mm in diameter. Care was taken to perform the measurement in the linear regime.

Results and Discussion

Figure 1 shows the modulus G' as a function of frequency for a series of adhesives with different diblock contents. The only adhesive, which clearly appears to have a lower modulus at low frequency, is the 54% diblock. All other adhesives are very similar in G', within that range of frequencies. By contrast, when a probe test was performed at a debonding rate of 100 µm/s, corresponding to an initial strain rate (V_{DEB}/h_0) of 0.8 s^{-1}, the four adhesives could be clearly distinguished, in particular with a different value of maximum tensile stress, σ_{max}, and with a markedly different level of stress in the plateau region of the stress-strain curve. The observed stress level at the plateau and the maximum extension before detachment ε_{max} decrease and increase respectively with increasing diblock content. The video images of the debonding clearly indicate that the plateau stress for these materials corresponds to the formation and elongation of the fibrillar foam. Images show that the average cell size is fairly independent of the diblock content in the blend so that differences in measured stress cannot be due to different microscopic structures of the foam.

Based on these results, it is obvious that the stress level necessary to extend the walls of the foam cannot be controlled by the shear modulus G' only.

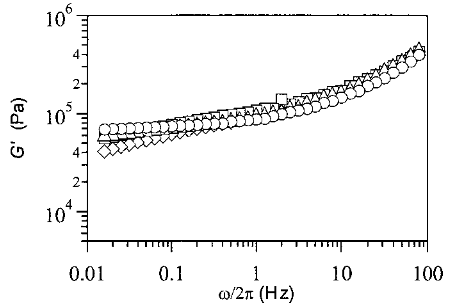


Figure 1. Elastic modulus G as a function of frequency for various SI contents, at T = 22°C. ○ : 0 wt.-% SI, △ : 19 wt.-% SI, □ : 42 wt.-% SI, ◇ : 54 wt.-% SI.

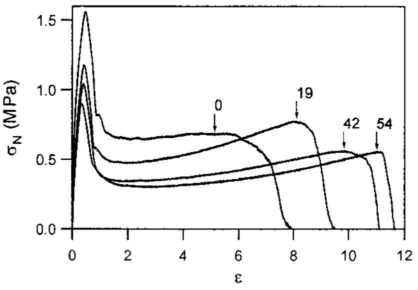


Figure 2. Nominal stress vs. strain curves at V_{deb} = 100 μm.s^{-1} for the four model blends (stainless steel, RT). Numbers indicate the diblock content of each blend.

In order to understand the results of Figure 2 it is necessary to examine the tensile test results. Figure 3 shows nominal stress vs. strain curves for the same series of adhesives at an initial strain rate of 0.5 s^{-1} (approximately the strain rate applied to the adhesive layer in the tack test at the beginning of the extension process of the foam). Again the four adhesive formulations are very well differentiated and the stress level at large strains decreases with increasing diblock content. An obvious question is, however what the effect of the viscoelasticity is. In that range of frequencies, the small-strain loss modulus G'' of the adhesives is far from being negligible and typically tan δ can be between 0.1 and 1. A good measure of the effect of viscoelasticity can be obtained by performing tensile tests at three different strain rates. Results are shown in Figure 3b. It can be seen that 2 decades in strain rate have less effect than a difference in diblock content. Such an elastic behaviour of the adhesive blend in large strain extension is also confirmed by relaxation tests. If a tack test is stopped while the fibrillar foam is fully formed, the stress does not relax to zero, as one would expect from a liquid capable of flow, but relaxes to approximately 70% of its initial stress before remaining constant. This result shown on Figure 4, clearly demonstrates that the fibrils are able to store elastic energy during their formation and only during detachment or fracture is this elastic energy released.

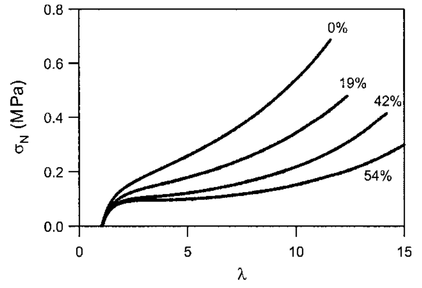


Figure 3a. Tensile curves at a crosshead velocity of 500 mm/min corresponding to an initial strain rate of 0.8 s^{-1} for the four copolymer blends.

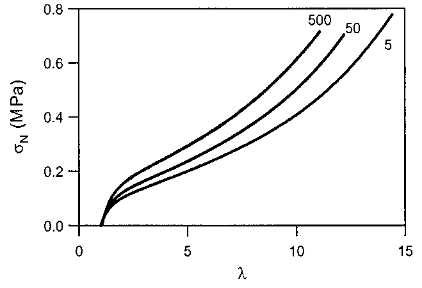
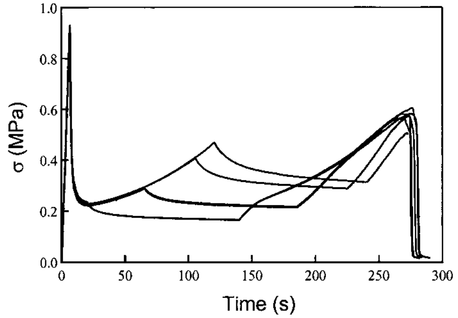


Figure 3b. Tensile curves for the 0% diblock blend at crosshead velocities of 5,50 and 500 mm/min corresponding to initial strain rates of 0.008, 0.08 and 0.8 s^{-1}.



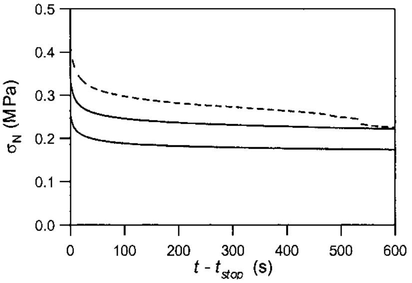


Figure 4a. Stress vs. time curves for probe tests with an intermediate stop for the 0 % diblock adhesive. The test is stopped for 120 seconds, then resumed. Note that the stress-strain curves are almost identical for all tests.

Figure 4b. Stress vs. t-t_{stop} curves obtained by stopping the driving motors in the fibrillation regime at three different stress levels for the 0 % diblock adhesive. The test is stopped here for 600 seconds.

The best way to quantitatively analyze the elastic behaviour in tension of the adhesive blends is with a model describing the non-linear elastic behaviour of rubbers. The microphase separated structure of these adhesives with PS hard domains and a soft PI + resin matrix can be assimilated to a loosely crosslinked rubber where the PS domains would be the crosslink points and the PI chains would provide the entropic springs between them.

The non-linear elastic behaviour of rubbers in uniaxial deformation has of course been the focus of numerous studies in the past[20] and is conveniently analyzed by representing the reduced stress, i.e.

$$\sigma_R = \sigma_N/(\lambda - 1/\lambda^2) \qquad (1)$$

where λ is the extension ratio l/l_0, and σ_N is the nominal stress F/A_0. The classical rubber elasticity model, also called the affine model, which considers that all crosslink points are fixed and every segment between crosslink points behaves as an entropic spring, predicts a constant reduced stress with increasing λ[20]. For real rubbery materials this is almost never observed and our adhesives are no exception. In particular, the simple affine model does not take into account the important role-played by entanglements.

More accurate representation of the role played by entanglements in the deformation of rubbers has been the focus of many years of research and has led to the development of several more elaborate models, well reviewed in reference[21]. Among those, the slip-tube model which represents entanglements as links that can slip along the polymer chain but not cross each other and combines the Doi-Edwards tube model with the phantom rubber elasticity model, provides a very clear physical picture of the role of entanglements. Within the framework of this model[21], the reduced stress can be approximately represented by:

$$\sigma_R = G_c + G_e/(0.74\,\lambda + 0.61\lambda^{-1/2} - 0.35), \tag{2}$$

where G_c represents the fixed crosslink points' contribution and G_e represents the entanglements' contribution. When $\lambda \geq 1$, $\sigma_R = G_c + G_e$, so that the sum of both contributions represents the small strain modulus G' measured in oscillatory shear.

A careful observation of equation 2 shows that with increasing λ, the role-played by entanglements decreases and the behaviour becomes dominated by the crosslink points. We have fitted the intermediate (100 – 400 % strain) portion of our stress-strain curves in the simple tensile tests (Figure 3) to the slip-tube model and the results of these fits are shown in figure 5. Clearly, for all adhesive blends, the largest contribution to the small strain modulus G' comes from entanglements and not from crosslink points. Even a substantial change in G_c (at least in relative terms) does not much affect the small strain modulus, in agreement with figure 1. On the other hand, during a tensile test the behaviour appears to be increasingly controlled by G_c as λ increases, which is observed in both Figures 2 and 3.

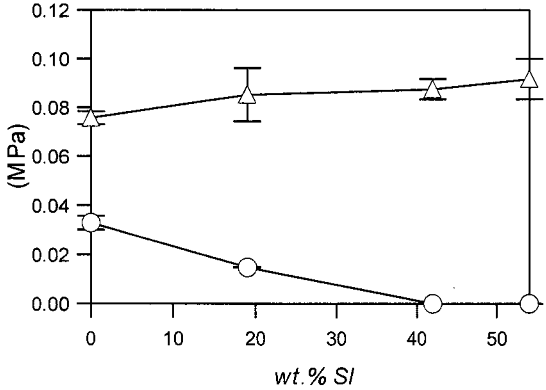


Figure 5. Slip-tube model coefficients: . -○-: G_c, -△-: G_e, as a function of SI content in the polymer blend.

From a molecular point of view, these results can then be qualitatively interpreted rather simply. The crosslink points represent the network formed by the styrene domains, connected by the isoprene midblocks of the SIS triblock copolymers. When a triblock is replaced by two diblocks, the average density of entanglements (which is controlled by the isoprene/resin structure only) does not change much. On the contrary, the average density of crosslink points decreases sharply when the amount of diblock is increased, reflecting the lesser number of tie molecules between PS domains. If the percentage of diblock is further increased, one expects even the network to disappear altogether when PS domains are no longer connected. Therefore one expects the connectivity between the PS domains (by bridging macromolecular chains) to play a major role in controlling the mechanical and adhesive properties of these soft adhesive blends. Such connectivity is amenable to predictive modelling if the χ parameters between the blend components are known[22].

Conclusions

We have shown that the fibrils which are formed during the debonding of a soft, block copolymer-based PSA from a rigid surface are mainly elastic and can be modelled, as a first approximation, by a constitutive equation describing a network of crosslink points formed by the styrene domains. The behaviour of such a network of PS domains would be analogous to that of a lightly crosslinked rubber network, with a homogeneous molecular weight between crosslinks and a very viscoelastic behaviour at small strains. Since the molecular weight of the isoprene block bridging two styrene domains is much larger than the average molecular weight between entanglements in the isoprene phase, the small strain modulus (in the linear viscoelastic regime) is then essentially controlled by the density of crosslink points, which, in turn, depends on the triblock/diblock ratio in the blend. Therefore, controlling the diblock/triblock ratio provides a convenient way by which to control the non-linear elastic properties of the adhesive, while the resin provides a convenient way by which to adjust the linear viscoelastic properties. Since the two parameters can be varied independently, the optimization of the adhesive properties is easier than for a homopolymer-based system.

Acknowledgements

We gratefully acknowledge funding from the European Commission within the 5th framework programme: Contract N° G5RD-CT 2000-00202. We have also benefited from helpful discussions with Galina Ourieva and Scott Milner from ExxonMobil Chemical and Christophe Derail from the Université de Pau et Pays de l'Adour.

[1] C. Creton, P. Fabre, in: *"The Mechanics of Adhesion"*, Vol. 1, Elsevier, 2002, pp. 535.
[2] A. Zosel, *Advances in Pressure Sensitive Adhesive Technology* **1992**, *1*, 92.
[3] L. Benyahia, C. Verdier, J. M. Piau, *J. Adhes.* **1997**, *62*, 45.
[4] S. F. Christensen, H. Everland, O. Hassager, K. Almdal, *Int. J. Adhesion & Adhesives* **1998**, *18*, 131.
[5] C. Derail, A. Allal, G. Marin, P. Tordjeman, *J. Adhes.* **1997**, *61*, 123.
[6] H. Lakrout, P. Sergot, C. Creton, *J. Adhes.* **1999**, *69*, 307.
[7] A. Zosel, *J. Adhes.* **1989**, *30*, 135.
[8] K. Brown, J. C. Hooker, C. Creton, *Macromolecular Materials and Engineering* **2002**, *287*, 163.
[9] C. Creton, H. Lakrout, *J. Polym. Sci., Part B: Polym. Phys.* **2000**, *38*, 965.
[10] A. Chiche, P. Pareige, C. Creton, *Comptes Rendus de l'Académie des Sciences de Paris, Série IV* **2000**, *1*, 1197.

[11] I. Chikina, C. Gay, *Phys. Rev. Lett.* **2000**, *85*, 4546.
[12] D. H. Kaelble, *J. Macromol. Sci., Rev. Macromol. Chem.* **1971**, *C6*, 85.
[13] M. Sherriff, R. W. Knibbs, P. G. Langley, *J. Appl. Polym. Sci.* **1973**, *17*, 3423.
[14] G. Kraus, K. W. Rollmann, *J. Appl. Polym. Sci.* **1977**, *21*, 3311.
[15] D. W. Aubrey, M. Sherriff, *J. Polym. Sci., Part A: Polym. Chem.* **1978**, *16*, 2631.
[16] S. F. Christensen, G. H. McKinley, *Int. J. Adhesion & Adhesives* **1998**, *18*, 333.
[17] C. C. Honeker, E. L. Thomas, *Chemistry of Materials* **1996**, *8*, 1702.
[18] E. Prasman, E. L. Thomas, *J. Polym. Sci., Part B: Polym. Phys.* **1998**, *36*, 1625.
[19] G. Josse, P. Sergot, M. Dorget, C. Creton, submitted to Journal of Adhesion.
[20] L. R. G. Treloar, in: *"The physics of rubber elasticity"*, Clarendon Press, Oxford 1975, pp. 210.
[21] M. Rubinstein, S. Panyukov, *Macromolecules* **2002**, *35*, 6670.
[22] K. Daoulas, D. N. Theodorou, A. Roos, C. Creton, submitted to Macromolecules.