

Polymer-polymer adhesion of uncrosslinked elastomers at short contact times

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Introduction

The polymer-polymer adhesion of uncrosslinked elastomers used in the tire industry is directly related to the cohesion of the different layers of a tire before the final crosslinking process, and is a key parameter for these materials. Despite this industrial relevance, only relatively few studies have been carried out on what is typically called “tack” and many aspects of the problem remain poorly understood. A key experimental obstacle in the study of the tack properties is the separation between surface and bulk contributions for such deformable materials.

Hamed studied the tack of elastomers on themselves using the classical peel test technique [1]. This technique allows the measurement of the tack properties, but only for long contact times. Furthermore it is well known that in a peel test, there is an important degree of coupling between bulk deformation, geometry and interfacial structure so that the desired interface effects may be difficult to interpret. Gent used another apparatus to study the tack at short contact times [2]. He studied the autohesive tack of elastomers by measuring the impact and rebound velocity of a rigid pendulum with a rubber sample at its tip impacting on another elastomer sample. With this experiment, very short contact times are accessible, but the contact time and the debonding velocity are not independent and the contact area is not exactly known.

We have developed the probe tack experiment used in the Pressure-Sensitive-Adhesive (PSA) industry as a powerful analytical tool to evaluate adhesion and cohesion of adhesives against rigid surfaces [3]. In this test, a flat steel probe approaches the adhesive layer at a constant velocity, applies a controlled compressive force during a set contact time and is removed at a constant debonding velocity while a CCD camera allows the observation of the debonding mechanisms. This technique cannot be directly applied to the study of autohesive tack of elastomers because the adhesion between the two polymers is greater than between the polymer and the substrate and the debonding occurs between the substrate and the elastomer. To avoid this, we used chemical grafting of mercaptosilanes to chemically bond the polymer to the substrates (glass or silicon wafer).

In the present work, results on the self adhesion of an SBR Rubber are presented. First we present the rheological properties of the material, and then the tack experiments results which are directly related to the bulk properties.

Experimental

Materials. We used a linear SBR Rubber (20% Styrene, 42% vinyl, 19% cis and 19% trans, $M_n=123000\text{g/mol}$, $\text{PDI}=1.09$) For rheological experiments, we used a sample of 1 mm thick and 8 mm diameter (parallel plate configuration). For the tack experiments, the polymer was grafted on glass or silicon by using a coupling agent.

Grafting of the SBR Rubber on the substrates. First, the substrates are cleaned in a piranha bath (30% hydrogen peroxide, 70% sulfuric acid at 150°C) during one hour. Then, they are put in a solution of 10% trimethoxy-mercaptopropyl-silane in toluene. The reaction is conducted under inert atmosphere (nitrogen) during 3 hours. The substrates are finally rinsed with absolute ethanol and dried with a nitrogen flux. A solution of 10% SBR in toluene is poured on the substrates, the toluene is slowly evaporated and the substrates are then annealed at 45°C during 2 days, to allow the reaction of the SH group with the double bonds of the SBR to take place.

Rheology The rheological properties of the SBR Rubber in the linear viscoelastic regime were measured on a RDA2 parallel plate rheometer from Rheometrics. We measured the storage and loss moduli in the range 0.1 Hz – 500 Hz for temperatures between the Tg (-35°C) and 80°C. By using empirical shifts of data obtained at different temperatures along a logarithmic frequency axis, we could construct master curves at room temperature.

Probe test experiments. We performed probe test experiments on our custom-designed apparatus with an MTS 810 hydraulic testing machine [4]. A typical probe test can be divided into three stages (**figure 1**). In the first stage, a flat, stainless steel probe with a silicon wafer coated with a ~ 1 μm thick SBR glued on its end, approaches a 100 μm thick SBR layer grafted on a microscope glass slide at a constant velocity. When the contact pressure of 1 MPa is reached, the probe stops during a contact time varying from 1 to 2000 s. The probe is removed during stage 3 at a constant debonding velocity varying from 1 to 100 μm/s.

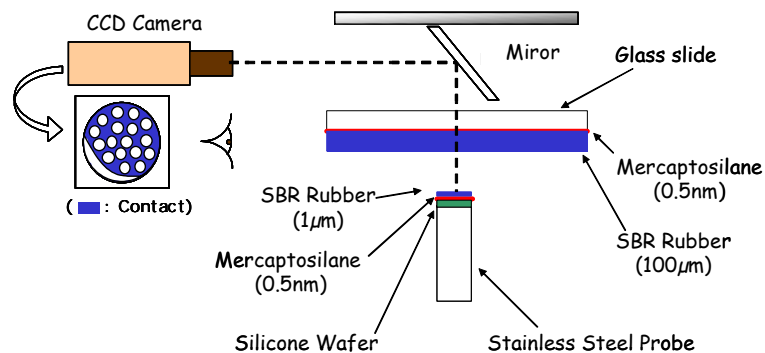


Figure 1. Schematic of the experimental setup for the probe test.

During this test, all experimental parameters are well controlled. The contact pressure, the contact time and the debonding velocity are independent parameters of the test and the contact area is measured with the video acquisition which also allows the detailed analysis of the debonding mechanism.

Results and discussion

Linear Viscoelastic Properties. The master curve obtained for the SBR at 20°C is shown on **figure 2** and is typical of monodisperse linear well entangled polymers.

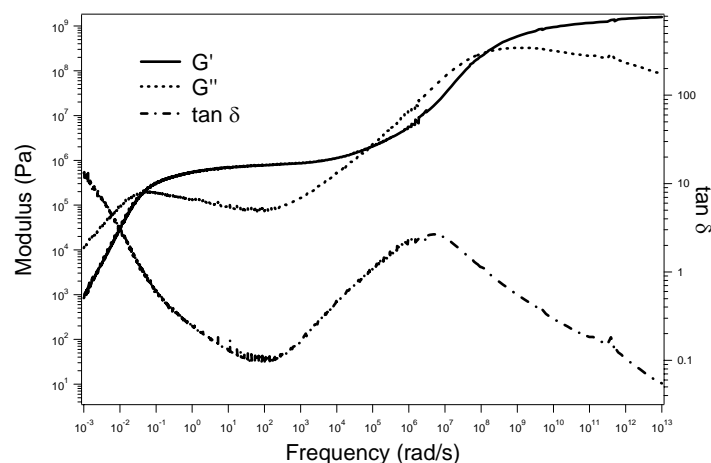


Figure 2. Master curves for the SBR Rubber at 20°C.

Using these master curves we measured several molecular and dynamic parameters of the rubber, and in particular the reptation time which sets the self-diffusion velocity of the polymer. This is a critical parameter during the process of healing of the interface as shown in neutron reflectivity studies [5]. The reptation time is found to be of approximately 160s.

Probe test. We studied the influence of two parameters on the tack properties. The first parameter is the time of contact and the second is the debonding velocity.

Figure 3 shows the evolution of the tack curves (stress versus strain) for a debonding velocity of 10 $\mu\text{m/s}$. For all contact times, the curves typically show a very moderate degree of deformation before failure in comparison with soft adhesives [4]. The maximum stress is of the order of a MPa, close to the elastic modulus of the elastomer at that deformation frequency. Both the maximum stress and the maximum strain increase with the time of contact so that the curves are self-similar and the adhesion energy (proportional to the area under the stress-strain curve) increases monotonically with contact time.

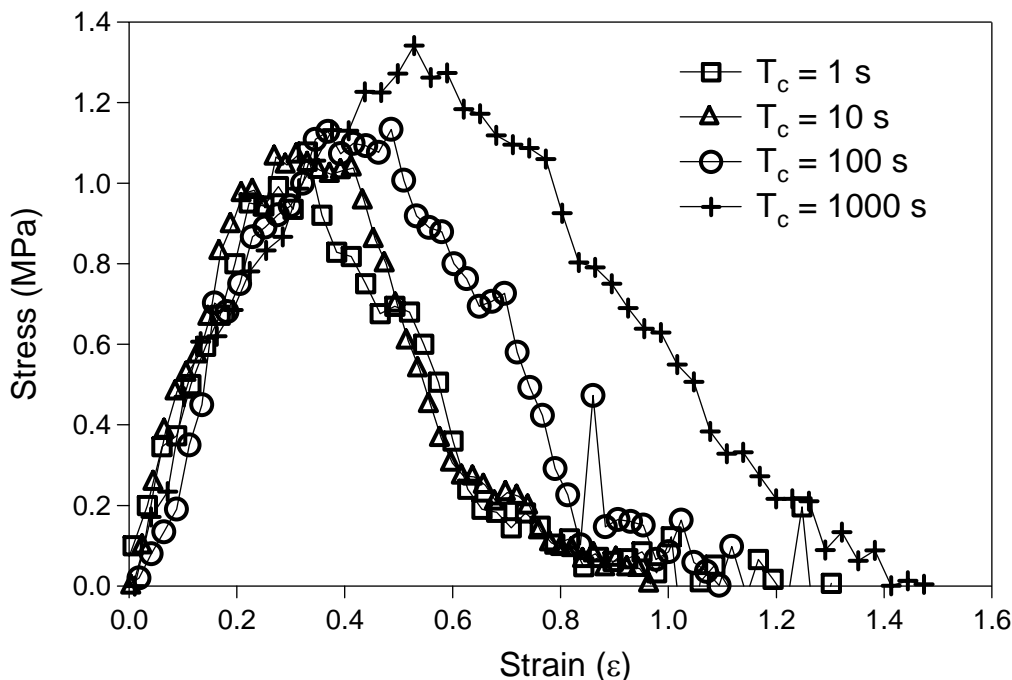


Figure 3. Evolution of the tack curves with the time of contact for a debonding velocity of 10 $\mu\text{m/s}$

If the debonding experiments are carried out at different probe retraction velocities, the results are quantitatively different. **Figure 4** shows the variation of the adhesion energy with the time of contact for three debonding velocities (1, 10 and 100 $\mu\text{m/s}$).

The adhesion energy first increase with contact time, and reaches a plateau value for times of contact greater than approximately 100s.

The effect of the debonding velocity is a viscoelastic effect. The faster the debonding occurs, and the greater is the adhesion energy, because of greater bulk dissipation.

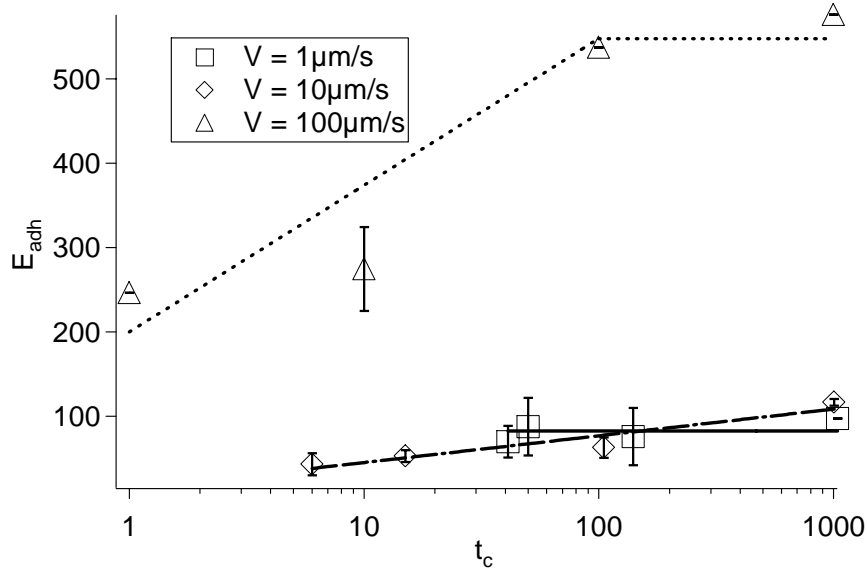
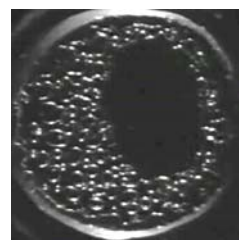


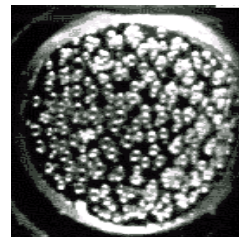
Figure 4. Evolution of adhesion energy with contact time for 3 debonding velocities

Nevertheless, the effect of the debonding velocity and time of contact are coupled. Depending on the values taken by these two parameters, we observed three different debonding mechanisms : for short times of contact and fast debonding, we observed the nucleation and propagation of multiple interfacial cracks and very low adhesion energies ; for longer contact times, cavitation occurred in the polymer, giving the highest adhesion energies and finally for very slow debonding rates, we observed a liquid-like mechanism of deformation, relatively insensitive to the interface structure and giving relatively low values of adhesion energy. The three mechanisms are described in **figure 5**.



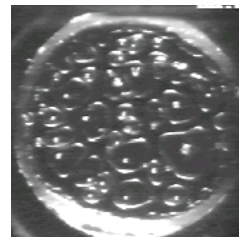
Interfacial crack propagation

The debonding occurs at low strain, without bulk deformation



Cavitation

The debonding is cohesive, not interfacial, and occurs at larger strain.



Liquid-like

The debonding is cohesive, occurs at large strain, but the velocity is so slow that the rubber has a liquid behavior

Figure 5.

It is clear that the energy of adhesion is directly related to the microscopic deformation mechanism with high energy for cavitation phenomena, intermediate energy for liquid-like debonding and low energy for interfacial crack propagation. We found also that the transition between these different mechanisms depended on the value of the time of contact and debonding velocity relatively to the terminal relaxation time.

Conclusion

A modification of the probe tack experiment used for PSA allowed us to study the self adhesion of an SBR rubber. We found that the adhesion energy was directly related to the debonding mechanism which depends on the value of the experimental parameters relative to the characteristic times extracted from the rheological measurements of the polymer, especially to the longest of these relaxation times also called reptation time. In fact, the reptation time sets the interdiffusion time at the interface as well as the boundary between elastomeric and liquid like behavior of the bulk polymer.

Acknowledgements

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