

INTERDIFFUSION AND TACK AT INTERFACES BETWEEN IMMISCIBLE POLYMER MELTS

Régis Schach¹, Yvette Tran¹, Alain Menelle², Costantino Creton¹

¹Laboratoire de Physico-Chimie des Polymères et Milieux Dispersés, E.S.P.C.I., Paris, France,
costantino.creton@espci.fr

²Laboratoire Léon Brillouin, CEA Saclay, France

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. In particular, while it is clear that the adhesion between miscible polymers is governed by the kinetics of interdiffusion, the situation is less clear for mutually immiscible polymers. In this case, the non-zero χ parameter between the two polymers causes the formation of a well-defined interface even at thermodynamic equilibrium.

A key experimental obstacle in the study of the tack properties is the separation between surface and bulk contributions for such deformable materials. Previous studies^{1,2} focused on the mechanical strength of the interface only and did not investigate the structure of the interface but only inferred it. Furthermore the mechanical test methods used (peel or tack pendulum) either did not give access to short contact times or were relatively poorly controlled in terms of experimental parameters.

We have combined the use of the probe tack experiment used in the Pressure-Sensitive-Adhesive (PSA) industry, with the technique of neutron reflectivity to analyze the degree of interpenetration of polymer chains at the interface. In our probe 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 mechanisms³. 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). Neutron reflectivity requires a deuterated polymer layer and has a relatively long data acquisition time. It is perfectly adapted to the characterization of the width of polymer interfaces at thermodynamic equilibrium. Our experimental strategy has been the following: we have characterized both mechanically and by NR, a series of polymer pairs with increasing

degrees of miscibility. Then the curve adhesion strength vs. interpenetration was used to interpret the increase in mechanical strength as a function of contact time data and extract information on the kinetics of formation of the interface.

Experimental

Materials. We used two SBR Rubbers specially synthesized for the study, a Polyisobutylene, a polydimethyl siloxane and an uncrosslinked epdm. All samples are linear and their molecular weights are larger than 80 kg/mole. Both SBR are monodisperse. For the tack experiments, the polymer was grafted on glass or silicon by using a coupling agent.

Grafting of the Rubbers 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% trimethoxymercaptopropyl-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.

Neutron reflectivity: Samples for neutron reflectivity studies were prepared as follows: a thin (50 nm) layer of deuterated PB was spin-coated on a thick 2” silicon wafer. Since all the polymers of this study are apolar and have T_g values well below room temperature, it was not possible to directly spin coat the second layer on top of the first or to transfer the layer by floating (because of dewetting from the water surface). Then the second layer had to be transferred by first preparing a bilayer of PMMA over which the desired hydrogenated polymer (500 nm thick) was spin-coated. This bilayer is then floated and transferred by flipping it onto the Si wafer. The PMMA layer is then dissolved with acetone and the bilayer for NR is ready. NR experiments were then performed at room temperature at the DESIR reflectometer at the Laboratoire Léon Brillouin in Saclay.

Probe test experiments. We performed probe test experiments on our custom-designed apparatus with an MTS 810 hydraulic testing machine. A typical probe test can be divided into three stages. In the first stage, a flat, stainless steel probe with a silicon wafer coated with a $\sim 1 \mu\text{m}$ thick polymer on its end, approaches a $130 \mu\text{m}$ thick layer of the second polymer 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 then removed during stage 3 at a constant debonding velocity varying from 1 to $100 \mu\text{m/s}$. 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.

In order to obtain meaningful comparisons of adhesion energy for the different fluid/fluid interfaces, we always performed the tests with a probe velocity during the debonding stage which imposed average strain rates to the samples, higher than the inverse of the longest relaxation time of both polymers. Furthermore the thickness ($130 \mu\text{m}$) and composition (a cis,1,4, polybutadiene with a molar mass of 420 kg/mole) of the thick layer was always kept constant. In those conditions the other polymers (in the $1 \mu\text{m}$ thick layer) acted as boundary conditions for the deformation of the PB layer but did not contribute to the adhesion energy.

Results and Discussion

Bilayers between deuterated monodisperse cis1,4 PB and all other polymers were prepared by the technique described above. NR Experiments were performed on interfaces at thermodynamic equilibrium and the results are presented in figure 1.

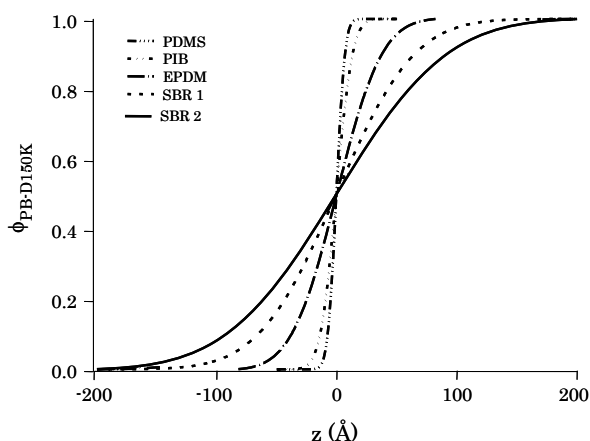


Figure 1: volume fraction of deuterated monomer as a function of distance along the interface for interfaces between a deuterated PB and various polymers.

Clearly the degree of interpenetration varies significantly for the different interfaces depending on the miscibility between the polymer pair. It is important to note that these values are quantitatively comparable to the radii of gyration of the polymers that we have used which vary between 10 and 25 nm.

The mechanical strength of the interface is then measured on the same interfaces by the probe tack tests. As an example of what is obtained for the probe tests, typical curves of probe tack as a function of contact time are shown on figure 2 in both linear and log scale.

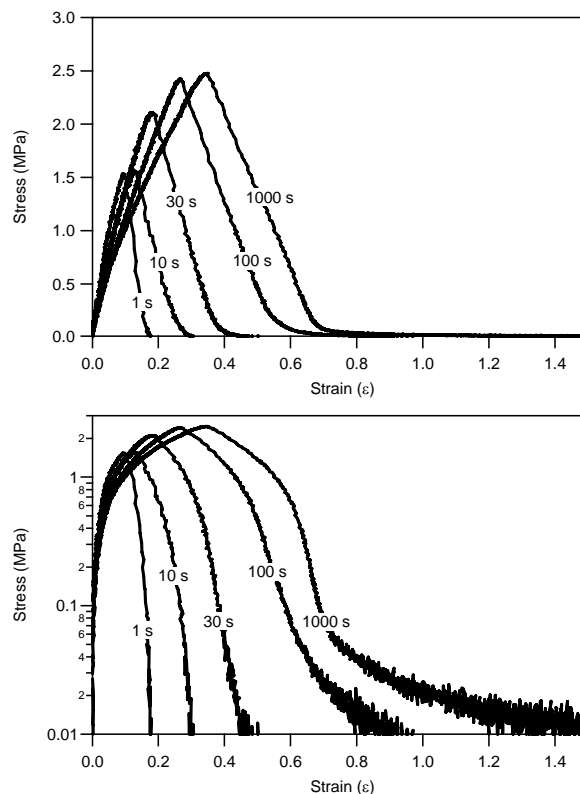


Figure 2: Series of probe tack curves for different contact times for the interface between PB and SBR1. a) in linear scale and b) in log scale.

From 1 to 30 seconds of contact time, the peak stress increases and fracture occurs in a brittle manner by the simultaneous and rapid propagation of multiple cracks. With increasing contact time these cracks propagate for higher levels of stress and increasingly slowly, a clear indication of the strengthening of the interface.

Because the deformed layer (the PB) is always the same, for all interfaces, the tack curves are very similar for all polymer pairs. However while the mechanical strength of all interfaces between immiscible polymers increases with contact time, the final magnitude of the increase and the rate of increase vary greatly. The adhesion energy, i.e. the integral under the stress-strain curve, is shown on figure 3 for the series of interfaces. For comparison we also in-

cluded the data for the self-adhesion of the PB (in this case the thin layer is also made of PB).

It is clear that regardless of the nature of the polymer the upper bound in terms of adhesion energy is the amount of energy necessary to fracture the PB layer cohesively, i.e. 120 J/m^2 . However this level of adhesion energy is only reached for the two interfaces with an SBR polymer. EPDM, PIB and PDMS never reach such a high value of adhesion energy even at thermodynamic equilibrium.

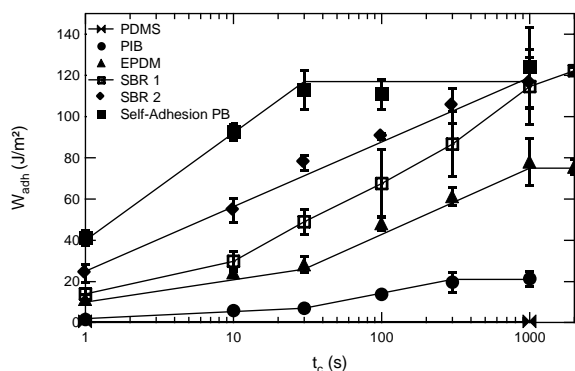


Figure 3: Adhesion energy W_{adh} as a function of contact time for a series of interfaces between PB and various polymers.

Comparing figure 1 and figure 3, it is immediately obvious that the stronger interfaces are also the interfaces where the degree of interpenetration at equilibrium is higher. In particular both SBR polymers have an interfacial width of the order of 15 nm with the PB. On the other hand the PIB and PDMS have a very narrow interfacial width with PB. An interesting check can be done by plotting the maximum achievable adhesion energy as a function of the interfacial width at thermodynamic equilibrium.

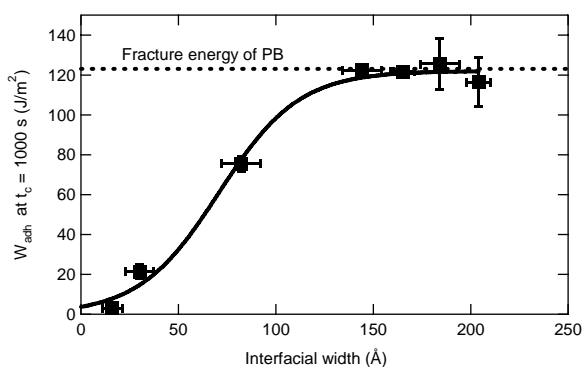


Figure 4: Adhesion energy W_{adh} as a function of interfacial width a_i at thermodynamic equilibrium for different polymer pairs.

This result is shown on figure 4 and clearly demonstrates that the adhesion energy between the fluid layers is controlled primarily by the degree of interpenetration at the

interface. This result has some interesting implications. For high molecular weight polymers in the strong segregation limit, the interfacial width between two polymers 1 and 2 varies as $1/\gamma_{12}$ so from the results of figure 4 one expects adhesion to vary approximately as the inverse of the interfacial tension⁴. This result can be at odds with the classical result found in textbooks for the reversible work of adhesion:

$$W_{rev} = \gamma_1 + \gamma_2 - \gamma_{12}$$

Since typically the surface tensions are much larger than the interfacial tension, we expect for example a low adhesion between two very immiscible but high surface tension polymeric fluids and on the contrary a high adhesion between two nearly miscible but low surface tension fluids.

A second interesting conclusion of figure 3 is the considerable slowing down of the rate of mutual diffusion with increasing degree of immiscibility. In particular if one compares the kinetics of increase in adhesion between the PB/PB interface and that of the EPDM/PB interface, there is almost a factor of 100 in equilibration time. If we assume that maximum adhesion is attained when the interfaces are at thermodynamic equilibrium, this implies a much lower mutual diffusion coefficient at the interface.

Conclusions

We have demonstrated that the level of adhesion between high molecular weight immiscible polymeric fluids is chiefly controlled by the degree of interpenetration, i.e. by the interfacial tension. Furthermore we have observed a dramatic decrease of the equilibration rates of the interface with increasing χ parameter for the polymer pair.

Acknowledgements

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References

Examples:

- (1) Hamed, G. R. *Rubber Chem. Tech.* **1981**, *54*, 576-595.
- (2) Gent, A. N.; Kim, H. J. *Rubber Chem. Tech.* **1990**, *63*, 613-623.
- (3) Lakrout, H.; Sergot, P.; Creton, C. *J. Adhes.* **1999**, *69*, 307-359.
- (4) Helfand, E.; Tagami, Y. *J. Chem. Phys.* **1971**, *56*, 3592-3601.