

Adhesion at Interfaces Between Immiscible Polymer Melts

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We have investigated the adhesion between immiscible polymer melts by combining a characterization of the width of the interface by neutron reflectivity (providing information on the formation of entanglements across the interface) and a macroscopic measure of adhesion by a probe test method. We found a direct correlation between the level of adhesion and the interfacial width between the two polymers regardless of the surface tensions of the two polymers. Furthermore we observed a significant slowing down of the interdiffusion rate at the interface with increasing χ parameter between the two polymers.

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^[1,2] 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.

We have combined the use of the probe tack experiment^[3] 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.

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. 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. A solution of 10% SBR in toluene is then 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. 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^[3]. 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 μm thick layer of the second polymer on a microscope glass slide at a constant velocity. When the desired contact pressure is reached, the probe stops during a contact time varying from 1 to 2000 s. The probe is then removed at a constant debonding velocity varying from 1 to 100 $\mu\text{m/s}$. The thickness (130 μm) 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 μm 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. The degree of interpenetration varied significantly for the different interfaces depending on the miscibility between the polymer pair.

The mechanical strength of the interface was 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 1.

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.

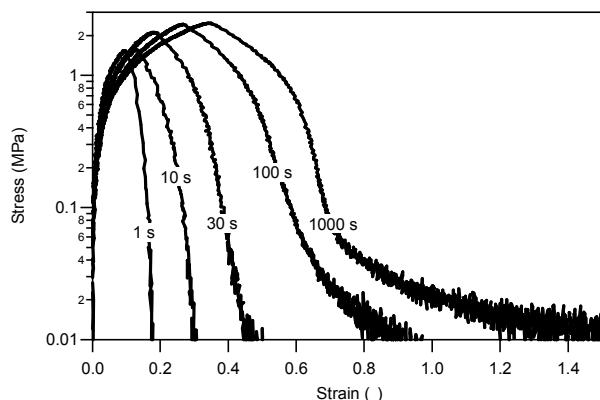


Figure 1: Series of probe tack curves for different contact times for the interface between PB and SBR1.

Because the deformed layer (the PB) is always the same, for all interfaces, the tack curves are very similar for all polymer pairs. 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 included the data for the self-adhesion of the PB (in this case the thin layer is also made of PB).

The upper bound in terms of adhesion energy is the amount of energy necessary to fracture the PB layer cohesively, i.e. 120 J/m². 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.

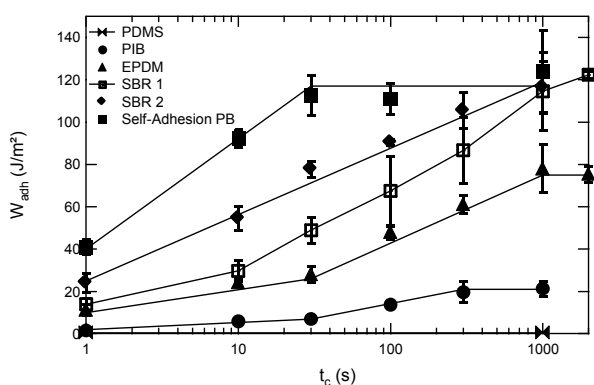


Figure 2: Adhesion energy W_{adh} as a function of contact time for a series of interfaces between PB and various polymers.

Comparing the NR results and figure 2, it is immediately clear 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.

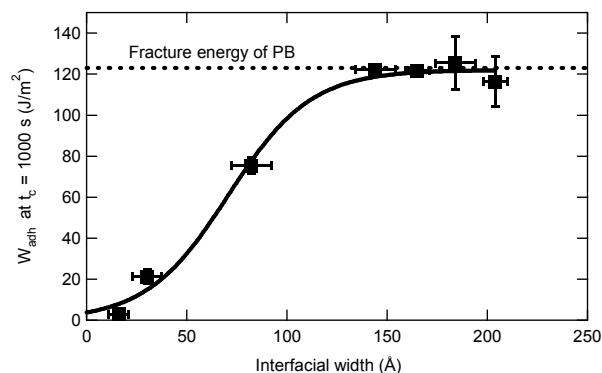


Figure 3: Adhesion energy W_{adh} as a function of interfacial width a_i at thermodynamic equilibrium for different polymer pairs.

This result is shown on figure 3 and clearly demonstrates that the adhesion energy between the fluid layers is controlled primarily by the degree of interpenetration at the interface. A second interesting conclusion drawn from figure 2 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.

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 parameter for the polymer pair.

Acknowledgements

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References

- [1] A. N. Gent, H. J. Kim, *Rubber Chemistry and Technology* **1990**, *63*, 613.
- [2] G. R. Hamed, *Rubber Chemistry and Technology* **1981**, *54*, 576.
- [3] H. Lakrou, P. Sergot, C. Creton, *Journal of Adhesion* **1999**, *69*, 307.