POLYMER-POLYMER ADHESION OF UNCROSSLINKED ELASTOMERS STUDIED BY NEUTRON REFLECTIVITY

R. Schach[*], C. Creton, Y. Tran

Physico-chimie des Polymères et des Milieux Dispersés. UMR 7516
Ecole Supérieure de Physique et de Chimie Industrielles
10, rue Vauquelin - 75231 Paris Cedex 05 – France
*Thèse financée par la Manufacture Française des Pneumatiques Michelin, commencée en janvier 2003

The polymer-polymer adhesion of uncrosslinked elastomers (i.e. polymers with a glass transition temperature below room temperature) 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 few studies have been carried out on the so-called "tack", and so many aspects of the problem remain poorly understood.

To understand these adhesion phenomena, we need to link the structure and the mechanical properties of the interface between two polymers. In the case of elastomers, these studies present major challenges. On the one hand, the interface and the bulk contributions to adhesive strength must be separated. On the other hand, the structure of the interface (essentially, the degree of interpenetration of polymer chains) and the stress necessary to extract the chains to separate the interface (which is likely to depend on friction coefficients) have to be distinguished. Thus, a precise knowledge of the structure of the interface is a necessary step to infer adhesion measurements in a less speculative way.

When two polymers are put into contact at a temperature higher than their glass transition temperature, they either diffuse into each other over long distances as a function of the contact time, if they are fully miscible, or they reach an equilibrium degree of interpenetration when they are immiscible. The adhesion between two polymers is directly related to this interpenetration width, and hence to the degree of miscibility.

Neutron reflectivity is very well suited to measure the interfacial width between two polymers. Interfaces between two glassy polymers have been extensively studied [1]. Adhesion experiments and neutron reflectivity studies confirmed that the interpenetration of two polymers is one of the most important parameters of these systems [2,3]. The aim of our work is to exploit this experimental technique to elastomer/ elastomer interfaces.

These experiments have never been performed on elastomers because of the extreme difficulty of preparing samples. To conduct neutron reflectivity experiments, double layers of polymers are needed. Usually, this double layers are obtained by the flotation technique : a first film, prepared by spin-coating on silicon substrate, pick up a second film which was also spin-coated and was floated off its substrate onto a deionized water surface. Unfortunately, this technique cannot be applied to elastomers, because of mechanical properties of these polymers. Actually, as elastomers are "liquids" contrary to glassy polymers, an elastomer film floated on water will flow and is not stable.

We investigated here the adhesion between a cis 1,4 polybutadiene (PB) and several other elastomers (styrenebutadiene rubber (SBR), poly-isobutylene (PIB) and poly-dimethylsiloxane (PDMS)). In order to satisfy the contrast conditions for neutron reflectivity studies, deuterated PB (PB-d, purchased from Polymer Source) was required. We also used four different SBR with various degrees of immiscibility with the PB. SBR samples were specially synthesized by Michelin with a narrow polydispersity : three SBR with a glass transition temperature of -35°C and three different molecular weights, 80000 g/mol, 160000 g/mol and 240000 g/mol (the higher the molecular weight and the more the SBR is immiscible with the PB) and a SBR with a glass transition temperature of -50°C and a molecular weight of 160 000 g/mol (this fourth elastomer has a lower styrene content than the 3 others and is less immiscible with PB). These four elastomers are weakly immiscible with the PB. The PDMS and the PIB can be considered as polymer models strongly immiscible with the PB.

We aim to determine the interpenetration depth at thermodynamic equilibrium between deuterated polybutadiene (PB-d) and the other elastomers by neutron reflectivity. A method to prepare double layers of elastomers was hence developed. The floating technique was a little modified. A first film of polybutadiene was prepared by spin-coating a solution of the polymer in toluene on silicon substrate. A double layer of polymethylmetacrylate (PMMA) and elastomer

(SBR, PIB or PDMS) was then spin-coated by using toluene as PMMA solvent and carbon tetrachloride as elastomer solvent and PMAA non-solvent. As PMMA is a glassy polymer at room temperature, this double layer can be easily floated. The double layer is then transferred on the first film to obtain a triple layer PMMA/elastomer/PB-d. Finally, the excess PMMA is rinsed with acetone which is a good solvent of PMMA but a non-solvent of the other polymers. This last step permits to remove the PMMA and to obtain a double layer of elastomers. Ellipsometry measurements were carried out at each step to verify the thicknesses of the resulting layers.

Neutron reflectivity experiments have been performed on the EROS spectrometer at the LLB to determine the interfacial width of these samples. The interfacial width is the sum of two contributions : the actual interpenetration of the polymers and the thermally excited capillary waves [4]. The relative contribution can be calculated using the results of Buff [5] for the capillary waves and Broseta [6] for the interpenetration. Finally, we find the deconvoluted interpenetration profiles (figure 1).

A wide range of interpenetrations is observed. For very immiscible systems such as the PDMS/PB interface, the interpenetration width, about 15 Å, is very weak whereas for SBR/PB systems (SBR with the glass transition temperature of -50°C), it is more than 200 Å. Actually, the key parameter is the comparison between the interpenetration and the size of the polymer. For example, the SBR with a Tg of -35°C and a molecular weight of 80 000 g/mol shows an interpenetration greater than its radius of gyration which is approximately 150 Å. Thus, the interface between the PB and this SBR at thermodynamic equilibrium may be probably as strong as the bulk. On the other hand, the SBR with a molecular weight of 240 000 g/mol shows an interpenetration of half its radius of gyration. This interface is expected to be less strong than the bulk. Of course interpenetration depth is only half the story since the stress that can be transferred across the interfaces depends probably of the friction coefficients at the monomer level. These friction coefficients have been measured for some glassy polymer pairs [7,8] but remain unknown for elastomer systems.

In conclusion, we have shown that the measurement of the interfacial width for elastomers/elastomers interfaces at thermodynamic equilibrium is possible and we expect that this information will be invaluable to interpret further adhesion experiments on same systems.

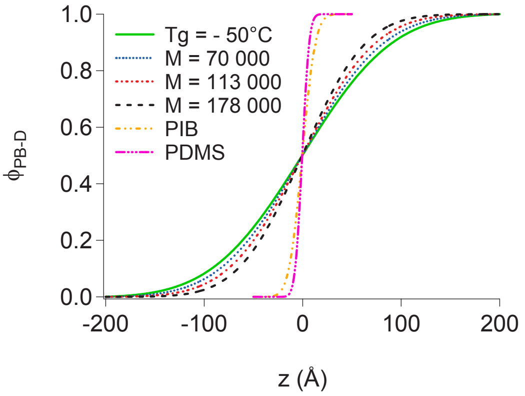

Figure 1. Interpenetration profiles of PB and six different elastomers. The PDMS/PB interface shows an interpenetration width of 15 Å, the PIB/PB 30 Å, the three SBR with a Tg of -35°C 145 Å, 165 Å and 185 Å (the wider interface corresponding to the lower molecular weight) and the SBR with a Tg of -50°C has an interpenetration width of 205 Å.

References

[1] M. Stamm and D. W. Schubert, *Annual Review of Materials Science* **25,** 325-356 (1995)
[2] R. Schnell, M. Stamm, and C. Creton, *Macromolecules* **31**, 2284-2292 (1998).
[3] R. Schnell, M. Stamm, and C. Creton, *Macromolecules* **32**, 3420-3425 (1999).
[4] K.R. Shull, A.M. Mayes, T.P. Russel *Macromolecules* **26**, 3929 (1993)
[5] F.P. Buff, R.A. Lovett and F. H. Stillinger *Physical Review Letters* **15**, 621 (1965)
[6] D. Broseta, G.H. Fredrickson, E. Helfand, L. Leibler (1990) *Macromolecules* **23**, 132
[7] J. Washiyama, E. J. Kramer, and C. Y. Hui, *Macromolecules* **26**, 2928-2934 (1993).
[8] J. Washiyama, E. J. Kramer, C. Creton, and C. Y. Hui, *Macromolecules* **27**, 2019-2024 (1994).]