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Adhesion promotion through controlled surface modifications

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SUMMARY: We present and discuss series of experiments conducted on systems controlled at the molecular level in order to identify the molecular mechanisms of polymer adhesion. A special emphasis is paid to 1) adhesion enhancement through block copolymers at an interface between two incompatible polymers (amorphous or semi-crystalline) ; 2) adhesion promotion between an elastomer and a solid, by soft end grafted connector polymer molecules able to interdigitate into the elastomer. We show that surface modifications based on surface anchored polymer chains are efficient for adhesion enhancement because they allow the interface to sustain mechanical stresses. The coupling between surface and bulk stresses is finally what governs the adhesion energy and we examine how one can understand and optimize this coupling.

Introduction

Molecular models have been proposed recently to describe how polymer molecules could promote adhesion between two different polymers or between a polymer and a solid surface. Such molecules, called connector molecules1), act in a different way depending on the fact that the polymers are soft (temperature T larger than the glass temperature Tg) or hard (T<Tg).

For soft polymers (cross-linked elastomers), it has been suggested that the extraction mechanism analyzed by Raphaël and de Gennes2) was at the origin of an adhesion energy larger than the thermodynamic work of adhesion, W, even if the connector molecules were not chemically attached to the elastomer. Due to cohesive interactions, the monomers of the surface chains tend to remain embedded in the monomers of the elastomer and the connector chains resist to the propagation of the fracture. When forcing the fracture to propagate, the connector chains are elongated and some of their monomers are exposed to air. The energy necessary to elongate and extract these monomers is finally dissipated when the connector chains collapse on the surface after the fracture has gone through. For low

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enough surface density of connector chains (so that they act independently of each other) the increment of adhesion energy is expected to be:

$$\frac{G-W}{W}=WN\Sigma$$

with G the adhesion energy at vanishing velocity of propagation of the fracture, N the polymerization index of the connector chains, and Σ their surface density (the surface density of connector chains is related to their number per unit area, ν, by $\nu=\Sigma/a^2$, with a the size of the monomers). For finite velocities of the fracture, the adhesive strength is further increased compared to the adhesion energy at zero fracture velocity, due to friction between elastomer and connector chains monomers.

The case of hard polymers is more complicated. The adhesion enhancement by block copolymer molecules at an interface between two amorphous polymers has been investigated both experimentally and theoretically [3 to 7)]. The copolymer molecules spontaneously segregate at the interface, and tend to link mechanically the two polymers as schematically represented in figure 1. As for soft polymers, the extraction of the block which is the easiest to extract is one possible mechanism for adhesion enhancement.

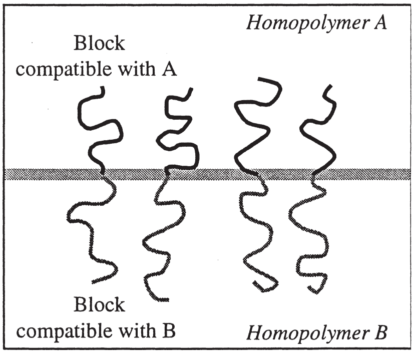

Fig.1: Block copolymers localized at an interface between two incompatible polymers A and B

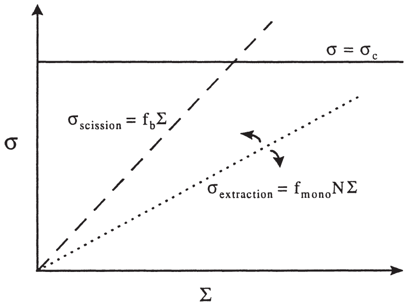

Fig.2: Stress for fracture, as a function of the surface density of copolymers for the three different rupture mechanisms.

The adhesion energy is then expected to increase linearly with both the surface density of block copolymer molecules at the interface and the length of the extracted block. This is not however the only possible mechanism for adhesion enhancement: three different modes can allow the fracture to propagate and are summarized in figure 2 in terms of the dependences of the stress σ associated with each fracture mechanism versus the surface density of copolymer, Σ. Obviously, the fracture will propagate through the mechanism corresponding to the smallest σ. If the force necessary to extract a block becomes larger than the force necessary to break a copolymer chain, the fracture will propagate through chain scission. Both extraction and chain scission lead to a constraint varying linearly with Σ, but the slope of the curve for extraction depends on the length of the extracted block, so that short connectors lead to easy extraction while long connectors rather lead to chain scission. A third mechanism is related with the formation of strongly deformed zones at the fracture tip (craze): when the constraint that the interface can sustain (without chain scission or chain extraction) becomes larger than the yield stress, σ_c, of one of the two polymers, the fracture proceeds through crazing. It has been observed that the adhesion energy was then varying with the surface density of connector chains like Σ^2. This Σ^2 law has been modeled, in a phenomenological way, by H. Brown5,8,9). When the fracture proceeds in this mode, the adhesive strength is much larger than for either chain extraction or chain scission, because the dimensions of the highly deformed zone ahead the crack tip are larger than molecular dimensions. The adhesion energy is essentially the energy necessary to create these deformed zones. To understand the relations between the organization of connector polymer molecules at an interface and the rupture mode of this interface thus appears as a key point if one wants to optimize adhesive properties. We analyze here in more details a few examples.

Adhesion promotion at an interface between two incompatible semi-crystalline polymers

We have investigated how block copolymer molecules formed in situ at the interface between polyamide 6 (PA6) and polypropylene (PP) were able to promote adhesion between these two incompatible polymers. The adhesion energy was measured (by an asymmetric double beam cantilever test) as a function of the surface density of copolymer molecules formed at the PP / PA6 interface during the annealing of the assembly, by reaction of chemically modified PP molecules on the NH_2 extremity of the PA6 chains. The surface density was measured a posteriori by XPS, after selective dissolution of the PA6 part of the assembly, thus only keeping on the PP surface the grafted PA6 part of the copolymer molecules(10). As for amorphous polymers, two mechanisms for adhesion enhancement do appear. For short PP blocks of the copolymer, the fracture proceeds through chains extraction of the PP block (PP is softer than PA6 and the fracture propagates close to the interface, in the PP part of the assembly). The adhesive strength grows linearly with the surface density of copolymer molecules at the interface(11). For long PP blocks, the adhesive strength is much larger, and grows as Σ^2 (10). Observations by electronic microscopy (in transmission), conducted in collaboration with C. Plummer at EPFL Lausanne, have allowed us to visualize that a crazing zone was then present ahead the crack tip, and that fibrils formed(12). We could measure the diameter of these fibrils and show, knowing the material constants of both PP and PA6, that the Brown's model was able to quantitatively account for the measured adhesive energy, as long as the highly deformed zones remained localized at the crack tip. For large surface densities of block copolymers, diffused deformed zones appeared all throughout the PP, and the Brown's model was no longer able to predict the adhesion energy.

For annealing temperature very close to the melting temperature of PA6, we have observed that the efficiency of the copolymer with long PP blocks to enhance adhesion was increased by a factor four compared to that of the same copolymer at lower annealing temperatures(13). This increased efficiency is not due to the nucleation close to the interface of an otherwise non stable crystalline form of the PP, contrary to what we first thought(13,11). It is not due to a change in the morphology of either the PP or the PA6 close to the interface(12). We thus think that this increased efficiency of the connector molecules which only appears in specific annealing conditions and for long PP blocks of the copolymer, is the signature of the semi-crystalline nature of the polymers and has to do with a co-crystallization of the copolymer with the bulk PP. X ray diffraction experiments under grazing incidence are presently underway in order to trace back possible epitaxy or co-crystallization effects.

We have also investigated how these same block copolymer molecules formed in situ could promote adhesion at an interface between PA6 and a thermoplastic vulcanized elastomer (TPV) in which the continuous thermoplastic phase was polypropylene(11). As shown in figure 3, the adhesive strength in these systems varies with the surface density of block copolymer in a way quite similar to what happens for pure PP – PA6 assemblies. The Σ^2 law is well observed, but for a given Σ, the copolymer molecules are more efficient for the PA6 – TPV system than for PA6 – PP one. By visualizing the plastically deformed zones at the crack tip (through optical microscopy of microtomed slices of the samples, embedded into an epoxy resin) we have shown that this increased efficiency of the copolymer had to be related to the coupling between interfacial and the bulk mechanical stresses. The max opening, δ, just at the crack tip can easily be measured, and falls in the tens of micrometers range. This is larger than for the corresponding assemblies with pure PP, due to the fact that TPV is softer than PP. In fact, knowing the yield stress for TPV, σ_c, which can be measured independently, we have shown that the adhesion energy in the TPV – PA6 systems could be estimated through the Dugdale formula, $G = \delta\sigma_c$, as shown in figure 4.

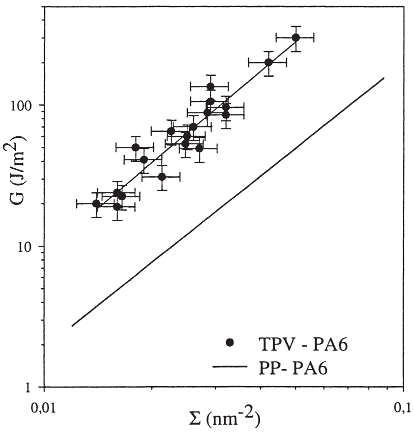

Fig.3: adhesion energy of TPV – PA6 assemblies as a function of the surface density of copolymers, and comparison with the case of PP – PA6 (full line) for the same copolymer at the interface.

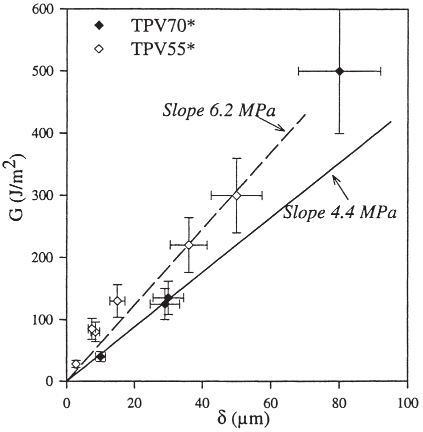

Fig.4: Adhesion energy as a function of the size of the plastically deformed zone at the crack tip, for two different TPV in contact with PA6. The values of the slopes agree with the modulus of the TPV

One can then understand why a given copolymer is more efficient at PA6 – TPV interfaces than at PA6 – PP ones: for a given interfacial strength (due to a given surface density of copolymer molecules at the interface where in both cases PP and PA6 are in contact[11)]), the highly deformed zones are much larger in the case of TPV than in the case of pure PP, because the yield stress is smaller for TPV than for PP. The adhesion energy, which is the product of the yield stress by the dimension of the deformed zone, is then larger for TPV than for PP. The present experiments clearly demonstrate that both the material properties and the molecular structure of the interface play together to fix the level of adhesion. In hard polymer systems, due to highly deformed zones at the crack tip, there is an interplay between interfacial structures and bulk mechanical deformations. To obtain a high adhesive level one needs to produce large plastically deformed zones, and this is easier in softer materials. If the constraint that the interface is able to sustain is weaker than the yield stress, no plastically deformed zones appear and the adhesion energy remains weak.

Adhesion at the interface between an elastomer and a solid surface covered by surface attached polymer chains

We have undertaken, for several years now, systematic experiments on the system polydimethylsiloxane (PDMS) – silica in order to test the de Gennes' model of adhesion promotion through extraction of connector molecules in soft polymers1,2). This experimental system presents many advantages: controlled cross-linked elastomers can be synthesized and surface anchored polymer layers can be formed with different internal organizations, adjusting independently the surface density and the length of the chains14). In particular layers of end grafted chains can be produced in a controlled manner (i.e. avoiding direct adsorption between the surface and the monomers of the end grafted chains). The cross-linked elastomers are transparent, and the JKR adhesion test can be used15). This is a convenient adhesion test, if used properly, because it can give simultaneously the thermodynamic work of adhesion, W, the Young modulus of the elastomer and the adhesive energy as a function of the velocity of the fracture16). We have shown that the evolution of the adhesive energy as a function of the surface density of connector molecules was more complicated than expected, as can be seen in figure 5: this adhesive energy first increases linearly with Σ, but rapidly a maximum is reached, and the connector molecules progressively loose their efficiency when Σ is further increased. This was not predicted by the first models and has been attributed to the fact that the adhesion promotion through

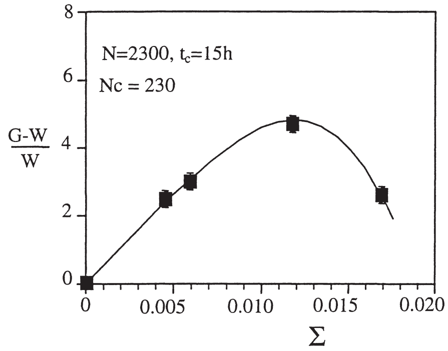

Fig.5: Adhesion enhancement as a function of surface density of grafted chains for a brush with a polymerization index N = 2300, an elastomer with a polymerization index between cross-links N_c = 230 and a contact time of 15h

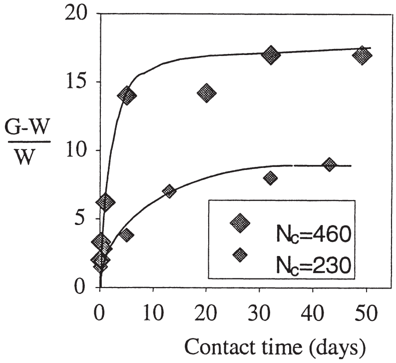

Fig.6: Evolution of the enhancement of adhesive strength with the time of contact between the brush and the elastomer for a brush with N = 1300 and $\Sigma = 8.10^{-3}$ in contact with two different elastomers

connector molecules is only possible if the connector molecules do penetrate into the elastomer. This penetration is easy at low Σ (it is entropy driven when, as it is the case in the present experiments, the surface attached chains and the elastomer have the same chemical nature), but it becomes more and more difficult when Σ is increased, due to the necessary swelling of the elastomer associated with the interdigitation process. For too high Σ, this swelling energy may prevent the penetration of the surface chains into the elastomer. A quite surprising result is shown in figure 6: the kinetics at which the adhesion enhancement develops after contact between the solid bearing the grafted chains and the elastomer is very slow17) (it seems that the process is not fully completed after two months!). This kinetics seems to be strongly affected by the molecular weight between cross-links in the elastomer17). Long interpenetration times have been predicted in such systems18) but not as long as experimentally observed. A consequence is that for many practical systems, the efficiency of the connector molecules cannot be described in terms of equilibrium interpenetration, and transients dominate the adhesive behavior of the system. During these transient stages, the level of adhesion appears dominated by the molecular weight between cross-links in the elastomer, and is only weakly affected by the length of the connector chains17). On the contrary, this length becomes the essential parameter for equilibrium adhesion.

Conclusions

We have discussed a few examples putting into evidence how macromolecules attached to an interface between two different polymers or between a polymer and a solid can act to enhance the mechanical strength of that interface. For soft chains, the extraction mechanism is what consumes energy to propagate a fracture at the interface. The energy depends on the molecular parameters of the surface anchored chains: their length and their surface density. In fact, it is the degree of interdigitation between the surface chains and the bulk which fixes the adhesion energy. The kinetics of this interpenetration process is very slow, not fully understood at present, and appears governed by the mesh size of the elastomer.

For hard polymers, we have more specifically investigated some semi-crystalline polymers and interface reinforcement by block copolymers. For short blocks, the surface anchored chains act through the extraction mechanism as for soft polymers. Long connector molecules are far more efficient, because the interface becomes able to support stresses which allow craze zones to form at the crack tip. Then the adhesive energy is amplified compared to the situation where short chains are used, by a factor more than ten, and the evolution of the adhesive energy as a function of the surface density of connector chains becomes non linear (Σ^2).

To understand in details how the stress the interface is able to sustain can induce or not the appearance of large plastically deformed zones in the bulk polymer thus appears as a key point to predict and control interfacial adhesion.

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