

ADHESION AND CRYSTALLINITY AT POLYPROPYLENE / POLYAMIDE 6 INTERFACES.

C. Laurens¹, R. Ober¹, C. Creton² and L.Léger¹

¹Laboratoire de Physique des Fluides Organisés
Collège de France, 11 place Marcelin Berthelot

75231 Paris Cedex 05, France

e-mail: Claire.laurens@college-de-france.fr

tel : +33 1 44 27 10 73

fax : +33 1 44 27 10 82

²Laboratoire de Physico-Chimie Structurale et
Macromoléculaire, ESPCI, 10 rue Vauquelin

75231 Paris Cedex 05, France

INTRODUCTION

The adhesion between two semi-crystalline polymers, polyamide 6 (PA6) and isotactic polypropylene (iPP) has been investigated. The interface is reinforced with PA6/iPP diblock copolymers formed *in situ* by chemical reaction between the -NH₂ end of polyamide molecules and modified polypropylene chains.

In such joints a strong increase of the efficiency of the copolymer to enhance adhesion has been observed in specific experimental conditions [1,2], (annealing over the melting temperatures of both polymers and copolymer of sufficient molecular weight). Such an effect, never observed for assemblies between glassy polymers, is presumably related to the crystallinity. However, subsequent studies [3,4] showed that this effect was neither due to a modification of the crystalline phase in the iPP matrix, nor to a change of the microstructure of the samples within the first micron from the interface.

All these results suggest that the crystalline structure very close to the interface could be responsible for this unexpected behavior. In particular the interfacial orientation and the ability of the copolymer to co-crystallize with the matrix could influence the adhesion. In the present study we will try to understand the role of these factors .

EXPERIMENTAL

Materials

The polyamide 6 was Ultramid B3 from BASF, with an average of one -NH₂ end per chain. Isotactic polypropylene 3050MN1 from APPRYL (M_n ≅ 57 kg/mol, M_w/M_n = 4.8) mixed with 5wt % of succinic anhydride functionalized PP (PP_f) was used for the other part of the assemblies. Such blends will be denoted PP* in the following.

Four PP_f synthesized by Atofina, having one average anhydride per chain, were used. PP_{f1} (M_n ≅ 23 kg/mol) and PP_{f2} (M_n ≅ 43 kg/mol) contain a few percent of ethylene, while PP_{f3} (M_n ≅ 45 kg/mol) and PP_{f4} (M_n ≅ 21 kg/mol) were obtained from pure iPP.

Sample preparation and characterization

✓ Thin films with a low interfacial roughness were prepared by spin coating and annealed under vacuum. The interfacial orientation was characterized by X-Ray diffraction, as described elsewhere [5].

✓ Macroscopic samples were used to test the adhesion. They were prepared by clamping sheets of PA6 and PP* together in airtight mold under slight pressure and heating the mold in a temperature-controlled furnace, varying the annealing time and temperature. The samples were stored in an atmosphere of controlled humidity for at least 48h before testing.

The adhesion energy G_c was determined using the Asymmetric Double Cantilever Beam test. We recorded the crack length using a video camera and calculated G_c using Kanninen's method [1].

✓ To determine the areal density of copolymer, we selectively dissolved the PA6 part of untested samples and evaluated the remaining amount of PA6 by dosing the nitrogen/carbon ration by XPS. The macroscopic samples were prepared as described by Boucher et al [1], and we used a simplified protocol to dissolve the PA6 films, involving only two formic acid baths. The samples were tested within 2 weeks of preparation.

The XPS spectra were collected on a SSX-100 Surface Science spectrometer using a monochromatized AlK_{α1} source. We recorded

the 1s peaks for carbon, oxygen and nitrogen, at a take-off angle of 35° between the sample and the detector and with an electron flood gun of 9eV. The areal density of copolymer Σ was evaluated with the following equation :

$$\Sigma = -\frac{N_A \rho \Lambda}{M_n} \ln \left[1 - \frac{I_N / I_C}{I_{N\infty} / I_{C\infty}} \right]$$

where N_A is Avogadro's number, ρ the density of PA6, Λ the escape length of the electrons, I_N , I_C , $I_{N\infty}$ et $I_{C\infty}$ the intensities of the nitrogen and carbon peaks of the sample and of pure PA6.

RESULTS AND DISCUSSION

Interfacial crystalline orientation

The comparison of diffraction spectra obtained for iPP films on bare silicon wafers or on PA6 films showed a specific crystalline orientation of iPP when deposited on PA6[5]. In such an orientation, the iPP and PA6 chains are locally parallel to the interface.

This epitaxy was observed whatever the annealing conditions and the used PP_f . Nevertheless, the degree of orientation was clearly influenced by the sample preparation. The degree of orientation increased with the PP_f length, the annealing time and temperature as shown in figure 1.

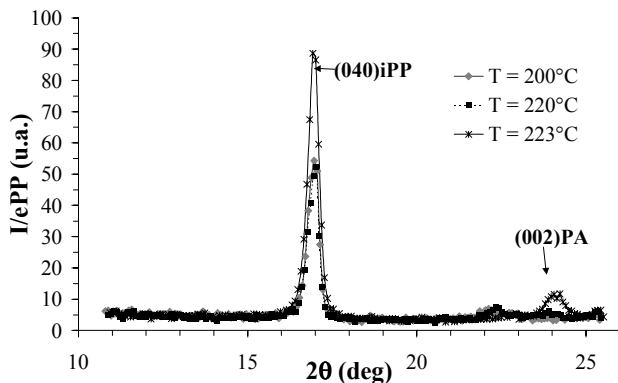


Figure 1: Influence of annealing temperature on the crystalline orientation of iPP and PA6. (Samples with PP_{f2} , annealed 90min).

As these factors both influence the epitaxy and the adhesion energy of macroscopic samples in the same way, we think that the two phenomena could be related. At the present time, we are not able to present a model explaining the relationship between both properties but we suspect that copolymer chains crystallized on

both faces of the interface probably play a role in this mechanism.

Influence of the copolymer structure : first steps

To vary the ability of the copolymer to co-crystallize with the matrix, we used different functionalized polypropylenes. The backbone of the first series contains a few percent of ethylene monomers, while the second series (PP_{f3} and PP_{f4}) has the same molecular weights but a pure iPP backbone.

These PP_f have shown very different rates of reaction with the polyamide. Figure 2 displays the kinetics of formation of the copolymers for films and macroscopic samples. From these data it is obvious that PP_{f3} and PP_{f4} react much faster than PP_{f1} and PP_{f2} , for both thin films and macroscopic samples. The areal density Σ saturates almost immediately for PP_{f3} and PP_{f4} , while it increases slowly for PP_{f1} and PP_{f2} . Besides, we noted that for low annealing temperatures the saturation is not reached for samples containing $PP_{f1/2}$, the maximum Σ value depending on the annealing temperature. Finally, one also remarks that PP_{f1} (short chains) react faster than PP_{f2} (long chains) while there is little difference between PP_{f3} and PP_{f4} .

Note that the different Σ_{max} for film and bulk sample are due to the different quantities of PP_f available in the two types of samples.

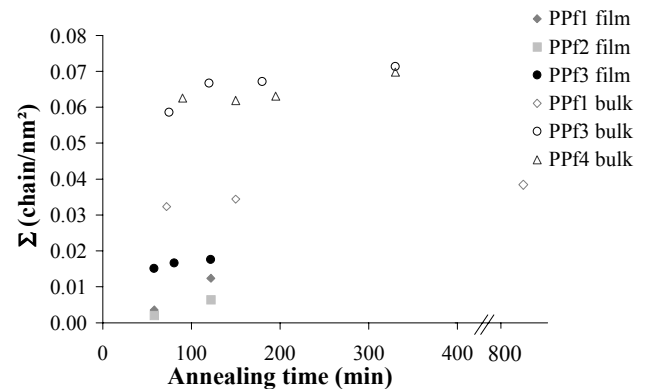


Figure 2: Copolymer formation kinetics for the different PP_f for films and macroscopic samples. Annealing temperature: 200°C.

These observations show that a low ethylene content in the PP_f chains changes radically its behavior. The presence of the ethylene monomers disturbs the diffusion of the grafted molecules into the matrix and thus the reaction

between PP_f and PA6. $PP_{f1/2}$ molecules can probably associate themselves. An equilibrium between free chains able to diffuse to react with PA6 and associated chains could then occur. That could explain the slower rate of copolymer formation observed for PP_{f1} and PP_{f2} , and the evolution of Σ with temperature.

These kinetic aspects are consistent with the adhesion measurements on the macroscopic samples. As shown in figure 3, the adhesion energy increases much faster for samples containing PP_{f3} than PP_{f2} (molecules of same molecular weight). Besides, G_c reaches a plateau for samples containing PP_{f3} , while such a saturation in G_c is not observed for PP_{f2} . This is consistent with a rapid saturation of the interface by the copolymer in the case of PP_{f3} and with a much slower diffusion of PP_{f2} towards the interface that doesn't lead to a saturation of the interface with copolymers.

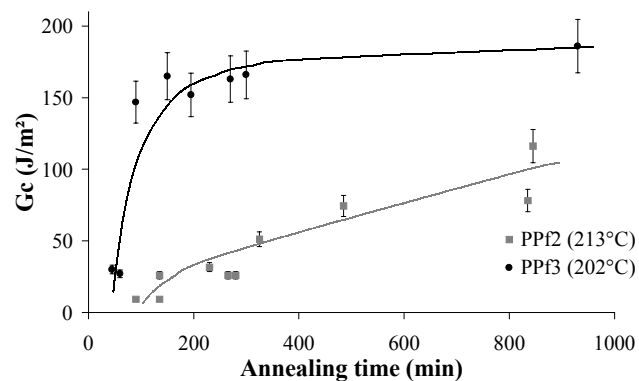


Figure 3: Increase of adhesion with annealing time for the two "long" PP_f chain types.

Perspectives

Subsequent experiments are underway to test the adhesion of $PP_{*3/4}$ samples with PA6 at different joining temperatures, to see if the maximum G_c is temperature dependent. In particular we will test whether samples annealed above the melting temperature of PA6 show a significant enhancement in G_c , as was observed for PP_{*2} [1,2].

From the detailed correlation between interfacial orientation, adhesion and areal densities of copolymer at the interface and the analysis of samples made with copolymers unable to co-crystallize with the iPP matrix, we also hope to be able to gain a better insight on the molecular

mechanisms of adhesion enhancement in these semi-crystalline systems.

CONCLUSIONS

Experiments on thin films have shown an epitaxy between iPP and PA6, which was influenced by the same factors as the adhesion energy of the joints.

We tried to elucidate the role played by the copolymer and by the interfacial organization in adhesion and interfacial crystalline orientation. We achieved this by varying the composition of the functionalized chains and then presumably their miscibility with the matrix. The first results show that small changes in the composition of the functionalized PP chains leads to important differences in the kinetics of the in situ formation of the copolymers and of adhesion enhancement.

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