

## MICROSTRUCTURE EFFECTS ON ADHESION AT POLYPROPYLENE/POLYAMIDE 6 INTERFACES

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### Introduction

The adhesion between semi-crystalline polymers, polyamide 6 (PA6) and both isotactic and syndiotactic polypropylene (iPP and sPP Respectively) has been investigated. The interface is reinforced with PA6/PP diblock copolymers formed in situ by chemical reaction between the -NH<sub>2</sub> end of polyamide molecules and modified polypropylene chains. In iPP/PA6 joints a strong increase of the efficiency of the copolymer to enhance adhesion has been observed in specific experimental conditions<sup>[1,2]</sup>, (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<sup>[3,4]</sup> 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 in the very vicinity of 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 seem able to influence the adhesion. We have previously shown that an epitaxial crystallization exists at the interface between iPP and PA6. This epitaxy appeared to be more pronounced under the annealing conditions leading to enhanced adhesion in macroscopic joints<sup>[5]</sup>. In the present study we try to understand how the interfacial orientation and the microstructure of the products play a role in this enhancement. We thus vary the structure of the PP matrix (iPP vs sPP) and that of the copolymer PP block. Thin film assemblies were used to determine the crystalline orientation and macroscopic samples allowed us to measure the adhesion and the areal density of copolymer

### Experimental

#### Materials

The polyamide 6 was Ultramid B3 from BASF, with an average of one -NH<sub>2</sub> end per chain. Isotactic polypropylene was 3050MN1 from APPRYL and syndiotactic polypropylene was an experimental product from Atofina. The main properties of the matrix are listed in Table 1.

Table 1. Main properties of the polymer matrix.

Polymer	M <sub>n</sub> g/mol	I	T <sub>m</sub>	χ	E GPa	σ <sub>y</sub> MPa
PA6	16 200	2.1	222°C	~ 30 %	dry: 2.9 wet: 1.0	65
iPP	57 000	4.8	165°C	~ 45 %	1.25	27
sPP	47 800	4.0	130°C	~ 18 %	0.40	16

Six functionalized PP, called PP<sub>f</sub>, were provided by Atofina. These maleic anhydride grafted chains bear an average of one anhydride per chain. Five PP<sub>f</sub> have an isotactic backbone and the last one was obtained by grafting the sPP matrix. The isotactic PP<sub>f</sub> were from three families : the first comes from a Ziegler-Natta ethylene-propylene copolymer containing a low ethylene content, the second from a Ziegler-Natta iPP and the last one from a metallocene iPP. The isotactic PP<sub>f</sub> were diluted in the iPP matrix while the sPP<sub>f</sub> was mixed with both iPP and sPP matrix. The main properties of all PP<sub>f</sub> are summarized in table 2.

Table 2. Names and main properties of the PP<sub>f</sub>.

PP <sub>f</sub>	M <sub>n</sub> g/mol	I	Microstructure
l-M <sub>n</sub> PE-PP <sub>f</sub>	22 600	2.7	EP copolymer (~13 % ethylene) Meso pentads: 84 %
h-M <sub>n</sub> PE-PP <sub>f</sub>	43 000	3.3	EP copolymer (~13 % ethylene) Meso pentads: 84 %
l-M <sub>n</sub> iPP <sub>f</sub>	21 400	3.3	iPP - Meso pentads: 85 %
h-M <sub>n</sub> iPP <sub>f</sub>	44 700	3.0	iPP - Meso pentads: 85 %
miPP <sub>f</sub>	69 700	3.1	Metallocene iPP Meso pentads: 80 % Many regio-irregularities
sPP <sub>f</sub>	35 800	3.5	sPP - Racemic pentads: 70 %

#### Sample preparation and characterization

Thin films with a low roughness were prepared by spin-coating and annealed under vacuum. The crystalline orientation was determined by X-Ray diffraction, as described in Laurens et al<sup>[5]</sup>.

Macroscopic samples used to test the adhesion were prepared by clamping sheets of PA6 and PP\* together in an airtight mold under slight pressure and heating the mold in a temperature-controlled furnace. The annealing time and temperature were varied. The samples were stored in an atmosphere of controlled humidity for at least 48h before testing to control the PA6 moisture sorption and modulus. The adhesion energy G<sub>c</sub> 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  $\Sigma$ , we selectively dissolved the PA6 part of our samples in a non fractured area as described by Boucher et al.[1] We evaluated the remaining amount of PA6 by dosing the nitrogen/carbon ratio by XPS. The samples were tested within 2 weeks of preparation. The XPS spectra were collected on a SSX-100 Surface Science spectrometer using a monochromatized  $AlK_{\alpha 1}$  source. We recorded the 1s peaks for carbon, oxygen and nitrogen, at a take-off angle of  $35^\circ$  and with an electron flood gun of 9eV.  $\Sigma$  was calculated as described by Boucher et al[1].

## Results and Discussion

### Crystalline orientation at the interface

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  $(010)_{iPP}$  and  $(002)_{PA6}$  planes are parallel to the film surface so that iPP and PA6 chains are locally parallel to the interface. This epitaxy was observed whatever the annealing conditions and the used  $PP_f$ . In particular we noted that

- sPP<sub>f</sub> mixed in the iPP matrix prevented the dewetting of iPP on PA6 as did the isotactic PP<sub>f</sub>
- the iPP-PA6 orientation was observed in the samples containing the sPP<sub>f</sub>.

The degree of orientation was also clearly influenced by the sample preparation. The degree of epitaxy increased with the isotactic PP<sub>f</sub> length (for both iPP<sub>f</sub> and PE-PP<sub>f</sub>), the annealing time and temperature in the same way as the adhesion energy of macroscopic samples.

Similar experiments were carried out on sPP films containing 5% sPP<sub>f</sub> and deposited on bare silicon wafers and on PA6 films. A specific orientation of sPP on PA6 was observed,  $(100)_{sPP}$  and  $(001)_{PA6}$  planes being parallel to each other and to the film surface. In this configuration, sPP and PA6 chains are locally parallel to the interface. The degree of orientation of this interface is influenced by parameters such as the cooling rate of the samples and the annealing time and temperature. Increasing these factors leads to a more important orientation of the interface. The influence of annealing time and temperature is comparable to the one observed on iPP-PA6 interfaces.

As the same factors influence both the epitaxy at PP/PA6 interfaces and the adhesion energy of macroscopic samples in the same way, we think that the two phenomena could be related. We also suspect that copolymer chains crystallized on both faces of the interface probably play a role in this mechanism.

### Influence of the copolymer structure on the interface reinforcement

To better elucidate the role played by the copolymer microstructure and by the possible co-crystallization of the

copolymer chains with the PP matrix, we used copolymers with various PP block structures, described above. We used pure isotactic PP<sub>f</sub>, metallocene PP<sub>f</sub> and PE-PP<sub>f</sub> less miscible with the Ziegler-Natta iPP matrix and a syndiotactic PP<sub>f</sub>, unable to co-crystallize with the iPP matrix but well miscible with the sPP one.

Figure 1 displays the kinetics of copolymer formation for the iPP matrix and all the PP<sub>f</sub> at 200°C. From these data it is clear that the two iPP<sub>f</sub> react much faster than the other PP<sub>f</sub>. The areal copolymer density  $\Sigma$  saturates almost immediately for iPP<sub>f</sub> while it increases more slowly for all the other PP<sub>f</sub>, less miscible with the iPP matrix. In these last cases, the reaction is probably limited by the PP<sub>f</sub> diffusion. This is coherent with the observation that the maximum  $\Sigma$  value depends on the annealing temperature for all PP<sub>f</sub> except l-M<sub>n</sub> iPP<sub>f</sub> and h-M<sub>n</sub> iPP<sub>f</sub>

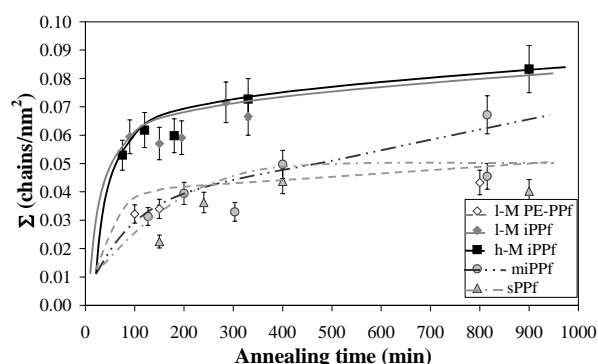


Figure 1: Influence of the PP<sub>f</sub> structure on the copolymer formation kinetics. Samples annealed at 200°C. The lines are guides for the eyes.

These observations are consistent with the adhesion measurements. As shown in figure 2, the kinetics of adhesion enhancement are also strongly dependent of the respective structures of the PP matrix and PP<sub>f</sub>.

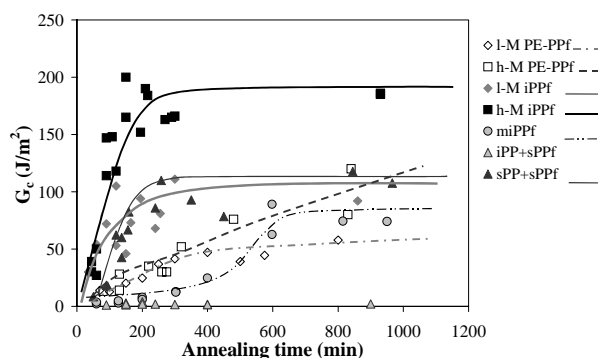


Figure 2: Influence of the PP<sub>f</sub> and matrix structures on the adhesion enhancement kinetics. Samples annealed at 205°C (except h-M<sub>n</sub> PE-PP<sub>f</sub>, annealed at 213°C). The lines are guides for the eyes.

When the PP<sub>f</sub> are fully compatible with the matrix (iPP+iPP<sub>f</sub> or sPP+sPP<sub>f</sub>, filled symbols and plain lines), the adhesion energy increases very fast and reaches a saturation regime. When the PP<sub>f</sub> is partially compatible with the

matrix (unfilled symbols and dotted lines), this increase is much slower and a plateau isn't always observed. This is consistent with the  $\Sigma$  measurements that don't show a saturation of the interface by the copolymers. Finally, when the matrix and the PP<sub>f</sub> are not miscible, the adhesion is very low whatever the annealing time, due to the lack of stress transfer between the matrix and the copolymer. The co-crystallization between matrix and copolymer is thus necessary to a good reinforcement of the interface, the presence of epitaxy at the interface is not sufficient. Another important point is that the maximum  $G_c$  is dependant on the length of the PP block of the copolymer in the iPP matrix case (for both iPP<sub>f</sub> and PE-PP<sub>f</sub>).

We then tried to determine the relation between the adhesion energy  $G_c$  and the interfacial density of copolymer  $\Sigma$  for our samples. This relation is characteristic of the fracture mechanism of the interface: if  $G_c \propto \Sigma$ , the interface breaks by extraction of the copolymer chains<sup>[6]</sup> while if  $G_c \propto \Sigma^2$ , the interface breaks by crazing and rupture of the copolymer chains<sup>[7]</sup>. Figure 3 shows  $G_c$  as a function of  $\Sigma$  for the high molecular weight PP<sub>f</sub> mixed with iPP.

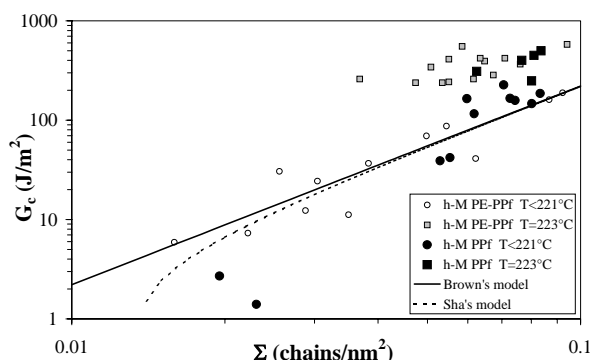


Figure 3: Energy of adhesion  $G_c$  as a function of the areal density of copolymer  $\Sigma$  for the high molecular weight PP<sub>f</sub>. The functions corresponding to Brown's model<sup>[7]</sup> and to its correction by Sha et al.<sup>[8]</sup> are drawn using the values determined by TEM for the fibril diameter and extension and the approximations suggested by Plummer et al. for the unknown mechanical parameters of the PP craze<sup>[4]</sup>.

This figure clearly shows that the data recorded for annealing temperatures below the melting temperature of PA6 are consistent with a fracture mechanism of crazing and chain scission for the two types of samples. Above this temperature, both showed an increase of adhesion compared to the predictions of the models. Such a behavior above 221°C was neither observed for shorter PP<sub>f</sub> in iPP nor in sPP-sPP<sub>f</sub> samples. The increase in adhesion is then correlated with the presence of sufficiently long chains at the iPP/PA6 interface whatever their microstructure; it also occurs for annealing conditions where the epitaxy is enhanced. It is probably related to the ability of the PP<sub>f</sub> to join several PP lamellae in the epitaxially crystallized zone (in this area the lamellae are closer than in the bulk). Such size effects, linked with the ability of the copolymer to join

several lamellae have also been recently suggested for the PE-sPP interface<sup>[9]</sup>.

Another important observation is that Brown's model does not fit all data. We have just seen that long PP<sub>f</sub> chains can give an adhesion energy greater than predicted by the model in particular annealing conditions. We have also observed that for samples containing miPP<sub>f</sub> or samples containing l-M<sub>n</sub> iPP<sub>f</sub> annealed below 195°C the adhesion is weaker than predicted by the models.

## Conclusions

Experiments on thin films have shown an epitaxy relationship between iPP and PA6 on the one hand and between sPP and PA6 on the other hand. Both of them are influenced by the same factors as the adhesion energy of macroscopic joints.

We tried to elucidate the role played by the copolymer and by the interfacial organization in the adhesion reinforcement. We achieved this by varying the composition and microstructure of the functionalized chains and hence their miscibility with the matrix. Strong microstructure effects appear on the kinetics of formation of the copolymers and of adhesion enhancement, the kinetics being much faster when the matrix and the PP block have closely matched microstructures. Besides, the copolymer efficiency is higher when the PP block is of high molecular weight, and particularly for high annealing temperatures. We related that effect to a synergy between the ability of the copolymers to connect crystalline lamellae and the increase of the crystalline orientation of the interface.

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