

ADHESION PROMOTION THROUGH DIBLOCK COPOLYMER FORMATION AT PP/PA6 CO-EXTRUDED INTERFACES

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Introduction

We present an investigation of the formation of polyamide 6 – polypropylene diblock copolymer molecules during the co-extrusion process, and we analyse their role in promoting adhesion of composite three layers PA6 – PP – PA6 films. The adhesion promotion at PP/PA6 interfaces reinforced by diblock PP/PA6 copolymer formed in situ has been widely investigated in the case of assemblies formed by annealing slowly above the melting temperature of the PP two sheets of these polymers tightly hold in contact [1-5]. These investigations have shown that the copolymer stabilizes the interface, and enhances adhesion, with an increased efficiency when the PP block has a microstructure close to that of the matrix and can cocrystallize with the matrix.

One important application of PP – PA6 assemblies is the formation of co-extruded films often used in packaging: then, the conditions of copolymer formation and the cooling conditions of the samples are completely different from what can be achieved in the lab. The chemical reaction leading to the formation of the copolymer occurs at higher temperatures, the open time for the reaction is much shorter (a few minutes compared to hours in the lab) and the cooling rate is far much faster (a few thousand °C/s instead of 10°/mn). These conditions may lead to a very different interfacial crystallization compared to joints prepared in the laboratory and thus possibly to quite different adhesion promotion mechanisms and quite different efficiency for the diblock copolymer molecules.

It is then interesting to characterize both the progressive building of an interfacial layer of diblock copolymers and the building of mechanical strength at such co-extruded thin films assemblies. We present

below part of the results of such a systematic investigation performed on three layers PA6 – PP – PA6 films obtained with various sets of co-extrusion parameters.

Experimental

Materials

The polyamide 6 (PA6) we used was Ultramid B3 from BASF, with an average of one – NH₂ per chain.

The binder was provided by Arkema, and composed by blending succinic anhydride functionalised polypropylene PP, called PP_f, with isotactic polypropylene in a twin screw extruder, a low fraction of PP_f.

Sample preparation

Multilayer samples were prepared using a coextrusion line.

Two single screw extruders fed a coextrusion block, which formed three horizontal layers (PA6/binder/PA6). The flow exited through a die (slit between 300 and 700 μm), covered a distance in air (air gap between 4 and 10 cm), passed on a water cooled steel roll (50°C), and was collected (see a schematic presentation of the exit of the die in figure 1).

This process was run using a die temperature of 250°C and produced a three layered structure (25/10/25 μm).

The copolymer could form by the reaction, in the melt state of the succinic anhydride with -NH₂ end groups of the PA6 [1] as soon as the PA6 and PP flux was in contact and until the film finally crystallized on the cold roll.

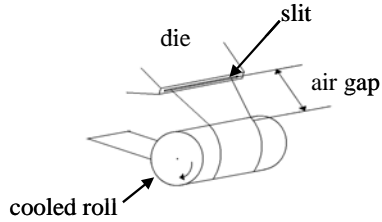


Figure 1: schematic presentation of the exit of the die and of the flow until the cold roll.

Characterization

To determine the areal density Σ of copolymer actually formed at the interface, we selectively dissolved the PA6 part of the three layers films. The amount of PA6 remaining on the PP film was determined through the nitrogen/carbon ratio by XPS and Σ was calculated as described in [1].

The adhesion energy G was determined using an Asymmetric Double Cantilever Beam test (G_c), with the three layer film reinforced by gluing on each side a 2 mm thick sheet of transparent PA11 as schematically presented in figure 2. We chose this reinforcement protocol in order to preserve the crystalline organisation of PA6 and PP films on each side of the investigated interface. The crack length was recorded using a video camera and G_c was calculated using Kanninen's method.

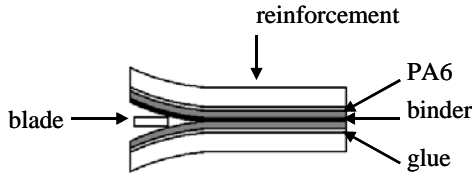


Figure 2: schematic representation of the sandwich reinforced samples used to characterize the adhesive energy G_c through a double beam cantilever test.

Results and discussion

Influence of the extrusion parameters on the formation of copolymer

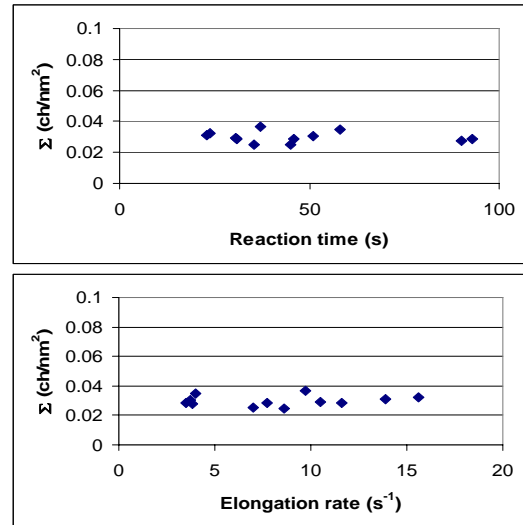
In a first set of experiments, we kept the materials constant (PA6 and binder) and modified the line speed, the air gap and the slit. Modifying these parameters allowed varying reaction time and elongation rate of the film in the air gap.

The surface density of copolymer appears to be insensitive to the extrusion parameters in the range investigated (figure 3).

The measured value of $\Sigma = 0.03 \text{ ch/nm}^2$ is smaller than the saturation value obtained for the same polymers on interfaces made in the laboratory ($\Sigma = 0.08 \text{ ch/nm}^2$) [4]. It is tempting to think that the

reaction time during the extrusion process is too short to saturate the interface.

We have first checked that the interface was indeed not saturated, by applying a subsequent annealing to the films at temperatures above the melting temperature of the PP. The surface density indeed rises quite rapidly to reach a value close to $\Sigma_{\text{max}} = 0.08 \text{ ch/nm}^2$, a value quite comparable to that obtained on samples prepared by compression in the laboratory [1-5].



Figures 3a and 3b : Evolution of the areal density of copolymers Σ as a function of reaction time (a) and elongation rate (b).

To go further in the understanding of the kinetics of formation of the copolymer in the extrusion conditions, we have measured directly the grafting kinetics without flow, but at temperatures comparable to those attained in the co-extrusion machine. The results are reported in figure 4.

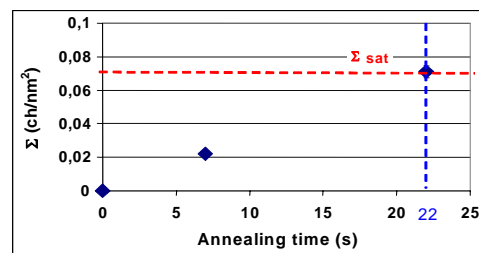


Figure 4: Kinetics of formation of the copolymer under conditions comparable to the co-extrusion, but without flow.

The time open for the reaction in the extrusion conditions we have explored is always larger than the time necessary to saturate the interface in the absence of flow. The reason of the non

saturation of the interface in the extrusion process is not a too short open time for the reaction.

In fact, the surface density of the copolymer, Σ , represents the total amount of copolymer formed during the whole time the PA6 and PP are in contact and in the melt state, divided by the total surface of interface created during the process. The flow during the extrusion produces interfaces, and this increase of area of interface acts in reducing the surface density of copolymers yet formed, by a kind of dilution process. In order to better track the origin of the non saturation of the interface during the extrusion, we have use a numerical modelling of the flow in order to quantify the amount of surface of interface created all along the flow, from the first contact between PP and PA6 down to the crystallization on the cold roll. This modelling has allowed us to identify in which parts of the flow pattern the creation of the surface of interface was mainly located. These are the regions of converging flow (inside the co-extrusion box and at the exit of the die) and in the air gap where the three layers film is submitted to an extensional flow.

The main result of this modelling is that, as soon as the geometry of the three layers film is fixed, whatever the extrusion parameters, the overall creation of surface of interface remains essentially fixed. The condition of fixed final thickness for the three layers, imposes a coupling between the different extrusion parameters which fixes the overall creation of the surface of interface. Then, the surface density of copolymers appears insensitive to the extrusion parameters.

Influence of the extrusion parameters on adhesion

ADCB experiments have been performed on all samples for which the surface density of copolymer had been measured. The results are gathered in figures 5 a and b. It appears clear that even if the surface density remains insensitive to the co-extrusion parameters, the adhesion is deeply affected and varies at fixed Σ . This is indicative of a different efficiency of the copolymer in reinforcing the strength of the interface, depending on the extrusion conditions. We cannot at the present stage produce definite arguments to explain why this is so, but, in view of the results obtained on samples formed in compression, we feel that this the signature of a different crystalline organization in the very vicinity of the interface, with different degrees of coupling between the PP part of the copolymer and the PP matrix. A detailed modelling of the cooling and crystallization of the three layers films has been undertaken to try to gain a better insight in the role of the different extrusion parameters on the efficiency of

the copolymers to promote adhesion at such interfaces.

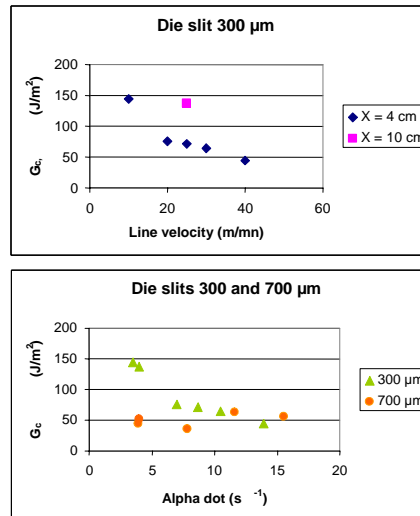


Figure 5 : a: G_c as a function of the flow rate (line velocity) for all samples with $\Sigma = 0.03 \text{ ch/nm}^2$ presented in figure 3, and for two different length of the air gap, x . b: G_c as a function of the rate of extension in the air gap, for two different die slits, 300 and 700 μm .

Conclusion

We have shown that the adhesion energy due to diblock copolymers at PP – PA6 interfaces formed by co-extrusion was depending on the extrusion conditions, while the surface density of copolymers was essentially fixed as soon as the geometry of the extruded film was fixed. This independence is the result of a fast chemical reaction and of an increased surface of interface all along the flow, especially in the converging flow at the die exit and in the air gap.

References

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