

ADHESION AT PP/PA6 INTERFACES : PART OF THE COPOLYMERS FORMED IN SITU AT THE INTERFACE IN SITUATION OF SHORT TIME ANNEALING REPRESENTATIVE OF COEXTRUDED JOINTS

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Introduction

The adhesion mechanisms at PP/PA6 interfaces reinforced by diblock PP/PA6 copolymer formed in situ has been investigated [1-5]. These studies showed the copolymer part in stabilizing the interface, the increase in efficiency of the copolymer when its PP block has a microstructure close to the matrix, and that this block can cocrystallize with the matrix. These previous studies have been realized on joints made in the laboratory with long time scales (hours), and slow crystallization kinetics (a few °C/mn).

One of the applications of these joints is the coextruded film : in that case, the kinetic and thermic conditions are completely different. The copolymer formation occurs at higher temperature, the open reaction time is much shorter (a few minutes) and the cooling kinetic is much faster (a few thousand °C/s). These conditions may lead to a very different interfacial crystallization compared to joints prepared in the laboratory.

It is then interesting to know if the trends showed on laboratory samples still hold. This is why we started a study to correlate the adhesive strength, the areal density of copolymers and the crystalline state at the interface on coextruded films.

Experimental

Materials

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

Isotactic polypropylene (PP) was PPH4050 from Total Petrochemicals.

The maleic anhydride fonctionnalised PP, called PP_f, was provided by ARKEMA : these grafted chains beared an average of 6.5 anhydride per chain (grafting process in solution).

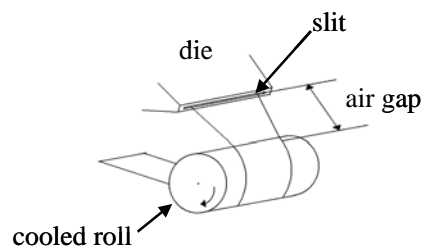
The binder was prepared by blending in a twin screw extruder a low fraction of PP_f in a PP matrix.

Sample preparation

Multilayer samples were prepared using a coextrusion system.

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.

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



The copolymer was formed by the reaction, in the melt state, of the succinic anhydride with -NH₂ groups of the PA6 [1].

Characterization

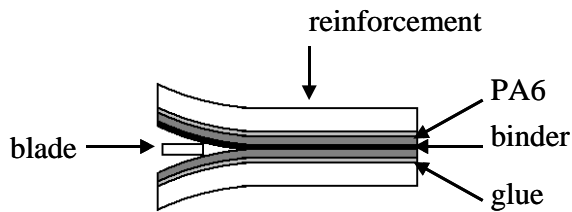
To determine the areal density of copolymer Σ , we selectively dissolved the PA6 part of our samples. We evaluated the remaining amount of PA6 by dosing the nitrogen/carbon ratio by XPS.

Σ was calculated as described by Boucher et al [1].

The adhesion energy G is determined using two complementary tests : 180° peel test (G_p) and Asymmetric Double Cantilever Beam test (G_c).

The peel test energy is $G_p = 2F/b$ with F the peel force and b the sample width. This test is convenient, but the peel energy contains interfacial contribution as well as dissipated energy in the PA6 arms. This can problematically mask interfacial effects.

The ADCB test seems to be more sensitive to the interface. Because the PA6 arms are very thin, they need to be reinforced to ensure elastic deformation. Furthermore the reinforcement protocole has to preserve the crystalline organisation of the PA6 films. A sandwich sample was realised by gluing two reinforcements of polyamide 11 (2 mm thick) on each side of the multilayer film. The crack length was recorded using a video camera and G_c was calculated using Kanninen's method.



Results and discussion

Influence of the extrusion parameters on the copolymer formation

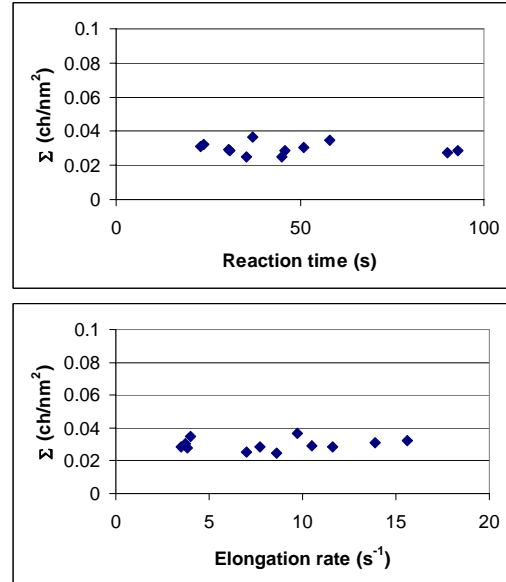
In a first case, we fixed the materials (PA6 and binder) and modified the line speed, the air gap and the slit. Modifying these parameters allowed to vary reaction time and elongation rate of the film.

The areal densities of copolymer appear to be not sensitive to the extrusion parameters (figures 1).

The measured value of $\Sigma = 0.03 \text{ ch/nm}^2$ is smaller than the saturation value obtained for the same polymers on joints made in the laboratory ($\Sigma = 0.08 \text{ ch/nm}^2$) [4]. The reaction time during extrusion seems too short to saturate the interface.

We confirmed this result by doing annealings of the film at temperatures above the PP fusion, to allow migration of reactive species towards the interface. For long enough annealing times, areal

densities of copolymers Σ_{max} of about 0.08 ch/nm^2 were measured. This result is satisfying in comparison with the values obtained on samples prepared by compression in the lab [1-5].



Figures 1a and 1b : Evolution of the areal density of copolymers Σ as a function of reaction time (a) and elongation rate (b).

Influence of the extrusion parameters on adhesion

Figure 2 presents peeling data as a function of reaction time. The peeling force depends of the coextrusion conditions, contrary to the areal density of copolymers.

It is then interesting to know if these effects are related either to a variation of the efficiency of the copolymers towards the adhesion promotion (local effect at the interface), or to a modification of the volumic mechanical properties of the peeled PA6 films.

ADCB experiments are in progress and should help to advance in the comprehension of these effects.

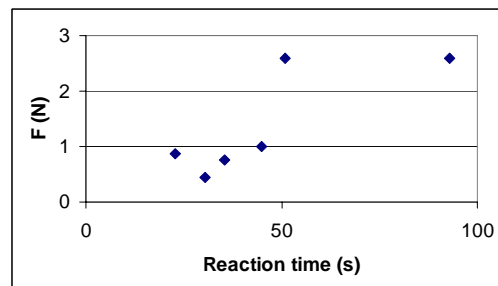


Figure 2 : Evolution of the peeling force as a function of reaction time.

Conclusion

Extrusion conditions influence adhesion energy measured by peeling, but not the density of copolymers created at the interface during extrusion.

This density of copolymers remains, whatever the extrusion conditions, inferior to the saturation.

Comparison of the fracture energy measured by peeling and ADCB test is in progress to determine on which level the extrusion parameters influence the crystalline organisation and the mechanical coupling between copolymer and matrix.

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