

FORMATION OF DIBLOCK COPOLYMERS AT PP/PA6 CO-EXTRUDED INTERFACES AND THEIR ROLE IN PROMOTING ADHESION

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Introduction

We present an investigation of the formation of polyamide 6 – polypropylene diblock copolymer molecules during the co-extrusion process, in relation with their role in promoting adhesion of composite three layer PA6 – PP – PA6 films. Polypropylene/polyamide 6 (PP/PA6) interfaces are commonly reinforced by diblock PP/PA6 copolymer formed *in situ* when the two polymers are pressed into contact and melted [1-6]. Both assemblies formed by moulding and by co-extrusion have recently been studied. For assemblies formed by moulding, it has been clearly shown that the efficiency of the copolymer in promoting adhesion was larger when the PP block had a microstructure close to that of the matrix, so that it could co-crystallize with the matrix [4,5]. The strength of the interface is then ruled by first the number of copolymers per unit area of interface, second, by the microstructure of the PP part of the diblock copolymers compared to that of the bulk PP and third, by the cooling conditions. For assemblies formed by co-extrusion, the conditions leading to the formation of the copolymers and the cooling rates are totally different. Several results have been established recently [6]. The copolymer is formed at much higher temperatures than for moulded samples, with a much shorter open time for the reaction (a few minutes instead of typically half an hour). Following the path of the materials along the process line from the point at which the two polymers are put into contact until the point at which the crystallisation is completed on the chill roll, the flow can be decomposed into different zones in which either the area of contact remains constant along the flow or zones in which the contact area increases, as a result of either converging flows or stretching of the extruded film. The surface density of copolymer at the end of the process then results from two competing effects: grafting of the

maleic anhydride modified PP on the NH₂ extremity of PA6 molecules at the interface, and dilution of the yet formed copolymers in the steps of the process corresponding to increasing contact area. Finally, the joint is rapidly cooled down and the crystallization occurs on the chill roll, under stretching stresses.

In order to try to quantitatively relate the extrusion conditions and the adhesion properties at PP/PA6 interfaces of co-extruded films, we have undertaken a systematic investigation of the kinetics of the grafting reaction of maleic anhydride modified PP on PA6 as a function of the grafting temperature, both without and with flow leading to an increase of the area of contact. We have also started to analyse in a systematic manner the role of stretching stresses on the crystalline organisation of the PP in the immediate vicinity of the interface.

We present below the first preliminary results of these investigations.

Experimental

Materials

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

The isotactic polypropylene (PP) matrix was two homopolymers provided by Total Petrochemicals.

The succinic anhydride functionalised PP, called PP_f, was provided by ARKEMA

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

Sample preparation

In order to achieve assemblies of PP and PA6 which could be heated rapidly enough above the melting temperature of both polymers, we have

worked with relatively thin films pressed into contact and hold in contact during the full heating step by a sample holder with a weak enough mass and a large enough thermal conductivity so that the temperature of the interface between both polymers could reach the melting temperature of PA6 in less than 20s after having been introduced in an oven regulated at 250°C. This sample holder is schematically presented in figure 1.

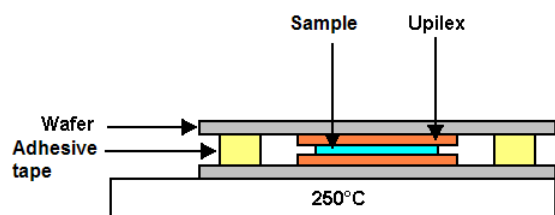


Figure 1: Schematic representation of the sandwich system used to assemble PP/PA6 films.

The different polymer films are maintained into contact and gently pressed together by sandwiching them between two silicon wafers, hold together by an adhesive tape resisting to high temperatures. Upilex films are intercalated between the PA6- PP films and the silicon wafers to prevent adhesion and provide easy demoulding. The total mass of the sandwich is kept small in order to allow for heating above the melting temperatures of both PP and PA6 faster than typical open times for the reaction in co-extrusion conditions.

The sandwich is prepared at room temperature and rapidly introduced into an oven thermally regulated at 250°C. A thermocouple placed at the interface between the two polymer films allows to monitor the rise of the temperature of the interface, and to identify at what time after introduction into the oven each of the melting temperatures are reached.

The samples are then extracted from the oven at various prescribed annealing times and rapidly cooled down to room temperature by deposition on a large metallic plate maintained at 22°C.

Characterization

To determine the areal density Σ of copolymer actually formed at the interface, we selectively dissolved the PA6 part of the sandwich film formed during annealing. 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].

Results and discussion

Kinetics of Formation of the copolymer

Typical results of kinetics of formation of the copolymer at the PP – PA6 interface are reported in figure 2 for various maleic anhydride modified PP mixed in the same PP matrix at various concentrations.

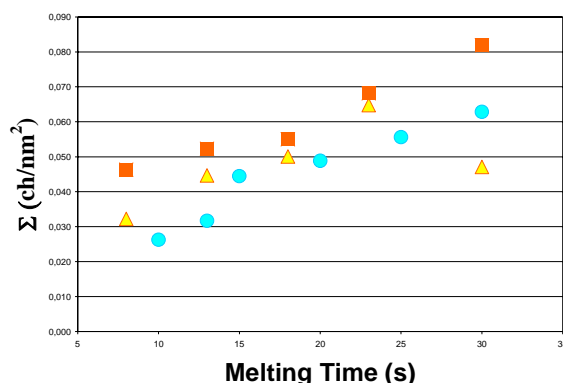


Figure 2: Kinetics of formation of PP/PA6 copolymers : ● functionalised PP in homopolymer 1; ■ ten times more functionalised PP; ▲ functionalised PP in homopolymer 2.

A first result is that even if the time allowed for grafting is short (less than 35s), grafting occurs, up to a grafting density close to the saturation grafting density for these polymers. Indeed, grafting is expected (and observed) to saturate when the number of chains pertaining to a copolymer molecule reaches the number (per unit area) of chains touching a surface in the melt of these chains. This saturation surface density only depends on the molecular weights of both polymers, and is of the order of 0.07 chains per nm² for the polymers used here. Second, one must emphasize that the reaction occurs in non isothermal conditions in the above reported experiments. After a first rapid rise, a slowing down of the grafting appears followed by a further increase when the temperature reaches and overcomes the melting temperature of PA6 (around 20s after the sandwich has been introduced into the oven). This probably reflects the fact that when the PA6 becomes liquid, more NH₂ extremities are able to reach the interface, meaning that the availability of NH₂ extremities is what limits the grafting density for the particular molecular weights used.

Crystalline organization at the PP surface

In order to investigate the incidence of the formation of the copolymers at the interface on the crystalline organization near the interface, we have

started a systematic analysis, through AFM, of the topography of the PP Surface, after selective dissolution of the PA6 film (in formic acid). Typical images are reported in figures 3.

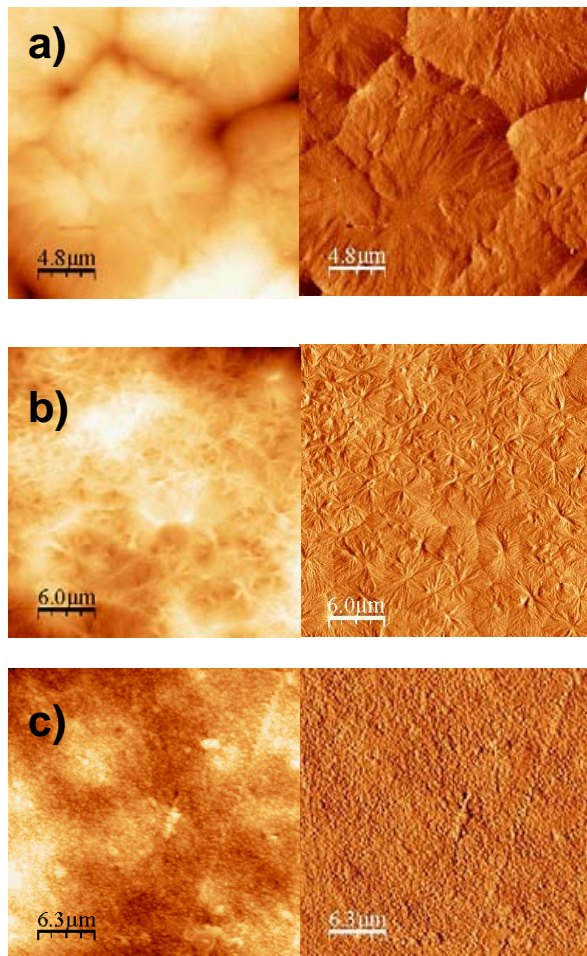


Figure 3: AFM images of the PP surface after selective dissolution of the PA6 film, as a function of the annealing time i.e. as a function of the surface density of dibloc copolymer present at the interface. Left images: topography; right images: phase. Annealing time: 10s (a), 18s (b) and 30s (c). Global RMS is approximately of 350 nm, and the peak to peak roughness increases gradually from a) to c).

It appears clearly that as the annealing time increases, i. e. as the surface density of copolymers at the interface increases, the spherulites present at the PP surface decrease in size. This is not the result of differences in the thermal history of the samples, as no such effect has been detected when pure PP was annealed pressed into contact with the same PA6, a situation for which the thermal history was quite similar, but no copolymer could form. The evolution of the crystalline morphology visible in figure 3 is the

result of the presence of copolymers formed at the interface. The more copolymers, the higher is the roughness of the interface and the smaller the size of the spherulites. The higher too is the adhesive toughness of the assembly.

We are now investigating in a systematic way the incidence of the microstructure of the grafted PP used to form the copolymers on the crystalline morphology at the PP surface, as this microstructure is known to influence adhesive toughness⁴. We will also try to correlate the crystalline morphology at the PP surface with other parameters of the co-extrusion process such as the stretching of the film before the crystallization.

Conclusion

We have started to investigate both the kinetics of formation of dibloc copolymers formed in situ at the interface and the resulting crystalline morphology at the surface for PP6PA6 assemblies formed at high temperature, in thermal conditions comparable to those experienced by the polymers during a co-extrusion process. The results will be used to model the co-extrusion process and identify the correlations between copolymer formation at the interface, crystalline organization, adhesive toughness and the co-extrusion parameters.

Acknowledgments

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