



HAL
open science

Evidences for flow-assisted interfacial reaction in coextruded PA6/PP/PA6 films

H. Kiparissoff-Bondil, S. Devisme, D. Rauline, F. Chopinez, Frederic Restagno, L. Léger

► **To cite this version:**

H. Kiparissoff-Bondil, S. Devisme, D. Rauline, F. Chopinez, Frederic Restagno, et al.. Evidences for flow-assisted interfacial reaction in coextruded PA6/PP/PA6 films. *Polymer Engineering and Science*, 2018, 59 (S1), pp.E44 - E50. <10.1002/pen.24841>. <hal-04030702>

HAL Id: hal-04030702

<https://universite-paris-saclay.hal.science/hal-04030702v1>

Submitted on 15 Mar 2023

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.



HAL Authorization

Evidences for Flow-assisted Interfacial Reaction in Coextruded PA6/PP/PA6 Films

H. Kiparissoff-Bondil,¹ S. Devisme,² D. Rauline,² F. Chopinez,² F. Restagno ,¹ L. Léger¹

¹Laboratoire de Physique des Solides, CNRS, Université Paris-Sud, Université Paris-Saclay, Orsay Cedex 91405, France

²CERDATO, Arkema, Serquigny 27470, France

We present an investigation of the progressive building of copolymer layers formed by chemical reaction at interfaces in multilayer coextruded polymer films. Analyzing the surface density of copolymers in the final films, we show that the interface always remains under-saturated in copolymers, even for coextrusion parameters such that the time open to the interfacial chemical reaction is well above the time necessary to reach saturation without flow. Based on a numerical analysis of the flow all along the coextrusion line, we show that this under-saturation of the interface, which may strongly affect the final adhesion between the different polymers, results from a competition between the interfacial chemical reaction and the dilution of yet formed copolymers in all the zones of the coextrusion line where surface of interface is increased, due to convergent, divergent or elongational flow. We also show that the coupling between flow and reaction kinetics needs be taken into account to control the final surface density of copolymers and precisely optimize the interfacial properties, through an optimization of the coextrusion parameters POLYM. ENG. SCI., 00:000–000, 2018. © 2018 Society of Plastics Engineers

INTRODUCTION

Multilayer polymer films in which several different polymers are joined in order to benefit from their complementary properties are present in a wide range of our everyday life habits. They represent however a challenge for their fabrication, essentially because most of polymer pairs are not miscible, and develop only very weak adhesion when forced into contact [1–3]. It is then necessary to develop tricks to enhance adhesion and provide ways of ensuring that mechanical stresses can be transferred through the corresponding interfaces, so that a multilayer material able to resist to manipulation is indeed formed. Quite commonly, such adhesion enhancement is produced by diblock copolymers, carefully designed so that each block is compatible with one of the materials in contact [4–7]. These copolymers, when accumulated at the interface, constitute what is often called an interphase [8, 9], that is, a zone with a non-zero thickness, and having properties that differ from those of each of the two polymers into contact. Such interfacial copolymers first decrease the interfacial tension between the two materials in contact, by spontaneously organizing at the interface [10]. Second, if long enough so that each block can entangle and possibly co-crystallize with each partner of the assembly, they strongly enhance adhesion, as it has been extensively demonstrated in the past, both for glassy and for semi-

crystalline polymers [11–15]. Multilayer polymer films are often produced by co-extrusion process. For evident practical reasons, the copolymers acting as adhesion promoters are then formed directly *in situ* at the interface, by an interfacial chemical reaction between reactive polymers precursors present on both sides of the interface [4, 16]. This is just because the diffusion process of yet formed copolymers from the bulk towards the interface is a too slow process to allow for an efficient formation of an interphase during the short time spent by the two materials in contact and in the molten state, inside the coextrusion. On the contrary, the chemical reaction of reactive species yet present at the interface may be faster to the time during which the different polymers are molten and in contact inside the coextrusion machine. The question of understanding how the interfacial copolymer layer progressively builds up all along the co-extrusion line then appears as a crucial question in order to be able to optimize the process parameters and efficiently produce multilayer polymer films with good mechanical properties [17, 18].

We have extensively investigated in the past the correlations between copolymer surface density and adhesion at polypropylene (PP)—polyamide 6 (PA6) interfaces, with a special attention paid to specific aspects related to the aptitude of these copolymers to cocrystallize with the matrix polymers [19, 20]. In all these investigations, the copolymer was formed *in situ*, at the interface, by the reaction of modified PP molecules, bearing few maleic anhydride groups, that we name PPg in the following, on the amine extremity of PA6 molecules. The PP-PA6 assemblies were formed in the lab, by molding techniques, with rather long annealing periods, and without any flow. We developed systematic ways of dosing the formed copolymers, through XPS analysis, after selective dissolution of the PA6 part of the assembly. We also analyzed the adhesion at such interfaces, through double beam cantilever tests, along with X rays grazing incidence investigations of the crystalline organization close to the interfaces [13].

More recently, we have developed new ways of annealing PP-PA6 assemblies made of rather thin films (typically 50 μm), and new ways of cooling down these assemblies so that the time open for the formation of the copolymer at the interface and the cooling rate were representative of co-extrusion conditions [19]. We thus have been able to characterize the interfacial reaction rate and to determine experimentally the surface density for multilayer films formed in the lab, but with temperature and time histories comparable to those found in a coextrusion line. For long enough contact times between PA6 and reactive PP mixtures, it has been shown that, as expected, the copolymer surface density saturates to a finite value, just because when the number of copolymers yet formed at the interface is sufficient to fill the surface zone close to the interface with chains all chemically bound to the surface and having their Gaussian equilibrium configuration, the reaction stops, due to the elastic

Correspondence to: F. Restagno; e-mail: frederic.restagno@u-psud.fr

Grant sponsor: Arkema

DOI 10.1002/pen.24841

Published online in Wiley Online Library (wileyonlinelibrary.com). c

TABLE 1. Molecular characteristics of the various tie layers investigated.

	PP ($M_w \text{ kg}^{-1} \text{ mol}^{-1}$)	PPg ($M_w \text{ kg}^{-1} \text{ mol}^{-1}$)	% PPg	Maleic anhydride (ppm)
LS1A	PP1: 310	PPg1: 48	High	13,480
LS2F	PP1: 310	PPg2: 60	Low	516
LS3A	PP1: 310	PPg3: 83.5	Low	356
LS3B	PP1: 310	PPg3: 54.5	Medium	1,032

PPg1, PPg2, PPg3 refer to different batch of synthesis of the grafted PPg.

penalty which has to be paid to further introduce new reactive chains inside this layer [19, 21–24]. The exact value of this surface density at saturation is thus fixed by the molecular parameters of both contacting polymers (molecular weights and average size of the monomers).

On the other hand, the diffuse interphase between compatible polymer has been extensively studied and modeled to try to understand both the rheological and the interfacial defects that can be observed in coextrusion process [2]. Rheology has been demonstrated to be a quite sensitive method to study the construction of an interphase [25–27]. Nevertheless, there is still a lack of direct characterization of the interphase in real coextruded films, in terms of composition and molecular organization.

In the present article, we show that, based on the same selective dissolution technique and for the same PP/PA6 interfacial reaction of maleic anhydride modified PP reacting on the NH₂ extremity of PA6 macromolecules, the surface density of interfacial copolymers in coextruded multilayer PA6/PP/PA6 films can be measured directly on industrial films. We then show that, whatever the process parameters used, this surface density of copolymers is always observed to remain well below the saturation density, even when the total time open for the reaction in the coextrusion line (i.e., the total time during which the two polymers are into contact and are well above their melting temperature), is much larger than the time necessary to attain this maximum surface density for assemblies molded in the lab. Numerically modeling the co-extrusion process, we show that this undersaturation of the final interface in coextruded multilayers is the consequence of a competition between the interfacial reaction and the dilution of the yet formed copolymers, in all the zones of the coextrusion line where the surface of interface is increased, due to converging, diverging or extensional flows. The numerical modeling of the process allows one to identify the few zones of the coextrusion line where the interfacial area increases significantly. The chemical reaction leading to the copolymer formation, on the other hand, takes place all along the coextrusion line, starting when the two molten polymers are put into contact, and going on all the time during which the interfacial temperature is large enough so that at least one of the two polymers remains molten. We finally show that a simple modeling of the process, taking into account the interfacial reaction kinetics as characterized without flow, and the dilution of the copolymer in the zones of the coextrusion line where the surface of interface is increased is insufficient to account for the experimentally measured final surface density of copolymers.

MATERIALS AND METHODS

Materials

The polymers used in the present work have been described in detail in Refs. 13, 19, 28. We recall here their main characteristics.

The polyamide 6 (PA6) was Ultramid B3 from BASF, with an average of one –NH₂ per chain. For this polymer, the Gel Permeation Chromatography (GPC) in hexafluoroisopropanol gave $M_w = 33.8 \text{ kg mol}^{-1}$ and a polydispersity index $I = 1.9$. Isotactic polypropylene (PP) was PPH4050 provided by Total Petrochemicals. Succinic anhydride functionalized PP, (PPg) was provided by ARKEMA. The anhydride reaction was conducted in solutions. The PPg chains contained an average of 6.5 anhydride groups per chain. Blends of a low weight fraction of PPg in a PP matrix were prepared in a twin-screw extruder and used as tie layers. The main characteristics of those blends are presented in Table 1. All blends gave results similar to those described below, which have been obtained with the blend LS1A.

Sample Preparation

Three-layer assemblies were obtained on the Collin coextrusion line at CERDATO. Two single screw extruders fed a coextrusion block, forming three horizontal layers (PA6/tie layer/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. Crystallization took systematically place when the film was touching the cooled roll. The reaction time open for the formation of interfacial copolymer is defined as the time elapsed between the first point where the two molten polymer join and the time at which crystallization on the cooled roll occurs. The flow distance is defined as the distance run by the flow in between these two times, the origin being taken where the join is formed.

This process was run using systematically a die temperature of 250°C and it produced series of three layers structures, PA6/tie layer/PA6, with respective thicknesses 25/10/25 and 75/10/75 μm .

For each coextrusion, it is possible to choose a set of independent tool parameters (speed of the extruders, air gap length, slit and cooled roll speed), as long as the extrusion remains stable. In the present series of coextrusions, it was decided to exclusively set the speed of extruders, (i.e., the entry rate of the system) to adjust the thickness. For a given geometrical structure of the final film, three tool parameters are then to be chosen: the air gap length, the slit size and the cooled roll speed (line speed). Choosing a set of tool parameters determines a set of dependent extrusion parameters: stretching of the film in the air gap, total time open to the interfacial reaction and crystallization rate. These three parameters are expected to control the formation of the interfacial copolymers, but they cannot be varied independently of each other, while keeping the final structure of the films fixed.

Characterization of the Surface Density of Copolymers

To determine the surface density of copolymers actually formed at the interface, Σ , we used X-ray spectroscopy (XPS) in a way very similar to previous investigations on the same PP/PA6 system [12, 13, 19, 29]. The method, first developed by Boucher et al. [13], involves selective dissolution of the PA6 part of a sandwich PA6/PP/PA6 film with three baths of formic acid, followed by a treatment with trifluoroacetic anhydride in the gas phase followed by a hydroxylation in de-ionized water. The selective dissolution of the PA6 was achieved using several solvents and reactive materials: Formic acid (Normapur®, purity > 99%), dichloromethane (analysis grade, purity > 99.9%) were purchased from VWR, trifluoroacetic anhydride (purity > 99%) was from Aldrich, and *n*-heptane (Purex PA), and absolute ethanol (PA-Purex) were from Carlo Erba. They were used as received. All the glass flasks were cleaned using Piranha solution (1:1 sulfuric acid [95%–97%, VWR-Merck for analysis] and 30% hydrogen peroxide [Prolabo-VWR]) for 15 min, rinsed with cascaded deionized water and then dried under nitrogen flux.

After the selective dissolution of the PA6, all samples were stored under controlled argon atmosphere in glass flasks previously cleaned in Piranha solution, and analyzed by XPS within 7 days from preparation, in order to minimize possible oxidation of the nanometric PA6 layer remaining on top of the PP layer before the XPS analysis. This remaining nondissolved PA6 only comes from PA6 chains having reacted at the interface to form PA6/PP copolymer molecules. Its amount was quantified through the nitrogen/carbon ratio dosed by XPS. The XPS spectra were collected with a SSX-100 Surface Science spectrometer using a monochromatic source (Al K α 1, $h\nu = 1,486.6$ eV.). Survey scans between 0 and 1,100 eV were first collected on each sample to check for surface contamination. The 1s spectra of carbon and nitrogen were then recorded on a clean area of the sample and used to estimate Σ , through:

$$\Sigma = -\frac{N_A \rho_{PA6} \lambda \sin \theta}{M_{nPA6}} \ln \left[1 - \frac{I_N / I_C}{(I_N / I_C)_{PA6}^\infty} \right] \quad (1)$$

With N_A the Avogadro's number, ρ_{PA6} the mass density of PA6, M_{nPA6} its number average molecular weight, λ the mean free path of N 1s photoelectrons, and θ the takeoff angle (35°). I_C , I_N , I_C^∞ , and I_N^∞ are respectively the intensities of the carbon and nitrogen peaks for the analyzed sample and for a thick PA6 film. The reproducibility of the Σ determination was $\sim \pm 10\%$ [13, 19].

SURFACE DENSITY OF COPOLYMERS IN CO-EXTRUDED MULTILAYER FILMS

Figure 1 reports the surface density of copolymers for various PA6/PP/PA6 films obtained on the line « Collin » at CERDATO, for one PP/PPg mixture (LS1A in Table 1) and for various exit slit sizes e and air gap lengths X . The coextrusion parameters were adjusted so that the final structure of the PA6/PP/PA6 three layers films remained fixed to 25, 10, and 25 μm , respectively.

The surface density of copolymers appears essentially insensitive to the geometrical parameters of the coextrusion line. This is a quite surprising result, as changing the tools parameters of

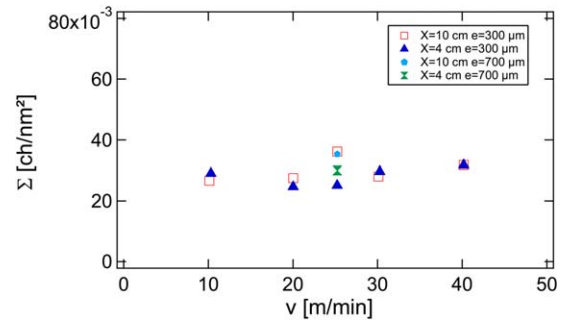


FIG. 1. Density of copolymer Σ , as a function of the line velocity for the tie layer LS1A and for various exit slit sizes e , and air gap lengths X , adjusting the co-extrusion parameters so that the final structure of the PA6/PP/PA6 three-layer film remains fixed to 25, 10, and 25 μm . [Color figure can be viewed at wileyonlinelibrary.com]

the coextrusion line allows one to span very different open times for the interfacial reaction. A second clear result is that the surface density of copolymer remains well below the saturation surface density, which is close to 0.075 chains nm^{-2} for the particular molecular parameters of the polymers used [1].

Figure 2 shows that similar results are also obtained for another tie layer, LS2 F in Table 1 (longer PPg molecules), again keeping the final structure of the three layers fixed to 25, 10, 25 μm .

Finally, the evolution of the surface density of copolymers with the time spent between the entrance into the co-extrusion box and the exit slit, t_2 , while the time spent in the air gap t_3 was essentially fixed, is reported in Table 2 for two different geometries of the final three-layer film.

The surface density of copolymers clearly decreases when increasing the time open to the interfacial reaction, for both geometries. This quite surprising result points out that some competing mechanism should come into play and counterbalance the grafting reaction.

We have checked that this decrease of the copolymer surface density was not the result of a decomposition of the reacting species. To do so, the set up proposed by C. Laurens et al. [30] has been used to post-anneal the coextruded films and the copolymer density has been measured as a function of the annealing time, at three different annealing temperatures, 180°C, 205°C, and 225°C. The results are reported in Fig. 3.

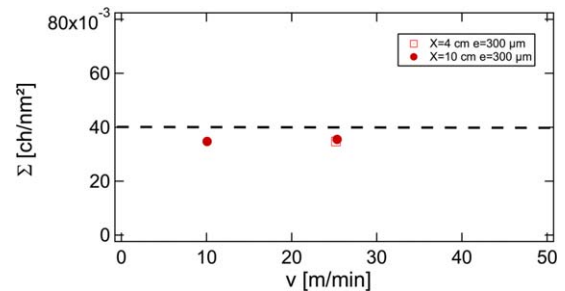


FIG. 2. Density of copolymer Σ , as a function of the line velocity for the tie layer LS2F for exit an exit slit sizes $e = 300$ μm , and for two different air gap lengths X , adjusting the coextrusion parameters so that the final structure of the PA6/PP/PA6 three layers film remains fixed to 25, 10, and 25 μm . [Color figure can be viewed at wileyonlinelibrary.com]

TABLE 2. Density of copolymer Σ , as a function of the time spent between the entrance into the coextrusion box and the exit slit t_2 .

Structure	t_2 (s)	t_3 (s)	Σ (ch nm ⁻²)
25/10/25	>136	0.36	0.006
	63.15	0.35	0.029
50/10/50	>77	0.39	0.041
	36.17	0.37	0.047

The time spent in the air gap t_3 was essentially fixed as can be seen in the 3rd column. The different final film geometries are in the first column for the tie layer LS2F.

The data reported in Fig. 3 clearly show that the undersaturation of the coextruded films is not due to a lack of PPg chains, as the post-annealing allows the interface to attain the surface density at saturation close to 0.07 chains per nm² for the particular molecular weights of the polymer used.

NUMERICAL MODELING OF A COEXTRUSION LINE

Analyzing the surface densities of copolymers for coextruded trilayers films PA6/PP/PA6, obtained with a range of different co-extrusion machine parameters, two quite surprising results were obtained.

First, the surface density of copolymers formed at the PP/PA6 interfaces appeared independent of the exact coextrusion parameters (line velocity, size of the exit slit, air gap length, and draw ratio) provided the final thicknesses of the various layers were maintained fixed. Second, the surface density in copolymer was observed to be smaller than the saturation density of the interface, even for coextrusion parameters such that the open time for the reaction was well above the time necessary to reach saturation when films were formed at rest [19].

A plausible explanation of this undersaturation of the interface could be a dilution of the yet formed copolymers in the zones of the process line where the surface of interface is increased, as for example inside the air gap where the film exiting the slit is stretched before its crystallization on the cooled roll. To gain a more precise insight in such a possible dilution of the yet formed copolymers, we have numerically modeled the flow all along the coextrusion line, with a special attention paid to the evolution of the area of interface. We present below the main results of that numerical modeling.

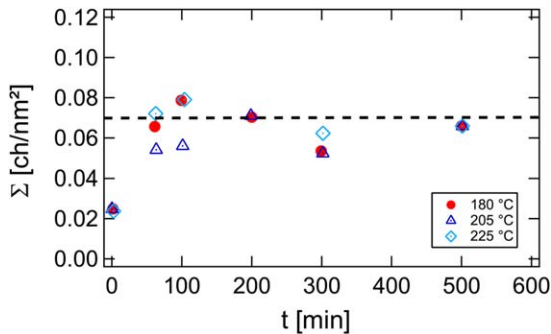


FIG. 3. Density of copolymer Σ , as a function of the annealing time for different heating temperatures. for assemblies made with tie layer LS1A. [Color figure can be viewed at wileyonlinelibrary.com]

We have used the three dimensions finite element numerical code REM3D [25]. Rem3D is a 3D injection-molding software. It solves the Stokes Equation in complex geometry with an adaptive automatic meshing and it allows one to take into account the free surfaces in the air-gap region. The geometry of the machine (here “a Collin” coextrusion line) can be accounted for, along with the coextrusion conditions (velocities, thicknesses...) and the rheological properties of the polymers. More precisely, to avoid extra-long calculation times, we assumed the same rheology for the two different polymers, PP and PA6, which is indeed a valid assumption at the co-extrusion temperatures used, and for the particular molecular parameters of those polymers. We thus have injected into the code the PA6 rheology as being that of the three layers system, with a Carreau-Yasuda law [31] and the WLF [32] law for the shear rate and thermal dependencies.

$$\eta = \eta_{\infty} + (\eta_0 - \eta_{\infty}) [1 + (\tau_s \dot{\gamma})^{\alpha}]^{\frac{m-1}{\alpha}} \quad (2)$$

With $\eta_0 = 279.513$ Pa.s, $\eta_{\infty} = 0$ Pa.s, $\alpha = 0.489$, $m = 1$, $\tau_s = 2.5 \times 10^{-3}$ s and

$$\eta = \eta_0(T_{\text{ref}}) \exp \left[\frac{A_1(T_{\text{ref}} - T_s)}{A_2 + (T_{\text{ref}} - T_s)} - \frac{A_1(T - T_s)}{A_2 + (T - T_s)} \right] \quad (3)$$

with $A_1 = 20.4$; $A_2 = 101.6$ K; $T_s = 349.3$; and $T_{\text{ref}} = 523.15$ [33].

The values used in the resolution are the one included in the software database. The origin was chosen as the point at which both injected materials PP and PA6 were meeting for the first time. The simulation has been performed with the help of Frank Gérard, CERDATO ARKEMA, imposing the dimensions of the co-extrusion box and the coextrusion parameters of the Collin extrusion line of CERDATO ARKEMA, on which most of the investigated tri-layer PA6/PP/PA6 films have been formed.

To trace back the evolution of the area of the interface along the coextrusion line, we have numerically evaluated the area stretch ratio TCSI. To evaluate TCSI, one needs to choose a reference surface, and to follow its evolution with time all along the co-extrusion line. TCSI is defined as the ratio of the value of that surface at time t to the initial area of the reference surface: $\text{TCSI} = \frac{S(t)}{S(t_0)}$, with $S(t_0)$ an elementary surface pertaining to the interface at the reference time t_0 . In fact, Ottino was the first using kinematical considerations to calculate this stretch ratio in any flow field geometry [1, 34]. The evolution of each element of interface is accessible through the 3D modeling of the flow field, so that the TCSI can be numerically computed along the flow.

We have run REM 3D for four different conditions, regarding the extrusion parameters, as sketched in Table 3, injecting

TABLE 3. Extrusion parameters used for running the numerical modeling of the evolution of the surface of interface with REM3D.

	Line speed (m min ⁻¹)	Gap (μm)	Structure ($\mu\text{m} \mu\text{m}^{-1} \mu\text{m}^{-1}$)
Case 1	10	300	15/10/25
Case 2	10	700	25/10/25
Case 3	40	300	25/10/25
Case 4	10	300	75/10/75

the rheological properties of the extruded polymer as specified above.

A typical result in terms of the evolution of the TCSI along the extrusion line is reported in Fig. 4, along with a schematic view of the extrusion machine, in order to facilitate the location of the different zones of interest inside the co-extrusion machine.

The results obtained for the four investigated situations of the coextrusion parameters presented in Table 3 are reported in Fig. 5, again in terms of TCSI as a function of the distance travelled inside the coextrusion line.

The total creation of surface of interface appears to be independent of the extrusion parameters provided the structure of the final multilayer film is fixed. To keep this final structure, the machine parameters need be adjusted (see comparison between Case 1 and 3) so that the draw ratio inside the air gap compensates for the die slit size in order to recover the final structure of the films. This is an interesting result, which may

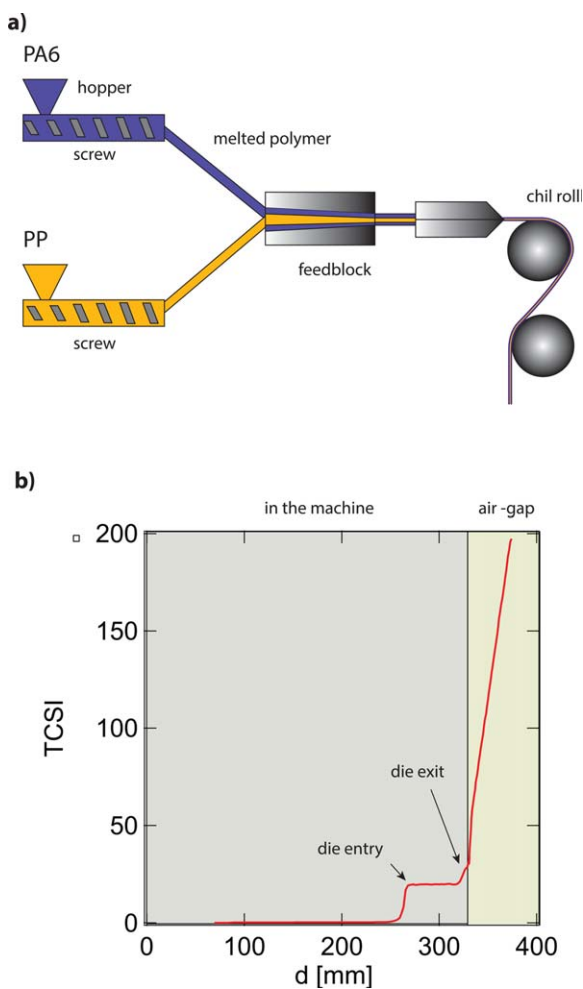


FIG. 4. (a) Schematic representation of the different parts of the extrusion machine. The origin of the coextrusion distance inside the machine is taken at the place where the two polymers meet. (b) Evolution of the rate of creation of surface of interface, TCSI, as a function of the distance travelled by the fluid inside the coextrusion line. It appears clearly in Fig. 4 that three zones of the line lead to noticeable increase of the surface of interface: the entrance of the die, the exit of the die, and the air gap, as a result of convergent, divergent, or elongational components of the flow. [Color figure can

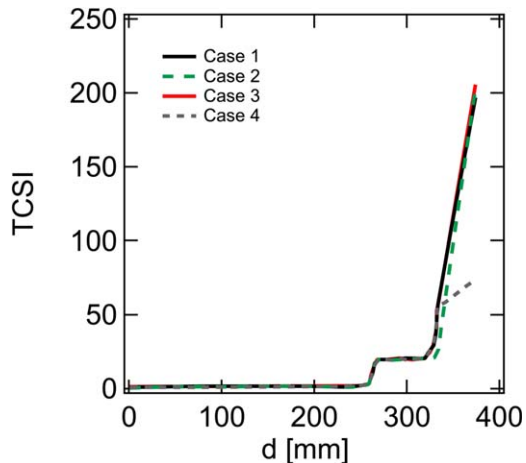


FIG. 5. Evolution of the rate of creation of surface of interface, TCSI as a function of the distance travelled inside the coextrusion line, for the various coextrusion parameters and film thicknesses presented in Table 3. [Color figure can be viewed at wileyonlinelibrary.com]

explain that the measured surface grafting density of three-layer films having the same final structure, but made with various combinations of extrusion parameters, is indeed the same. To be more precise, it is possible to use REM 3D to try to evaluate the surface grafting density all along the coextrusion line, provided few simplifying assumptions are made.

In a first simplified approach, one can assume that in all the zones of the coextrusion line where there is no substantial creation of surface of interface (TCSI close to 1), the grafting reaction takes place in a way quite similar to what happens in annealed samples without flow. The kinetics of the grafting reaction without flow has been investigated [13, 19], for molecular parameters of PP, PA6, and PPg polymers and concentration of PPg molecules in the PP matrix comparable to those of the present study. The main results of these studies can be summarized as follow. First, the final surface density of copolymer is limited by the number of PA6-NH2 extremities available at the interface. To be available a PA6 chains needs to be located at a distance from the interface smaller than its radius of gyration. Indeed, the limiting possible density of Gaussian polymer chains able to reach and touch an interface without being obliged to stretch, is then given by $\nu = 1/\sqrt{Na^2}$, with N the polymerization index of the chains and a the size of a monomer. With the molecular parameters of the polymers used in the present study, and neglecting the polydispersity, this leads to $\nu_{PA6} = 0.03 \text{ nm}^{-2}$ and $\nu_{PPg} = 0.3 \text{ nm}^{-2}$. This factor of 10 is mainly due to the larger size of the PA6 monomers compared to PP monomers. Second, the initial stages of the interfacial reaction are controlled by the diffusion of PPg chains from the bulk PP towards the interface, as the reactive PPg chains are highly diluted inside the PP matrix, so that the initial number of PPg chains located in the very vicinity of the interface is well below the number of NH2 extremities of PA6 chains initially located at a distance of the interface smaller than a radius of the PA6 chains. As yet noticed above, there is a saturation grafting density, Σ_{∞} , which results from the drastic slowing down of the grafting reaction when PPg chains yet grafted to PA6 chains have consumed all PA6-NH2 extremities pertaining to PA6 chains located close enough to the surface to form a dense layer

of Gaussian chains. This is due to the fact that, in order for any additional PPg chain to find a NH2 extremity, it is necessary to stretch the yet grafted PA6 chains to allow for new PA6 chains to enter into the layer from the interface having a thickness comparable to the size of the PA6 chains. The entropy penalty corresponding to such a stretching essentially stops the grafting reaction. With the molecular parameters of PPg and PA6 chains used in the present study, this limiting surface density has been experimentally determined to be $\Sigma_{\infty}=0.075$ chains/nm². One can notice that this experimental value is two times larger than the simple estimate of ν_{PA6} given above. We think that this is due to the polydispersity of the PA6, which can favor an enrichment in small chains close to the interface.

Then, the initial formation of the interfacial copolymer is governed by the diffusion law:

$$\Sigma = 2c_0\Sigma_{\infty}b_02\sqrt{\frac{Dt}{\pi}} \quad (4)$$

with c_0 the concentration in PPg chains inside the tie layer and $D = 3.8 \cdot 10^{-15} \text{ m}^2 \text{ s}^{-1}$ the diffusion coefficient of PPg chains inside the PP matrix, as estimated by extrapolating to 250°C the data obtained by E Boucher et al. [13] for similar molecular parameters, between 180°C and 235°C. The term $\Sigma_{\infty}b_02$, with $b_0^2 = 0.176 \text{ nm}^2$ the surface of a PP monomer, has been added to the conventional diffusion law in order to take into account the finite fraction of surface sites available for the reaction, as a result of the finite number of NH2 extremities of PA6 chains available close to the interface. Finally, concerning the reaction kinetics, the saturation of the interface is reached in <22 s, at 250°C in the absence of flow [19]. This is shorter than the total time open for the reaction in all the coextrusion experiments analyzed in the present study, as yet said above.

Then, relying on both these results on the building of the copolymer interfacial layer in the absence of flow and on the

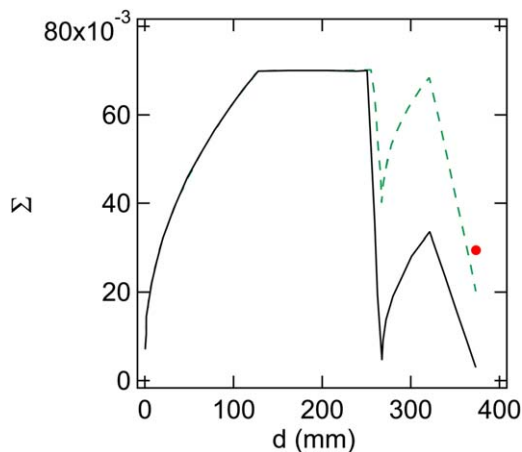


FIG. 6. Evaluation of the grafted density along the coextrusion line, taking into account the dilution of the yet formed copolymers in the zones of the coextrusion line where surface of interface is created, and assuming (1) no grafting by diffusion of the reactive species towards the interface (blue curve) or (2) grafting only by diffusion towards the interface and no convection inside the zones of creation of surface of interface (green curve). For comparison, the red point is the measured value of the grafted copolymer density on the corresponding trilayer film. [Color figure can be viewed at wileyonlinelibrary.com]

numerical modeling of the evolution of the surface of interface along the coextrusion line, we have constructed a first simplified description of the progressive building of the copolymer interfacial layer inside the coextrusion machine, based on the following assumptions:

- Diffusion of PPg chains towards the interface takes place all along the coextrusion line, and the corresponding contribution to the surface density of copolymers is ruled by *Eq. 4*, with a saturation at Σ_{∞} .
- In the zones where surface of interface is created, two additional competing phenomena take place: the copolymers yet present at the interface are diluted, due to the increase of the surface of interface, and if the flow lines are concentrated close to the interfacial regions, the grafting reaction can be accelerated by the convective transport of reactive species towards the interface. In the absence of any precise information on this possible coupling between flow and grafting, we have, in a first step, neglected the convective transport. We thus have run REM3D to quantify locally the evolution of the surface of interface and used these area data to estimate the surface density in copolymers at the end of each of the four zones of the co-extrusion line identified in Fig. 4, going from one zone to the following one by assuming the continuity of the surface density of copolymers when crossing the zone boundaries. At the end of zone 1, the surface density has reached saturation, as the time spent in zone 1 is larger than 22 s. Entering in zone 2, the surface of interface is increased, diluting the copolymers yet present at the interface by a factor directly related to the area stretch ratio, while grafting due to diffusion of PPg chains towards the interface starts again as soon as the surface has sufficiently increased so that it is desaturated in copolymers. We have estimated this grafting contribution assuming that *Eq. 4* is obeyed during the time spent in zone 2, and so on going from zone 2 to 3 (no creation of new surface of interface in zone 3) and from zone 3 to 4.

In Fig. 6 we present the results of such an approach for the extrusion parameters of Case 1 (Table 2), in terms of evolution of the surface density of copolymers at PP/PA6 interface, inside the coextrusion line, as a function of the position along the coextrusion line, and deduced from the numerical simulation with the above specified assumptions.

It appears clear in Fig. 6 that first, it is possible to approximately predict the final grafting density, taking into account the dilution of the yet formed copolymers due to creation of new surface of interface in the specific zones of the coextrusion line where the flow is convergent, divergent or elongational. This dilution process is crucial to understand how the co-extrusion parameters impact the final surface grafting density of copolymers. A second result appears in Fig. 6: the final copolymer surface density seems under estimated when dilution and diffusion alone are taken into account, omitting convection assisted grafting inside the zones of the co-extrusion line where dilution takes place. At this stage, it is however fair to notice that the modeling of the grafting kinetics through *Eq. 4* remains approximate, in particular because the value of the diffusion coefficient of the PPg chains in the PP matrix we have used is only an estimate deduced from the work of E Boucher et al. [13].

These results anyhow point out the clear need of a better description of the coupling between flow and grafting kinetics if

one wants to trace back in a precise manner how the coextrusion parameters do impact the final surface density of copolymers.

CONCLUSIONS

Measuring the surface density of copolymers formed at the PA6/PP Interface of co-extruded PA6/PP/PA6 three-layer films, we have shown that first this surface density was essentially insensitive to the coextrusion parameters, provided one keeps the final three layers structure fixed. In particular, the observed surface density is not correlated to the time open to the interfacial reaction of the Succinic anhydride modified PP Molecules on the NH₂ extremities of the PA6 molecules inside the coextrusion line. Second, we have also observed that this copolymer surface density was always lower than the surface density at saturation for these polymers, even when the time open to the reaction was longer than the time necessary to reach this saturation in films obtained in the lab without flow.

On the basis of a numerical modeling of the coextrusion flow, we have been able to show that this under saturation of the interface was the result of a competition between the interfacial reaction and the dilution of the yet formed copolymers in all the zones of the coextrusion line where the surface of interface was increasing, due to convergent, divergent or elongational flow. The numerical modeling of the flow allows one to precisely identify in which zones of the coextrusion line the surface of interface is increased, and to quantify this increase. Then, introducing both the flow and the interfacial reaction in a simplified way, that is, assuming that diffusion and not convection dominates the transport of reactive species to the interface, we could show that indeed, it is possible to approximately account for the experimentally measured surface density in the coextruded films. We could also show that it is necessary to better understand the coupling between flow and interfacial reaction rate (i.e., the importance of convective transport of reactive species towards the interface) if one wants to correctly optimize the coextrusion parameters in order to obtain films with optimized amount of interfacial copolymers acting as adhesion promoters at PA6/PP Interfaces. Systematic experiments on the same PA6/PP/PA6 system, performed with a specially designed apparatus allowing one to rapidly heat, stretch and quench three layers assemblies and directly investigate the respective role of diffusion and convection on the interfacial reaction rate are presently underway and will be reported in a forthcoming paper.

ACKNOWLEDGMENTS

The authors thank Arkema for providing the samples and financing the research. They acknowledge C. Creton and J.-F. Agassant for fruitful discussions.

REFERENCES

1. Z. Tadmor and C. G. Gogos, *Principles of Polymer Processing*, Wiley, Hoboken, New Jersey (2013).
2. H. Zhang, K. Lamnawar, and A. Maazouz, *Polym. Eng. Sci.*, **55**, 771 (2015).
3. C. Rauwendaal, *Polymer Mixing: A Self-Study Guide*, Hanser Publishers, Munich (1998).
4. C.W. Macosko, H.K. Jeon, and T.R. Hoye, *Prog. Polym. Sci.*, **30**, 939 (2005).
5. P.L. Beltrame, A. Castelli, M. Canauz, M. Canetti, and A. Seves, *Macromol. Chem. Phys.*, **196**, 2751 (1995).
6. H. Pernot, M. Baumert, F. Court, and L. Leibler, *Nat. Mater.*, **1**, 54 (2002).
7. S. Lyu, T.D. Jones, F.S. Bates, and C.W. Macosko, *Macromolecules*, **35**, 7845 (2002).
8. A. Ajji, and L.A. Utracki, *Polym. Eng. Sci.*, **36**, 1574 (1996).
9. S. Wu, *Polymer Interface and Adhesion*, M. Dekker, New York, New York (1982).
10. T.P. Russell, *Curr. Opin. Colloid. Interface Sci.*, **1**, 107 (1996).
11. H.R. Brown, *Macromolecules*, **22**, 2859 (1989).
12. E. Boucher, J.P. Folkers, C. Creton, H. Hervet, and L. Léger, *Macromolecules*, **30**, 2102 (1997).
13. E. Boucher, J.P. Folkers, H. Hervet, L. Léger, and C. Creton, *Macromolecules*, **29**, 774 (1996).
14. C. Creton, E. J. Kramer, H. R. Brown, and C.-Y. Hui, *Molecular Simulation Fracture Gel Theory*, Springer, Berlin, 53 (2002).
15. L. Leger, and C. Creton, *Philos. Trans. R. Soc. Math. Phys. Eng. Sci.*, **366**, 1425 (2008).
16. G.H. Fredrickson and S.T. Milner, *Macromolecules*, **29**, 7386 (1996).
17. J. Song, R.H. Ewoldt, W. Hu, H. Craig Silvis, and C.W. Macosko, *AIChE J.*, **57**, 3496 (2011).
18. J. Zhang, S. Ji, J. Song, T.P. Lodge, and C.W. Macosko, *Macromolecules*, **43**, 7617 (2010).
19. T. Barraud, F. Restagno, S. Devisme, C. Creton, and L. Léger, *Polymer*, **53**, 5138 (2012).
20. C. Laurens, R. Ober, C. Creton, and L. Léger, *Macromolecules*, **34**, 2932 (2001).
21. P. Auroy, L. Auvray, and L. Léger, *Macromolecules*, **24**, 2523 (1991).
22. C. Ligoure, and L. Leibler, *J. Phys. Fr.*, **51**, 1313 (1990).
23. P. Auroy, Y. Mir, and L. Auvray, *Phys. Rev. Lett.*, **69**, 93 (1992).
24. P.G. Ferreira, A. Ajdari, and L. Leibler, *Macromolecules*, **31**, 3994 (1998).
25. B. Lu, K. Lamnawar, and A. Maazouz, *Soft Matter.*, **13**, 2523 (2017).
26. H. Zhang, K. Lamnawar, and A. Maazouz, *Macromolecules*, **46**, 276 (2013).
27. H. Zhang, K. Lamnawar, and A. Maazouz, *Rheol. Acta*, **51**, 691 (2012).
28. H. Bondil, Etude de l'adhésion Aux Interfaces Polypropylène/Polyamide-6: Rôle Des Copolymère Formés in Situ En Situation de Recuits Courts Représentatifs Des Assemblages Coextrudés, Université Paris VI - Pierre et Marie Curie, (2006).
29. F. Kalb, L. Léger, C. Creton, C.J.G. Plummer, P. Marcus, and A. Magalhaes, *Macromolecules*, **34**, 2702 (2001).
30. C. Laurens, C. Creton, and L. Léger, *Macromolecules*, **37**, 6814 (2004).
31. C. W. Macosko, Ed., *Rheology: Principles, Measurements, and Applications*, VCH, New York (1994).
32. M. Rubinstein and R. H. Colby, *Polymer Physics*, Oxford University Press, Oxford, New York (2004).
33. J. E. Mark, Ed., *Polymer Data Handbook*, Oxford University Press, New York (1999).
34. J.M. Ottino, W.E. Ranz, and C.W. Macosko, *AIChE J.*, **27**, 565 (1981).