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Controlling interfacial instabilities in PP/EVOH coextruded multilayer films through the surface density of interfacial copolymers

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Abstract

Co-extruded polypropylene/tie/ethylene vinyl alcohol/tie/polypropylene (PP/tie/EVOH/tie/PP) films often exhibit optical defects which appear as randomly distributed scattering objects, in the sub-millimeter range. These defects may strongly affect the film transparency and prevent their practical use in packaging. Based on an objective optical test aimed at quantifying the film transparency, and on a systematic analysis, through optical microscopy, of transverse cuts of films obtained in various co-extrusion conditions, the nature of the defects could be identified as resulting from a modulation of the thickness of the inner EVOH Layer, with no variation in the overall thickness of the multilayer films. Thanks to a recently developed method to dose the surface density of interfacial copolymers, a clear correlation between the amplitude of the thickness modulation of the inner EVOH layer and the density of co-polymer molecules formed *in situ* at the EVOH/tie layer interface during the co-extrusion process was established. These results open the way to a better design of tie layers composition to avoid these kinds of defects.

KEYWORDS: Controlling interfacial instabilities in PP/EVOH coextruded multilayer films through the surface density of interfacial copolymers.

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I. INTRODUCTION

Nowadays, industries often need to design composite materials offering specific complementary properties. Due to their light weight, polymers are one of the most used materials to answer this type of demand. However, the successful association of different polymers in order to benefit from their different properties (for example mechanical, dielectric or optical properties) [1–4] within a unique material is still a challenge because most of polymer pairs are not miscible, and develop only very weak adhesion when forced into contact [5]. One possibility is to form multilayer polymer films. The fabrication of these multilayered materials is not simple as the interfaces need to be reinforced mechanically. Such necessary adhesion enhancement is usually produced by diblock copolymers that are carefully designed so that each block is compatible with one of the materials in contact. The copolymers tend to assemble at the interface and they stabilize it. [6–12]. For practical applications, these copolymers are created *in situ* during the mixing process by an interfacial chemical reaction between reactive polymers initially mixed within each of the joined polymers.

Food packaging often uses multilayer films made of PP/EVOH, to form transparent films, allowing one to see what is inside the package, and displaying good mechanical and oxygen barrier properties. In such PP/EVOH multilayer films, the interface is stabilized by ethylene vinyl alcohol-co-polypropylene grafted maleic anhydrid (EVOH-co-PP-g-AM) copolymers formed at the interface during the co-extrusion process (Figure 1). To achieve this goal, a tie layer is inserted between PP and EVOH layers. The tie layer is a mixture of a small quantity of maleic acid grafted PP (PP-g-AM) with unmodified PP (that can be different from the external PP, but fully miscible with it). The cohesion between the tie layer and the PP layer is ensured by inter-diffusion of PP chains through the PP-tie layer interface when both are into contact and heated above the melting transition temperature of PP. The ethylene vinyl alcohol-co-polypropylene grafted maleic anhydrid (EVOH-co-PP-g-AM) copolymers is synthesized *in situ* during the coextrusion process by the chemical reaction of PP-g-AM chains on EVOH chains, as schematically shown in figure 1. This final five layers polypropylene/tie/ethylene vinyl alcohol/tie/polypropylene (PP/tie/EVOH/tie/PP) presents good mechanical and barrier qualities. However, the corresponding co-extruded films often show optical defects which affect the film transparency. Surprisingly enough, these defects are not observable with other quite similar associations, like for example polyamid6/polypropylene. These defects lead a grossly frosted glass aspect, identified in this

article as *granities*. The associated loss of transparency is not acceptable for a number of food packaging applications. A typical example of *granities* defects is given in figure 2, where two multilayer assemblies with different transparency qualities are shown. Both tested films are placed at 20 millimeters from the book entitled "PHYSICAL POLYMER SCIENCE" [13]. The title can easily be read through film a) and with difficulties through film b).

The goal of the present paper is to describe a systematic investigation of multilayer PP/Tie/EVOH/Tie/PP films, aimed at identifying the mechanisms that can explain the nature and the origin of transparency defects in coextruded films. As these defects reveal themselves through scattering of light, they could be due either to local variations of the optical properties of one or several of the constituting polymers, or to interfacial instabilities that would modulate the total thickness of the film or the thickness of the internal layers.

Interfacial instabilities in co-extrusion process have been widely studied in the case of non-reactive polymers. In some experimental approaches, based on the analysis of extrudates formed in industrial configurations, stability charts function of process parameters and/or relative rheological parameters of the polymers were proposed [14–17]. Those studies showed that stable/unstable transitions were characterized by the development of wavy interfaces between polymers. In further experimental studies, the development of instabilities within the flow was investigated [18–22]. Main results show that viscoelastic stresses stratification across the interface is the dominant factor in the instability [23]. However, apart for simple asymptotic cases (extremely long or short waves), the exact physical mechanisms at the origin of the instability are still unknown. Moreover, it was recently shown that interfacial chemical reactions can drastically affect the stability of an interface. The impact of interfacial reaction in co-extrusion still needs to be understood [24, 25].

Several studies point out clear links between the contrast in rheological properties of joined polymers and the interfacial instability. However, rheology alone cannot explain the observed different sensitivities to *granity* between PP/tie/PA6/tie/PP and PP/tie/EVOH/tie/PP. Other mechanisms should contribute that need be identified. Recently, in close collaboration with the results presented in the present paper, Bondon *et al.* [26] have analyzed, on lab-formed assembly, the interphase formed between EVOH and tie layer (PP-g-AM plus PP) through electronic microscopy. They have evidenced a roughening of the interface at nanometric scale when the interfacial reaction between EVOH and PP-g-AM was developing. This roughening of the interface was found to be associated to an anormal mechanical

relaxation of the interphase as measured by rheometry [24, 25].

In order to fill the gap between lab formed and extruded films, we present below the results of systematic experiments aimed at identifying the nature of the optical defects responsible for the appearance of *granities* defects, and trying to better pin point the role of interfacial copolymers. To do so, we have analyzed in a systematic manner these *granities* defects, proposing an objective test to quantify the loss of transparency. In order to identify more precisely the origin of that loss of transparency, we have analyzed in detail optically thin cuts of multilayer films, to try to answer the following questions: which microscopic parameters cause this macroscopic optical defect? Why, using the same materials, but varying the co-extrusion parameters, the optical quality of the films can be so different? What are the parameters controlling the appearance of *granities* defects? We present here the main results of this investigation.

II. MATERIALS

The studied coextruded films are five layers multimaterials PP/Tie/EVOH/Tie/PP (50/10/8/10/50 μm). They were kindly provided by ARKEMA. Tie layers are mixtures of PP-g-AM in PP. Nine samples were investigated. They differ from the process conditions and formulations of PP-g-AM (PPg1 or PPg2 or PPg3). PPg1 is the commercial grade, PPg2 was formulated in reactive extrusion and PPg3 in solution. The precise characteristics of the different polymer cannot be divulged for confidentiality reasons. The properties of the nine samples used are summarized in table I. The type of formulation together with the process conditions (PP processing temperature, PPg processing temperature, EVOH processing temperature and residence time (*i.e.* the time during which the materials are inside the feed-block and in the air gap before crystallization) are identified. The residence time is the time during which the tie layers and EVOH are molten and into contact, *i.e.* the time during which the interfacial copolymers can be formed. PPg1, PPg2 and PPg3 were synthesized by ARKEMA, PP was PP RD204CF from BOREALIS (Total Petrochemicals) and EVOH was EVASIN 3251FS provided by ARKEMA.

In order to quantify the surface density of the interfacial EVOH-co-PP-g-AM copolymers in the EVOH/PP multilayers, a selective dissolution of the EVOH part of the coextruded films was needed. This step was achieved by several solvent and reagents: dichloromethane amylene stabilised (CarloErba Reagent), acetyl chloride (AC) (Sigma Aldrich) reagent grade,

98%. These reagents were purchased and used without any further treatment.

III. FILM TRANSPARENCY AND INTERNAL LAYER THICKNESS

III.1. Method

III.1.1. Classification of the films

Several practical tests to characterize the ability of an object to transmit light and to quantify its transparency exists. These tests are separated into two categories: clarity meter and haze meter [27, 28]. A loss of transparency means that light is deviated by the object, due to scattering, diffraction or refraction, depending on the nature and on the size of the heterogeneities responsible for local changes in the light/object interactions. The length scale of these optical heterogeneities fixes the cone angle inside which light is deviated. The optical aspect of a coextruded film presenting defects depends on the angle at which the light is deviated when crossing the film: small angles (less than 2.5°) refer to clarity and wider angles refer to haze. The first one affects the resolution when observing an object through the film, and the second one has an impact on the contrast. We decided not to perform these existing tests, because the *granities* defects impact both the resolution and the contrast. A test directly relevant for the application has thus been developed, *i.e.* quantifying the ability to clearly see an object located at a given distance from the film, when observing this object through the film.

The method is detailed in the following. A sheet (figure 3) with letters of different sizes is observed through the film. The letters are sorted by size so that each line contains one size of letters. Each line (each size) corresponds to a note, going from 1 to 11 (1 for the line with the biggest letters and 11 for the line with the smallest letters). When looking to the sheet through a given sample, the smallest letters the observer is capable of distinguishing will specify the note affected to the sample. The more transparent is the sample, the smaller are the letters which can be distinguished by the operator and the higher is the note attributed to the sample. Three operators were involved in the present study. The respective distances between the sheet and the film and between the film and the eyes of the observer were fixed to respectively 100 mm and 500 mm . These distances were kept constant during all series of experiments in order to compare samples meaningfully. One advantage of this setup is its few space-consuming aspect, so that it can be settled directly on-line at the exit of the

process machine. It should be pointed out that it is crucial to fix the same distances between the film and the letters and the film and the operator for all experiments for the sake of comparison. The absolute note can slightly differ according to the operator, but the raking between samples remains the same. Statistical data analysis of the notes from different operators has not been done.

III.1.2. Microscopic Characterization

As already mentioned in the introduction, a rapid and easy examination of the samples showed that the studied defects are not due to a degradation of the external surfaces quality of the samples (roughness, thickness of the overall multilayer assembly...). Then, in order to identify the origin of the loss of transparency, systematic observations of the transverse section of the films were performed by optical microscopy.

For each sample, sections were cut to obtain around 10 μm thick chips. These cuts were performed at CNRS Imagif in Gif-sur-Yvette, with a cryogenic microtome LEICA, working at $-80\text{ }^{\circ}\text{C}$ with a glass knife. These chips were immersed in a drop of a immersion oil (refractive index 1.518), sandwiched between two glass slides and observed with an optical microscope (Olympus BS51) with $\times 20$ or $\times 50$ magnifications. A particular attention was paid to the orientation of these chips with respect to the direction of extrusion and are labeled in the following as: transversal (T), longitudinal (L) and random orientation (A). For each co-extruded film, twelve chips, four of each orientation were investigated.

III.2. Results and discussion

III.2.1. Notes

All samples were assigned a note according to the optical quality test described above. These notes are summarized the second column of the II. In this table, samples are organized from the note 5 (the most transparent samples) at top, down to the note 1 (the less transparent samples) at the bottom of the table. Only notes 5, 4, 3 and 1 were attributed, samples corresponding to the other quality note were not in the series of film available. Regarding samples 5 and 7I and for all operators, some letters could be read through the film but not all of the letters in this line noted 4. This heterogeneity of the results obviously came from the heterogeneity of optical quality within the same film. It has been decided to

gather samples 5 and 7I (note 4) with the group with the note 3. Regarding notes 5 and 1, appreciation of all operators were consistent. All examined co-extruded films can thus be organized in three groups of different optical quality. Finally, sample 7 exhibits obviously two areas with two different qualities: the lateral extremities of the film (7E) and the center (7I). These two parts were analyzed separately.

III.2.2. Microscopic observation

Two most representative pictures of the chips, for each group of optical quality, are displayed in figure 4.

These pictures reveal two phenomenally responsible for a loss of transparency: spherulites appear in the PP layer of some of the samples and also thickness irregularities of the inner EVOH layer. Indeed, the transverse sections of the samples can be schematically drawn as in figure 4g. As the refractive index of PP and EVOH are different, the thickness variation of the EVOH layer would locally transform the film in a succession of converging and diverging lenses, which will contribute to deviate light in all directions, altering the imaging capacities of the film. Both the amplitude and the wavelength of these thickness variations of the inner layer should affect the degree of light deviation, making the film more or less hazy.

In order to identify which phenomena was mostly responsible for the loss of transparency of the films, the presence or the absence of spherulites has been spotted for each sample and the waviness of the inner layer has been quantified, measuring the wavelength and the amplitude of the thickness variations of the inner EVOH layer. The results are summarized in table II. The wavelength λ reported for each orientation is the average of λ_{\min} and λ_{\max} both defined in figure 4g. For some samples, the wavelength could not be measured either because the wavelength is bigger than the size of the chip or because it could not be determined owing to the accuracy of the pictures or also because the number of observable thickness oscillations was too small to allow for an estimated average. These cases are symbolized with a slash in table II.

The amplitude of the thickness variation of the inner layer has been defined as follows:

$$\frac{\Delta E}{E} = \frac{\bar{E}_{\max} - \bar{E}_{\min}}{\bar{E}} \quad (1)$$

With \bar{E}_{\max} and \bar{E}_{\min} respectively the average of E_{\max} and E_{\min} as defined in figure 4g and \bar{E} the average of all thickness measured. The $(\frac{\Delta E}{E})$ reported for all orientations is the

average of $\frac{\Delta E}{E}$. The lines corresponding to samples containing visible spherulites at the scale of observation are filled in gray in figure II, while lines for which spherulites were not observable are unfilled.

Samples 8 and 9 with a note 5 and sample 7 with a note 3 (for a cut located at the center of the sample: 7I) or 1 (for a cut located at the extremity of the sample: 7E) display spherulites. Spherulites can thus be found whatever the optical quality, meaning that they are not responsible for the loss of transparency of the films, at least at first order.

Concerning the wavelength of the thickness oscillations of the inner EVOH layer, the quality of the data (number of thickness oscillations) collected in this study is not sufficient to distinguish a possible correlation between the value of this wavelength and the lack of transparency. The number of sections per sample should be increased to reasonably be able to conclude on this point.

The most relevant parameter which emerges from the analysis of the chips appears to be the amplitude of the thickness variation of the inner EVOH layer: whatever the orientation, this amplitude is observed to be in the range 0.0-0.3 for all samples noted 5; 0.1 to 0.5 for the samples noted 3-4 and 0.6-1.4 for the samples noted 1. There is thus a clear correlation between the amplitude of the thickness variation of the inner EVOH layer and the optical quality of the films. This correlation appears even clearer in the histogram shown in figure 5, which gathers all the collected data. The larger is the amplitude of thickness variation, the less transparent is the film.

One can notice that the amplitude of the thickness oscillations of the inner EVOH film observed in real coextruded film is much larger than observed on the same polymer sandwiches but made with no shear [26].

Another interesting result is revealed by the histogram in (figure 6). This histogram keeps the orientation L and T tracking, with amplitude of the variations of the inner layer thickness reported in blue for the longitudinal orientation and in red for the transverse orientation. The amplitude of the thickness variation appears significantly larger for the longitudinal than for the transverse orientation. There is thus an anisotropy in the destabilization of the thickness of the inner EVOH Layer, with an enhanced destabilization in the direction of extrusion. We address in more details this phenomenon below.

IV. FILM TRANSPARENCY AND COPOLYMER GRAFTING DENSITY

Even if not suitable for any application, as the different layers spontaneously delaminate, multilayer films made of pure EVOH and PP, for which thus no interfacial copolymers are formed during the co-extrusion, do not show instabilities of the thickness of the inner EVOH layer. It is thus natural to search for a possible correlation between the amount of interfacial copolymer and the severity of the optical granities defect. In order to do so, it is necessary to quantify the quantity of interfacial copolymers actually present at the tie/EVOH interface. We briefly describe below principle of the dosage method we have developed [29], and then correlate the analysis of the thickness variation of the inner EVOH layer to the surface density of copolymers formed at the tie/EVOH interface during the co-extrusion process.

IV.1. Method

IV.1.1. *Selective dissolution*

To access the surface density of EVOH-co-PP-g-AM copolymer molecules present at the end of the co-extrusion process at the buried tie/EVOH interface, parts of the multilayer films should be selectively dissolved, in order to exhibit the copolymer layer, and then to dose it through spectroscopic techniques. To do so, small pieces of a co-extruded multilayer films were brought inside a container with AC vapor for a one-night reaction. The reaction modifies the EVOH layer, transforming alcohol functions into ester functions. This esterification contributes to weaken the hydrogen bonds between EVOH chains so that each five layers PP/Tie/EVOH/Tie/PP film can be splitted into two PP/Tie/EVOH parts. Then, all EVOH chains not chemically linked to PPg were removed by immersions of three successive stirred baths of dichloromethane. At the end of the selective dissolution process, two sheets of PP films (S1 and S2 in figure 7) are obtained with esterified EVOH-co-PP-g-AM interfacial copolymers on one of their surfaces. The ester groups corresponding to this nanolayer of EVOH-co-PP-g-AM copolymers, are then quantified by FTIR. Knowing the average molecular weight of the EVOH used, it is then possible to convert the Infra-Red (IR) height peak ratio into surface density of EVOH-co-PP-g-AM. The precise protocol has been described in [29].

IV.1.2. FTIR quantification of EVOH-co-PP-g-AM

To enhance the sensitivity of the analysis and meaningfully quantify the surface density of copolymers, the SI or S2 films obtained after the selective dissolution were folded several times, and conditioned in discs of 20 mm diameter and 202 μm thickness. These discs were analyzed in transmission and the ratio of the height peaks at 1738 cm^{-1} (from ester signal) over that at 900 cm^{-1} (from PP signal) X was determined. This peak ratios were converted into surface density Σ through the following relation:

$$X = \frac{\rho_{\text{PA6}}}{\rho_{\text{PP}}} \frac{\Sigma N a^3}{h} \quad (2)$$

With h the thickness of PP.

IV.2. Results and discussion

The surface density of copolymers versus the note of the samples are displayed in the histogram in figure 8.

A clear correlation between the surface density of copolymer and the optical quality of the films is visible in figure 8: increasing the surface density of copolymers decreases the optical quality of the films (except for sample 7, which we shall discuss separately in the next paragraph). One can also notice that all the worst films (noted 1) correspond exclusively to one kind of tie: PPg3. We can conclude that the formulation of the tie is a key parameter if one wants to process films with good optical quality. But the formulation alone is not enough to determine the optical quality of the films: some of the films formulated with PPg1 have obtained the note 5 (sample 8) or the note 3-4 (sample 1 and 4), a result also visible for PPg2 (noted 5 for sample 9 and noted 3-4 for samples 2 and 5). Anyhow, for each type of PPg, the best films are those made with the smallest surface density of copolymers, as shown in Table I: all best films noted 5 have been made with a small residence time (7 seconds) inside the co-extrusion line, a condition which corresponds to a short open time for the grafting reaction between PP-g-AM and EVOH, and ensures a small surface density of copolymers.

The sample 7 demonstrates that the surface density of interfacial copolymers is not the only parameter influencing the optical quality of the final film. Indeed, within the same sample, the surface density of interfacial copolymers is significantly homogeneous, while for sample 7, the optical quality was depending on the area investigated. The differences

in stress/flow history in the various zones of a film can be responsible for this additional dependence of the optical quality on the location in the whole co-extruded film. We have at present no more precise analysis of the influence of the flow conditions on the final optical quality of the films. However, we have pointed out the importance of the flow conditions, through two observations: variation of the optical quality with the location within the film, and evidence of anisotropy in the amplitude of the modulation of the inner layer thickness, with an enhanced instability in the direction of the main flow along the co-extrusion line.

V. CONCLUSION

One category of optical defects observed in co-extruded multilayer films used in food packaging has been investigated. These defects, identified as granities, because they give to the film the aspect of a grossly frosted glass, are responsible for a loss of transparency of the film, which can be particularly disadvantageous for packaging applications. These granity defects, independent from thermal/oxidative degradation, develop on the specific association PP/EVOH materials without any variation of the overall thickness of the film, contrary to a number of other co-extrusion defects widely studied and usually attributed to dynamically induced instability of the co-extrusion flow. We have focused our attention on first identifying the nature of these defects and second on investigating the possible correlations between the degree of severity of these defects and the molecular structure and quantity of the copolymers formed *in situ* during the co-extrusion process, to mechanically strengthen the interfaces between the different polymers constituting the multilayer films. Our work has been centered on PP/EVOH multilayer films, for which these interfacial copolymers are formed by a chemical grafting of few PP molecules modified with maleic anhydride groups and for which a spontaneous nanometric undulation of the surface had been previously reported.

Optical microscopic observations of chips of films cut perpendicularly to the surface of the film reveal that the presence of visible spherulites inside the PP part of the films is not the main factor at the origin of the loss of transparency. These observations through optical microscopy have, however, lightened that fluctuations of the thickness of the inner EVOH layer were the main cause of loss of transparency, due to the corresponding deviation of light rays. The larger the amplitude variation in thickness is, the more locally converging or diverging appears the film, and the worst the optical quality is. The deviation of light

is affected by the local curvature of the inner interfaces, and should also be affected by the wavelength of these thickness instabilities. Unfortunately, this wavelength is comparable to the size of the chips we could form, and with the number of samples investigated, we could not conclude whether or not the wavelength of the variation of the inner layer thickness plays a role in the optical quality of the films. We have proposed a simple method allowing to objectively compare the optical quality of films formed with various co-extrusion parameters, and various kinds of reactive PPg chains, in order to be able to search for possible correlations between the structure, the surface density of copolymers and the co-extrusion process parameters, and the optical quality of the films. We have thus put into evidence a general rule: the larger the surface density of interfacial copolymers EVOH-co-PP-g-AM is, the worst the optical quality is.

However several results demonstrate that the interfacial copolymers surface density is not the only parameter governing the optical quality of the multilayer films. This shows up through two different results: the optical quality depends on the position on the overall film, with a better quality in the central part of the film than in along the lateral edges of the film, while both parts of the film contain the same surface density of EVOH-co-PP-g-AM copolymers. This suggests that stress and flow history during the coextrusion process are also important parameters. This reflects in the fact that we have put into evidence that the amplitude of variation of the inner layer thickness is higher for the chips cut along the co-extrusion line (longitudinal section) than when cut transversally (transverse section).

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DATA AVAILABILITY

The raw/processed data required to reproduce these findings cannot be shared at this time due to intellectual properties limitations.

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FIGURES

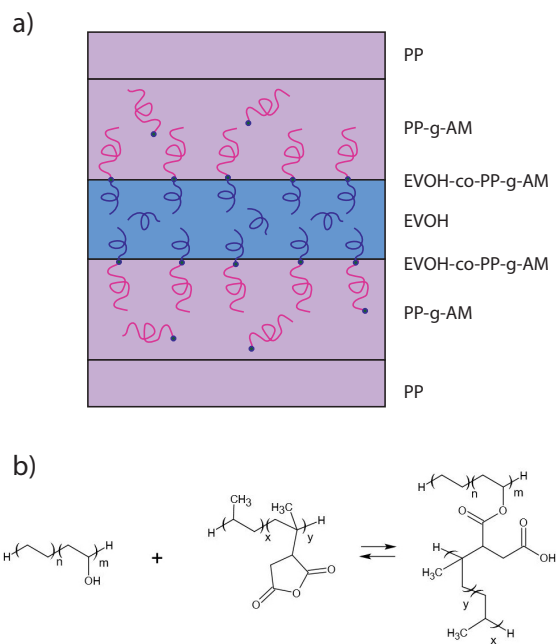


FIG. 1: a) Schematic of a five layers film: PP/tie/EVOH/tie/PP. EVOH-co-PP-g-AM copolymer is created at the interface. b) Chemical reaction of the copolymer formation.

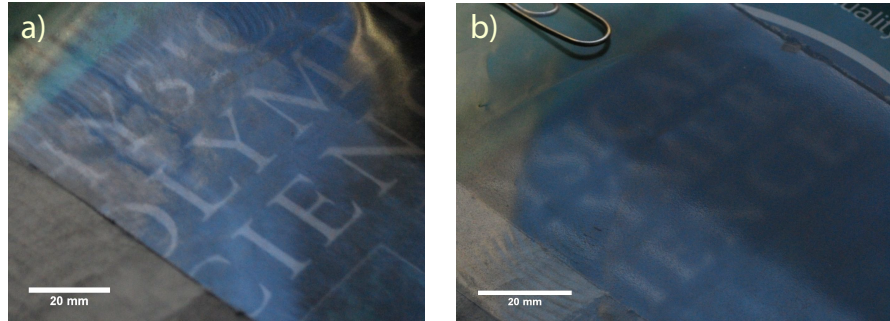


FIG. 2: Coextruded PP/Tie/EVOH/Tie/PP films with different degrees of severity of defects. One should notice that the zoom of the picture a) is slightly higher than the picture b).

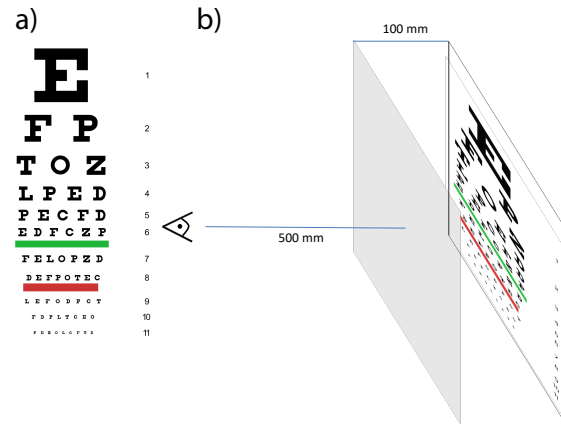
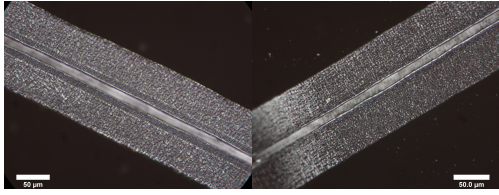
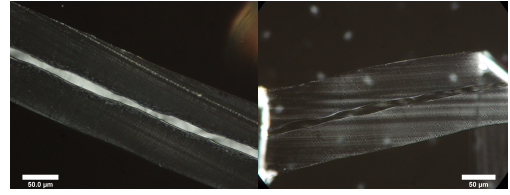


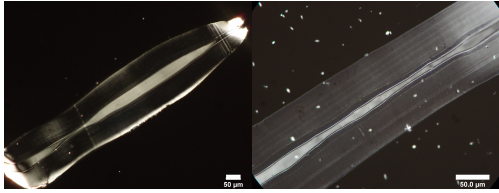
FIG. 3: a) Pattern to classify the quality of the samples. b) Testing setup.



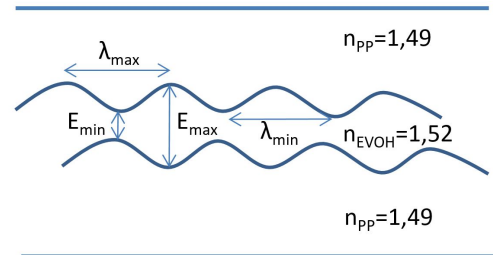
(a) Sample 8: note 5.(b) Sample 9: note 5.



(c) Sample 1: note 3.(d) Sample 2: note 3.



(e) Sample 6: note 1.(f) Sample 7: note 1.



(g) Schematic representation of the transversal section of the samples.

FIG. 4: Typical pictures of microscopic observations: the films in the first line (4a and 4b) were attributed note 5, the films in the second line (4c and 4d) were attributed note of 3 and the films in the third line (4e and 4f) were attributed note 1.

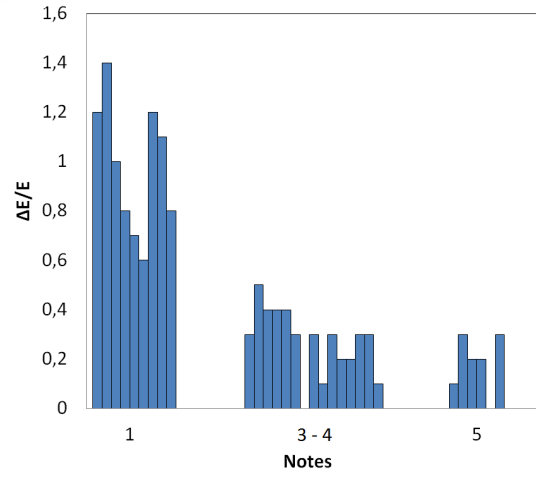


FIG. 5: Amplitude of variation of the inner layer thickness versus notes of all the samples studied in this article.

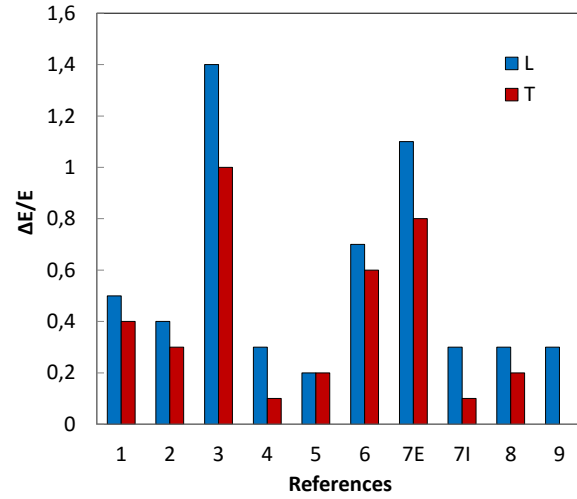


FIG. 6: Amplitude of variation of the inner layer thickness for all samples, longitudinal orientation in blue and transversal orientation in red.

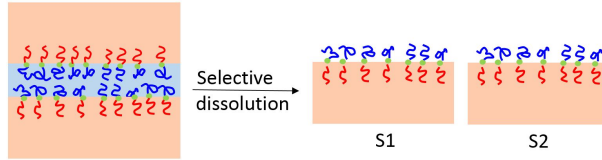


FIG. 7: After EVOH selective dissolution of coextruded films, two sheets S1 and S2 are obtained.

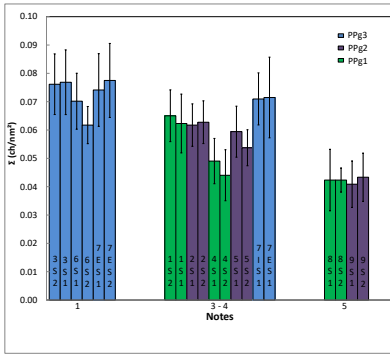


FIG. 8: Surface density versus notes. Samples formulated with PPg1 is represented in green, with PPg2 in purple and with PPg3 in blue.

TABLES

Samples	Tie layers	T_{PP} ($^{\circ}\text{C}$)	T_{PPg} ($^{\circ}\text{C}$)	T_{EVOH} ($^{\circ}\text{C}$)	Residence time (s)
1	PPg1	220	225	190	33
2	PPg2	220	225	190	33
3	PPg3	220	225	190	33
4	PPg1	200	200	190	31
5	PPg2	200	200	190	31
6	PPg3	200	200	190	31
7	PPg3	225	225	210	7
8	PPg2	225	225	210	7
9	PPg1	225	225	210	7

TABLE I: Formulation and process conditions of the samples.

Samples	Notes	$\left(\frac{\Delta E}{E}\right)$	$\left(\frac{\Delta E}{E}\right)$	$\left(\frac{\Delta E}{E}\right)$	λ (μm)	λ (μm)	λ (μm)
		A	L	T	A	L	T
8	5	0.1	0.3	0.2	54.0	40.9	/
9	5	0.2	0.3	0.0	84.2	/	/
1	3	0.3	0.5	0.4	6.9	86.6	98.2
2	3	0.4	0.4	0.3	110.5	61.7	98.2
4	3	0.0	0.3	0.1	/	/	76.0
5	4	0.3	0.2	0.2	77.6	41.8	85.1
7I	4	0.3	0.3	0.1	107.3	/	/
3	1	1.2	1.4	1.0	/	/	/
6	1	0.8	0.7	0.6	/	/	111.7
7E	1	1.2	1.1	0.8	/	/	/

TABLE II: Table of notes for all samples in regards with the amplitude of the undulation of the internal layer thickness. The samples containing spherulites are highlighted in gray.