

Microstructure variations of Polylactide Fibres with Texturing conditions

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ABSTRACT: *The characterization of the microstructure of synthetic fibres is necessary to identify changes in properties produced by differences in the production variables. To this end, two physico-chemical tests (iodine sorption and differential solubility) easy and rapid to implement were employed to study the differences in the microstructure of polylactide false-twist textured multifilaments. The results enabled us to identify variations in microstructure induced by texturing conditions and were related to processing variables. These tests were compared with more expensive and complicated techniques to quantify crystallinity and orientation of filaments. Both tests enabled us to identify microstructure variations between substrates.*

KEY WORDS: *polylactide, physico-chemical techniques, crystallinity, orientation*

INTRODUCTION

Poly lactide (PLA) is a biodegradable polymer whose monomer, lactic acid, is obtained mostly from corn starch. It is an annually renewable resource. Thermoplastic fibres, such as polylactide, undergo changes in their microstructure during the heat treatments of the manufacturing and processing in the textile industry that affects their crystallinity and/or orientation.

Texturing, which is applied to confer textile handle to thermoplastic filaments, can affect their microstructure resulting in problems of acceptance of treated goods. Texturing can be applied through several processes, the most common of which are the air-jet and the false-twist methods. In false-twist texturing, a POY (Partially Oriented Yarn) multifilament yarn feeds the texturing equipment. Two variables control the process: the draw ratio determined by rate between delivering and feeding rate and the temperature at which the twisted yarn is heat set. Depending on the different values of draw ratio and texturing temperature, significant differences in microstructure can be produced, resulting in different characteristics of yarn volume, elasticity and brightness.

The most important parameters defining the global fibre microstructure are crystallinity and orientation. These factors considerably affect the mechanical characteristics, the dyeing behaviour and the final application of the textile substrates.

Crystallinity can be determined by different methods, the most common of which are differential scanning calorimetry (DSC), density and X-ray diffraction. Orientation of the macromolecules along the axis of the fibre can be determined through the determination of sonic modulus, birefringence or X ray diffraction.

On the other hand, microstructure of man-made fibres and the variations induced by textile processing can be studied using different physico-chemical tests such as iodine sorption and differential solubility. The former concerns the capacity of the substrates to absorb foreign particles and depends on the compactness (crystallinity/orientation) of the fibre: iodine sorption decreases as compactness increases¹⁻².

Differential solubility concerns the swelling or solubility behaviour of a given substrate in a solvent non-solvent mixture. Because of the high sensitivity of the fine structure of synthetic man-made fibres to variations in their manufacturing or processing conditions, their response to a swelling/solvent mixture depends on their thermal, thermomechanical or hydrothermal history. The higher the intensity of the thermal treatment, the lower the differential solubility.

Relationship between microstructure measured by iodine sorption and/or differential solubility and the different processing variables have been studied for polyester³⁻⁶ and polyamide fibres^{7,8}. In this paper, both methods are applied to textured polylactide (PLA) substrates.

EXPERIMENTAL PART

Materials

Experiments were performed on false-twist textured samples obtained from a melt-extruded partially oriented PLA multifilament 167dtex/68 POY yarn supplied and textured by ANTEX (Anglès Textil, S.A.). The polymer used is polylactide for fibres grade with a proportion of D/L lactide 1.4/98.6 and a melting temperature of 165-170°C, supplied by NatureWorks LLC. Substrates were textured at different temperatures (135, 150 and 165°C) and draw ratios (1.30, 1.35 and 1.40). Eight different textured yarn samples were obtained and Table 1 shows sample references and the level of draw ratio (DR, X₁) and texturing temperature (T, X₂) arranged according to the experimental conditions.

Table 1. Temperature and draw ratio conditions of the texturing process.

Substrate	Draw ratio	Texturing temperature (°C)
A1	1.30	135
A2	1.30	150
A3	1.30	165
B1	1.35	135
B2	1.35	150
B3	1.35	165
C1	1.40	135
C2	1.40	150

The effect of texturing on the molecular mass, mechanical properties and thermal properties of the textured polylactide multifilaments compared with those of the original were studied in previous papers^{9,10}. After texturing the molecular mass decreased from $38.9 \pm 0.3 \text{ kg mol}^{-1}$ to $32.5 \pm 0.2 \text{ kg mol}^{-1}$ in accordance with its poor resistance to hydrolysis¹¹. Texturing^{9,10} increases breaking stress up to 245.6 MPa and decreases breaking strain to 30.2%.

Characterization methods

Differential scanning calorimetry (DSC)

Thermograms were obtained according to the following conditions:

- initial temperature 40°C,
- final temperature 200°C,
- heating rate $20^\circ\text{C} \cdot \text{min}^{-1}$
- Nitrogen purging gas ($2 \text{ kg} \cdot \text{cm}^{-2}$).

Crystallinity was measured by the sum of the exothermic crystallization enthalpy (negative) and the endothermic melting enthalpy (positive) that yields the original enthalpy of the sample (ΔH). The melting enthalpy of a 100% crystalline polylactide is $93.6 \text{ J} \cdot \text{g}^{-1}$. Consequently, the percentage of crystallinity is calculated through the relationship^{12,13}:

$$\text{Crystallinity (\%)} = \frac{\Delta H}{93.6} \cdot 100 \quad (1)$$

X-ray

Wide Angle X-ray Scattering experiments (WAXS) were performed using X-ray synchrotron radiation at the BM16-PX CRG Beam line at the European Synchrotron Radiation Facility (ESRF) in Grenoble (France). The experimental setup includes a WAXS measurements detector mounted on a 2Theta circle at 300 mm distance. $\text{CuK}\alpha$ radiation, with a wavelength of $\lambda = 0.154 \text{ nm}$, was employed. Nominal Energy was 12.6 keV.

From WAXS pattern (Figure 1), diffractograms of intensity versus diffraction angle, 2θ , were determined by the FIT2D program¹⁴. Then, crystallinity was calculated from the relationship¹⁵:

$$\text{Crystallinity (\%)} = \frac{I_t - I_a}{I_t} \cdot 100 \quad (2)$$

where: I_t is the total area of the diffractogram, and I_a is the area of the amorphous halo

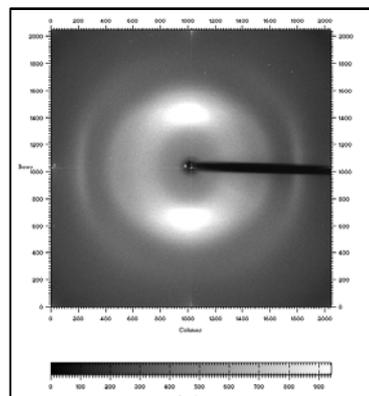


Fig. 1. WAXS pattern of substrate A1.

Sonic modulus

When polymer molecules in a high polymer sample (fibre or film strip) are oriented by stretching, the sound velocity along the direction of stretch increases progressively with orientation¹⁶.

Sonic velocity was determined by using the Dynamic Tester PPM-SR (H. M. Morgan Co, Inc.), measuring the time elapsed through a continuous filament by applying a sonic pulse and its reception at a determined distance.

Sonic modulus, E , of a long, thin rodlike specimen (e.g., a fibre) is related to the sound velocity by the equation¹⁷.

$$E = k \cdot c^2 \quad (3)$$

being the sonic modulus measured in units of force per unit linear density and c the sound velocity.

If E is expressed in cN/dtex and c in km/s , the value of the constant k is 9.97.

The sonic modulus is related to the macromolecular orientation along the fibre axis. The higher the sonic modulus, the higher the orientation⁸.

Iodine sorption

The iodine sorption of polylactide fibres corresponds to the milligrams of iodine sorbed per gram of sample after being in contact at a given temperature for 20 minutes in iodine dissolution (127 g I_2 , 200 g KI, 100 ml acetic acid and 5 ml phenol 90% per litre). Determination is made by titration of the sample with sodium thiosulphate after dissolution with 65/35 phenol/2-isopropanol².

Differential solubility

The differential solubility of PLA is the percentage of fibre dissolved in a 55/45 phenol/2-isopropanol (w/w) mixture at different temperatures for 30 minutes¹.

Modelling

Variations of the different parameters according to texturing conditions and test temperature were modelled by multiple linear regressions. To better analyse the influence of each parameter, coded factors were used according to Equations 4, 5 and 6, for draw ratio (DR, X1), texturing temperature (T, X2) and test temperature (TT, X3 for odd and X3' for even count of experimental temperature levels), respectively.

$$\bar{y} = \mu + \sum_{i=1}^k \alpha_i X_i \quad (4)$$

$$\bar{y} = \mu + \sum_{i=1}^k \alpha_i X_i + \sum_{j=1}^{k-1} \beta_j X_j^2 \quad (5)$$

$$\bar{y} = \mu + \sum_{i=1}^k \alpha_i X_i + \sum_{j=1}^{k-1} \beta_j X_j^2 + \sum_{l=1}^{k-1} \gamma_l X_l X_{l+1} \quad (6)$$

where \bar{y} are the mean of the factors levels and α_i are the difference between two consecutive levels for each factor.

The influence of the factors on each response Y (crystallinity, sonic modulus, iodine sorption and differential solubility) was analyzed through regression analysis, fitting the empirical model shown in Equation 7.

$$Y = \beta_0 + \sum_{i=1}^k \beta_i X_i + \sum_{ij=1}^k \beta_{ij} X_{ij} + \varepsilon \quad i, j = 1, 2, 3 \text{ (4)}; i \geq j \quad (7)$$

Where β_0 , β_i , β_{ij} are the coefficients to be estimated with the regression analysis and ε is the disturbance term (noise). The significance of the model was assessed by the Analysis of Variance¹⁸ and the non-significant coefficients (95% confidence level) were removed from the model to obtain the "best" regression equation¹⁹

RESULTS AND DISCUSSION

Crystallinity and orientation

Results of crystallinity and orientation are shown in Table 2.

Table 2. Crystallinity obtained by DSC and X-ray and sonic modulus of the studied substrates.

Substrate	Crystallinity		Sonic modulus (cN/dtex)
	DSC (%)	X-Ray (%)	
A1	24.8	21.6	26.1
A2	26.1	23.5	32.7
A3	30.5	28.8	38.0
B1	26.2	23.5	30.4
B2	29.5	26.2	35.2
B3	33.4	32.2	37.4
C1	26.9	25.3	37.6
C2	31.1	27.7	38.9

As regards crystallinity, a very good linear correlation ($r=0.973$) between the two measuring methods (DSC and WAXS) was observed (Figure 2).

WAXS yields crystallinity values that are 5% lower than DSC although both techniques were useful to compare the evolution of crystallinity according to different treatment conditions. Crystallinity values are very low and correspond to a low crystalline fibre as shown in the patterns (Figure 1).

Figures 3 and 4 show the evolution of crystallinity measured by DSC and WAXS according to the texturing conditions.

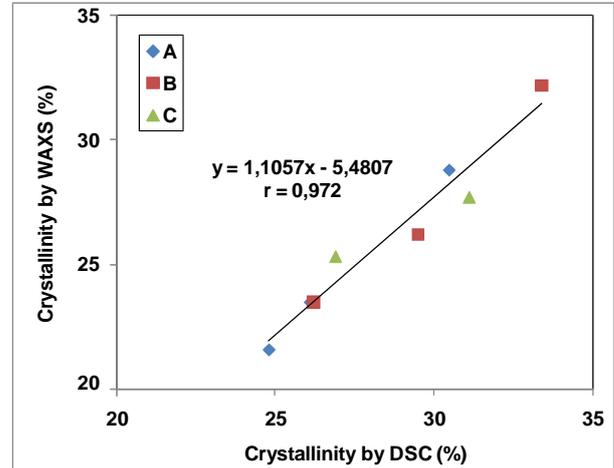


Fig. 2. Relation between crystallinity obtained by WAXS and by DSC.

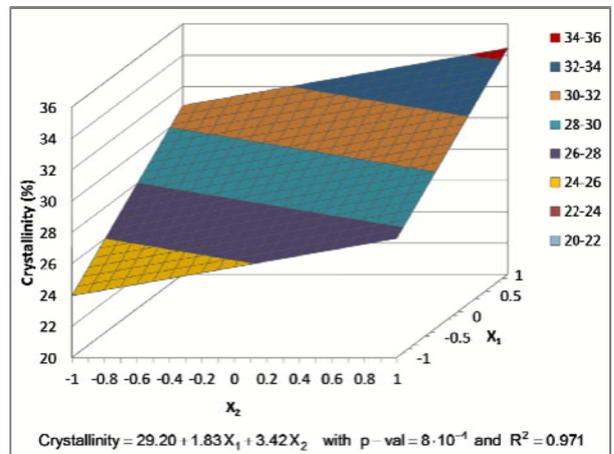


Fig. 3. Response surface and fitted regression model for crystallinity obtained by DSC as a function of draw ratio (X1) and texturing temperature (X2).

Draw ratio and texturing temperature significantly influences crystallinity and the positive coefficients show the direct relationship between texturing temperature and draw ratio with crystallinity. The texturing temperature has a greater effect than draw ratio on the increase in crystallinity. This is demonstrated by the value of coefficients affecting both variables. Crystallinity measured by DSC only shows linear terms but when measured by X-Ray a quadratic term affecting texturing temperature appears. This enables the model to better represent the influence of texturing temperature on crystallinity: an even increase in the texturing temperature produces higher

increases in the crystallinity at higher temperature levels.

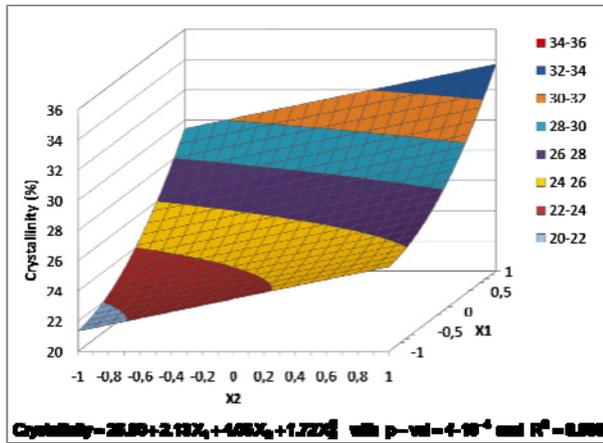


Figure 4. Response surface for crystallinity obtained by WAXS (X_1 : codified factor of draw ratio, X_2 : codified factor of texturing temperature)

Figure 5 shows the evolution of orientation according to texturing variables. Draw ratio and texturing

temperature cause the orientation to increase. The negative interaction between both parameters means that the effect of one factor on the orientation depends on the level of the other one.

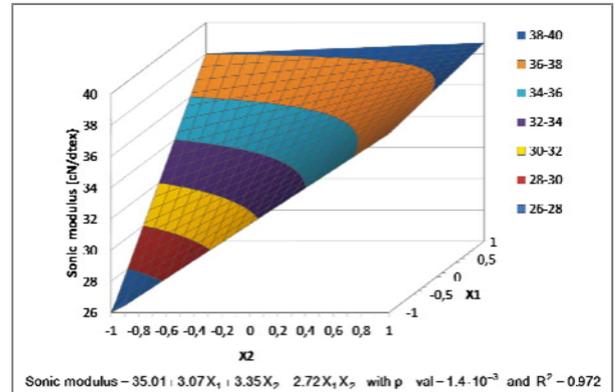


Figure 5. Response surface for sonic modulus (X_1 : codified factor of draw ratio, X_2 : codified factor of texturing temperature)

Physical-chemical tests

The Iodine sorption and the differential solubility of the samples at different test temperatures are shown in Table 3.

Table 3. Iodine sorption and differential solubility at different test temperatures of the studied substrates

	Iodine sorption (mg/g)						Differential solubility (%)				
	Test temperature (°C)						Test temperature (°C)				
	25	30	35	37.5	40	45	50	25	30	35	40
A1	18.8	82.4	154.9	170.1	147.3	110.8	107.2	12.5	22.5	36.0	51.4
A2	12.3	72.3	141.9	151.1	135.4	107.1	102.9	11.5	21.6	33.7	42.6
A3	4.5	55.0	133.8	148.3	134.8	102.2	92.0	9.5	17.3	29.4	36.4
B1	11.8	60.5	129.4	152.2	139.5	101.3	99.8	15.6	25.8	41.0	53.1
B2	8.7	46.7	114.3	129.1	130.1	92.0	91.2	14.7	21.9	35.1	50.6
B3	3.5	22.4	93.5	107.8	121.3	88.6	88.0	13.8	19.5	30.9	38.5
C1	8.1	49.6	114.0	131.9	110.3	92.6	85.4	20.2	27.4	44.3	52.8
C2	5.0	35.5	97.0	114.3	108.8	81.8	82.3	15.6	23.0	35.4	48.1

Iodine sorption

The iodine sorption curves of the samples as a function of the test temperature evolve in the same way as the sorption curves in earlier studies on polyester and polyamide²⁻⁷. The evolution of the iodine sorption with test temperature of samples A1, A2 and A3 is shown in Figure 6. Two parts of the curve may be distinguished. In the first part, iodine sorption is very sensitive to the variation of the testing temperature with the result that the unitary increase in temperature leads to a large sorption increase. In the second part, when a more or less defined maximum is exceeded, iodine sorption decreases as testing temperature increases.

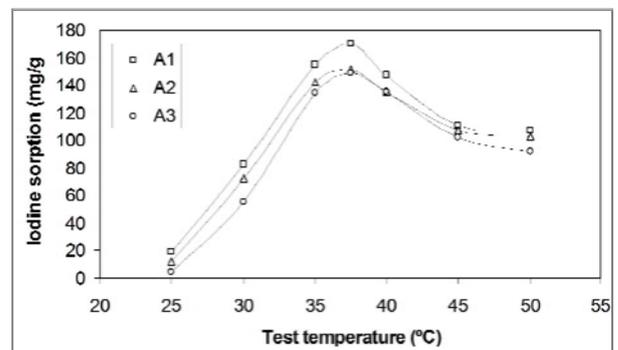


Figure 6. Evolution of iodine sorption with test temperature (samples A1, A2 and A3)

Note the ascending part of the curve and the maximum sorption. The two main factors that favour the increase in iodine sorption when the testing temperature is raised are a dilatation or fibre opening, facilitating the penetration in the substrate, and a higher penetration capacity of iodine because of the dissociation and/or speed of the molecules and/or iodine atoms.

On the other hand, an increase in temperature could cause a reduction in iodine sorption as a result of a decrease in iodine sorption in the equilibrium. When the maximum temperature is exceeded, thermal shaking could allow the deformation of molecular segments of the amorphous zones. In this case, when neighbouring segments are arranged in parallel, cohesion between them could be established, leading to an increase in the crystalline fraction and subsequently to a decrease in the amount of fixed iodine.

To study the influence of the test treatment on the iodine sorption values, only temperatures of the ascending part of the curves (25°C, 30°C and 35°C) were chosen.

The fitted regression model of iodine sorption (IS) versus draw ratio (DR, X1), texturing temperature (T, X2) and testing temperature (TT, X3) is the following:

$$IS = 46.07 - 14.79X_1 - 12.01X_2 + 54.79X_3 - 9.76X_1X_3 - 5.02X_2X_3 + 5.79X_1^2 + 12.67X_3^2 \quad \text{with } p\text{-val} = 5 \cdot 10^{-16} \text{ and } R^2 = 0.993 \quad (8)$$

Figure 7 shows the evolution of iodine sorption at the three testing temperatures (25, 30 and 35°C).

Iodine sorption decreases with texturing intensity. Since iodine sorption is related to the free volume of the fine structure of the fibres, and hence to their amorphous regions, this decrease may be attributed to an increase in the compactness (smaller accessibility) of the amorphous regions because of the ascent of draw ratio and/or texturing temperature.

The greater the testing temperature (X3), the higher the iodine sorption. Given the negative interaction between testing temperature and texturing variables (draw ratio and texturing temperature), the higher the testing

temperature, the greater the negative effect of draw ratio and texturing temperature on iodine sorption. The results show that the effect of draw ratio and texturing temperature on iodine sorption is more marked when the test is carried out at the highest temperature, facilitating the detection and analysis of variations in the microstructure of the polymer.

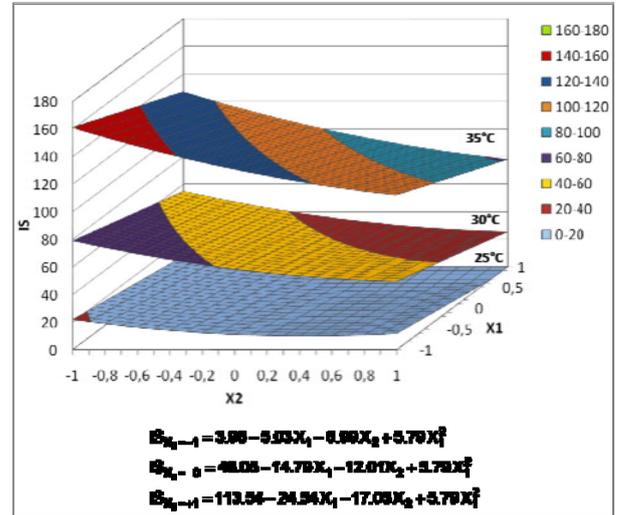


Figure 7. Iodine sorption response surface for the substrates studied at different test temperatures (X1: codified factor of draw ratio, X2: codified factor of texturing temperature)

When iodine sorption is related to crystallinity measured by X-ray and orientation measured by sonic modulus (Figure 8) a negative linear correlation is obtained with a correlation coefficient in both cases of about -0.77. This means that iodine sorption is inversely related to crystallinity and orientation. The more compacted (crystalline) and the more ordered (orientation) the microstructure, the lower the iodine sorption due to the decrease in the fibre free volume. The fact that iodine sorption is considerably influenced by the microstructure of the textured fibres is corroborated by the results²⁻⁷.

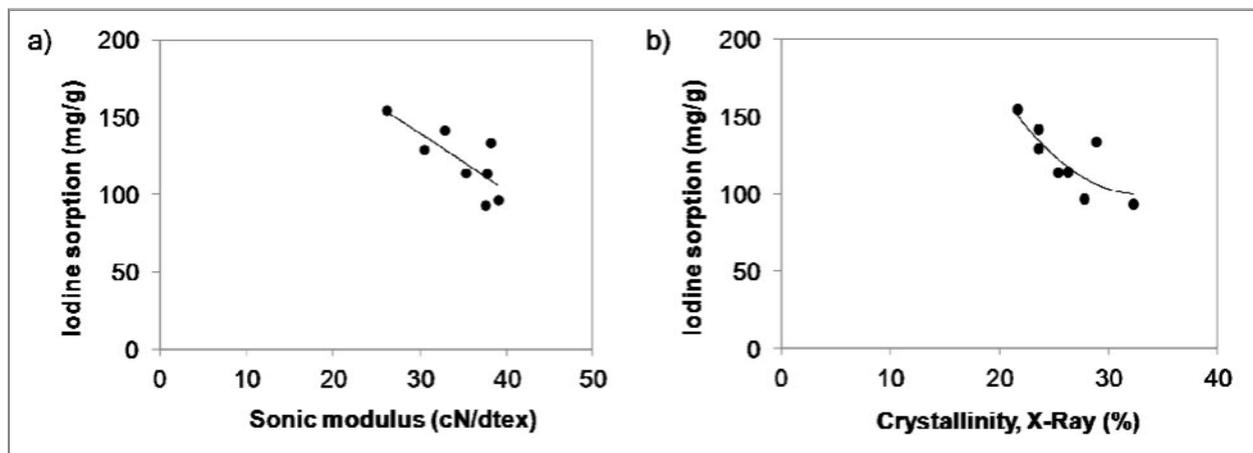


Figure 8. Relation between iodine sorption and a) crystallinity and b) sonic modulus

Differential solubility

Differential solubility increases with testing temperature. This is due to the higher penetration of the solvent/non solvent mixture in the more compact regions when testing temperature increases.

The fitted regression model of differential solubility (DS) versus draw ratio (DR, X1), texturing temperature (T, X2) and testing temperature (TT, X3) is:

$$DS = 28.66 + 2.22X_1 - 4.02X_2 + 5.44X_3 - 0.86X_2X_3 + 0.17X_3^2 \quad (9)$$

with p-val = $6 \cdot 10^{-23}$ and $R^2 = 0.985$

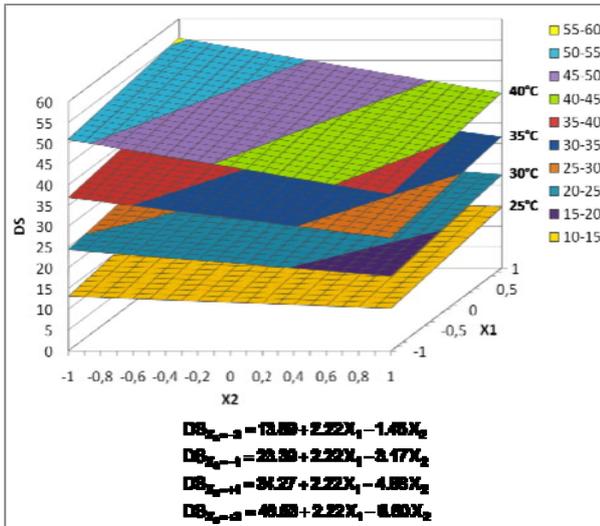


Figure 9. Differential solubility response surface for the substrates studied at different test temperatures (X₁: codified factor of draw ratio, X₂: codified factor of texturing temperature)

Figure 9 shows the positive effect of draw ratio and the negative effect of texturing temperature on the differential solubility at different testing temperatures.

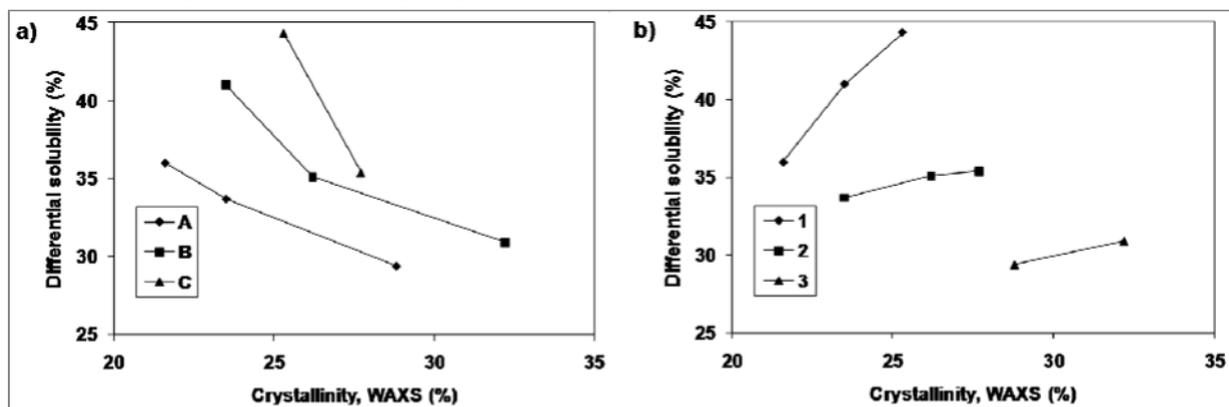


Figure 10. Relation between differential solubility and crystallinity by WAXS a) as a function of texturing temperature (A: 135°C, B: 150°C and C: 165°C) and b) as a function of draw ratio (1: DR 1.30, 2: DR 1.35 and 3: DR 1.40)

4. CONCLUSIONS

Global parameters of the microstructure, crystallinity and orientation (sonic modulus), increase when temperature and/or draw ratio of textured yarn are raised.

The higher the testing temperatures, the greater the negative effect of texturing temperature on the differential solubility. As expected, the higher the testing temperature (X₃), the greater the solubility, and the speed at which differential solubility increases.

The effect of draw ratio on the differential solubility is independent of the test conditions, whereas the effect of the texturing temperature is more marked for higher testing temperatures. This means that the detection of differences in the microstructure between substrates due to changes in texturing temperatures can be improved at higher testing temperatures.

There is no clear relationship between differential solubility and crystallinity and orientation and, hence with microstructure.

The opposite behaviour of differential solubility on varying draw ratio or texturing temperature is very useful when production defects occur, in order to ascertain whether the origin of the problem is due to an error in draw ratio or in texturing temperature. It is therefore necessary to determine crystallinity, CR, (by DSC, for example) and differential solubility (DS) of two substrates: one obtained in normal conditions (substrate A) and one obtained in unsettled conditions (substrate B). Then, the following increases can be calculated:

$$(10)$$

$$(11)$$

Thus, the following criteria, based on figure 10, can be applied:

If — , an error in draw ratio has occurred

If — , an error in texturing temperature has occurred.

- Two physic-chemical tests to characterize textured polylactide fibres were studied: iodine sorption and differential solubility:
- Iodine sorption decreases when draw ratio and texturing temperature increase and is related to the microstructure of the fibre: the higher the iodine

sorption, the lower the crystallinity and the orientation.

- Differential solubility is closely related to texturing variables: it increases with draw ratio and decreases with texturing temperature. The different behaviour of this parameter with both variables allows us to detect errors in production in the case of a controlled or uncontrolled variation of one of the two variables.
- Results of iodine sorption are influenced by testing temperature. The higher the testing temperature (prior the maximum sorption), the easier it is to assess the effect of both draw ratio and testing temperature on the microstructure. As regards differential solubility, testing temperature facilitates the detection of the effect of texturing temperature on the microstructure.

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