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MODELING OF THE INFLUENCE OF THE THERMOMECHANICAL MODIFICATION PARAMETERS ON THE STRUCTURAL CHANGES IN POLYESTER FIBERS

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Abstract: *In the present work is proposed an attempt for modeling of the complex influence of the heat mechanical treatment parameters on the structure developments in as-spun polyester fibers.*

Freshly molded poly(ethylene terephthalate) (PET) filaments with different preliminary orientation were subjected to simultaneously thermal and mechanical treatments. PET yarns were sequentially undergoing to uniaxially strain-stress with values of 40 MPa, 80 MPa, and 120 MPa at three different temperatures in a narrow temperature range from 85^0C to 95^0C.

Differential scanning calorimetry (DSC) has been used to study the structural rearrangements in the heat-mechanically processed PET fibers.

Response equations have been obtained showing the relationship between the parameters of the thermal deformation experiment and the desired degree of crystallinity of the studied PET fibers.

Key words: *poly (ethylene terephthalate), fibers, heat - mechanical treatment, tensile stress, strain-induced crystallization, modeling, differential scanning calorimetry.*

1. Introduction

It is well known that anisotropic systems such as crystals [1, 2] and oriented polymeric materials have specific physical properties. The final properties of the oriented polymeric materials are highly dependent on their super molecular structure [3÷6].

In the case of the polymeric fibers, the end structure is mainly due to the melt spinning conditions and the subsequent heat mechanical treatment too. During the moulding process into the fibers arise formations with enhanced

order, meso-phases, as well as zones containing crystalline phases with a different perfection which at appropriate conditions can be converted into crystal nucleus, and they are the so-called semi-crystalline nuclei. Another result of the filaments spinning is the formation of areas with frozen stresses in them. Often, with purpose to improve the fibers mechanical properties they are subjected to heat mechanical orientation modification. The simultaneous thermal and mechanical processing of oriented polymer systems is extremely complex and based on statistical and probabilistic processes. Poly (ethylene terephthalate) (PET) is a crystallizable thermoplastic polymer with relatively high glass transition temperature and low crystallization rate and therefore with large practical usages very often in the form of filaments and folios. The role of some basic parameters of heat-mechanical orientation modification parameters such as the tensile force, strain rate and temperature on the phase development of PET have been well studied and reported. There are publications regarding uniaxially oriented PET subjected to isothermal treatment without application of stress [7,8], isothermal treatment with application of stress and to non-isothermal treatments under stress [9,10]. Regardless of the great number of carried out investigations the optimal realization of high-temperature orientation modification of PET fibers remains not yet sufficiently studied process. Are not yet sufficiently studied relationships between the interrelated processes strain-induced crystallization and stress–strain behaviour of PET filaments. Moreover, there is not a clear answer if the final filament structure depends mainly on the applied stress or on the heat treatment itself. The effect of the preliminary molecular orientation and combined heat mechanical treatments in the temperature region immediately above the glass transition temperature from 85^0C to 95^0C on the structural reorganization of PET yarns is also not been investigated enough. Part of the above questions can be clarified using response surface methodology (RSM) [11]. The RSM allows us to develop a mathematical model that represents all variations in the expected value of the degree of crystallinity as the values of processing temperature and the strain stress are varied. The resulting model can be used for the purposes of optimization, determination of the main effects and interactions of the factors. Here we present part of the experimental results pertaining to the relationships between the basic heat-mechanical modification parameters and the structural development in freshly moulded poly (ethylene terephthalate) (PET) filaments with different preliminary orientation. Furthermore the present work is an attempt for modeling of the influence of the heat mechanical modification parameters on the structural changes in partially crystalline PET fibers.

2. Materials and methods

2.1. Materials

Poly (ethylene terephthalate) (PET) fibers named S1 and S2 were used as precursor samples. PET yarns were prepared by melt spinning on the industrial spinning machine Furnet (France) using variable take-up velocities and under production conditions as follows:

- melt output of 10.8 *g/min;*
- number of the fibers in yearn 32;
- yearn linear density $\rho_l = 48$ *dtex*.

The basic characteristics of the original filaments are shown in Table 1. All fibers characterizations given in Table 1 were carried out before the heat mechanical treatments.

Table 1. *Basic characteristics of the investigated filaments.*

Sample	V_L, *m/min*	d, μm	$\Delta n.10^3$	α, %
S1	4110	11,0	6,35	36.9
S2	2805	13,0	5,35	28.8

1. Sample; 2. V_L, m/min – take-up velocity; 3. d,μm – diameter of the single fiber; 4. Δn – birefringence; 5. α, % - degree of the sample crystallinity.

As it can be seen from the table the selected specimens are spun at different spinning speeds and thus with different preliminary orientation. So they are suitable for the achievement of the above-defined purpose of the present study.

2.2. Methods

2.2.1. Birefringence

The birefringence measurements of the studied PET fibers were performed using a polarizing interference microscope equipped with a CCD camera [12]. The main element of the experimental set-up is the system of a polarizer (P), analyzer (A) and birefringent fiber (F) in between and it is the so-called "P-F-A" system. The transmitting directions of the polarizers P and A are mutually perpendicular (crossed polarizers). The studied fiber can be rotated round the optical microscope axis.

2.2.2. Differential scanning calorimetry (DSC)

Structural development occurred in the studied fibers as a result of the simultaneous thermal and mechanical modifications were investigated using differential scanning calorimetry (DSC). The samples degree of crystallinity α was calculated using the data obtained by DSC. A Mettler-Toledo DSC-820 heat-flux module equipped with liquid nitrogen accessory was used for the calorimetric studies. The furnace was purged with nitrogen at a flow rate of 80 $ml.min^{-1}$. Temperature calibration was done using the onset melting temperatures of indium and zinc, and the energy calibration was based on the heat of fusion of indium. Fibers were cut in pieces of less than 1 *mm* and sealed in standard 40 μl aluminium pans. The value of the bulk heat of fusion of crystalline PET was taken from the literature.

2.2.3. Heat-mechanically modification

The thermal and mechanical treatments were carried out using an apparatus constructed and produced in our laboratory. The gear involves a horizontal stand with rails, a movable cylindrical oven located on the rails and a device for the sample deformation reading. The heat-mechanical treatment includes PET bundle annealing during ten minutes at the needed temperature followed by the sheaf loading with well defined tensile stress during 120 seconds (Table 2).

Table 2. *Temperatures and strain stresses of the heat mechanical fibers treatments.*

t, ^0C	σ, *MPa*		
85	40	80	120
90	40	80	120
95	40	80	120

The structural characterizations of the studied fibers are realized after the above described heat-mechanical treatment experiments, using DSC and birefringence measurements.

2.2.4. Mathematical Modeling

The mathematical models describe the functional relationship between independent variables (input factors) and the corresponding prediction of the responses. According to our preliminary study, the degree of crystallinity of samples (α_{S1} and α_{S2}) can be represented by means of incomplete third - order polynomials:

$$\alpha_S = b_0 + b_1 x_1 + b_2 x_2 + \\ + b_{12} x_1 x_2 + b_{11} x_1 x_1 + \\ + b_{22} x_2 x_2 + b_{112} x_1 x_1 x_2 \quad (1)$$

where:

α_S – degree of crystallinity responses of samples 1 and 2, % ;

x_1, x_2 – independent variables processing temperature, ^0C and the strain stress, *MPa,* respectively;

$b_0, b_1, b_2, b_{12}, b_{11}, b_{22}, b_{112}, b_{211}$ – regression coefficients.

The selection of the levels for the factors (Table 3) was carried out based on the results obtained in our preliminary studies [10, 12].

Table 3. *Independent variables and their levels expressed in coded and natural units*

Independent variables	Levels		
	$x_i = -1$	$x_i = 0$	$x_i = 1$
Processing temperature x_1, ^0C	85	90	95
Strain stress x_2, *MPa*	40	80	120

All experiments were performed using symmetrical block design for the two factors given in Table 3.

3. Results and Discussion

The experimental design and the obtained results are presented in Table 4.

Table 4. *Matrix of the experiments and the results*

Encoded values of factors		Degree of crystallinity α, %	
x_1	x_2	Sample 1	Sample 2
1	1	42.5	42.8
-1	1	38.8	42.0
1	-1	37.0	39.8
-1	-1	37.1	36.0
1	0	41.0	39.2
0	1	41.7	42.0
-1	0	40.4	40.4
0	-1	34.7	37.4
0	0	40.0	38.4

Seven additional experiments in the centre of the plan were conducted in order to evaluate the significance of the linear and interaction coefficients. The calculations indicate that all of them are statistically significant (Table 5). The coefficient b_{112} of sample 2 has low value of 0,05 and therefore should be excluded.

The experimental results were fitted to the incomplete third-order model (1) and the following regression coefficients were computed (Table 5).

The adequacy of the model was verified by evaluating the coefficient of multiple correlations R [11]. The results at significance level $\alpha = 0.05$ are shown in Table 5.

Table 5. *Values of the regression coefficients*

SAmple №	Values of the regression coefficients		$(\nu S_\varepsilon)^{0.5}t$, $(gS_\varepsilon)^{0.5}t$,	R^2	R	F	F(α, ν1, ν2)
1	b_0=40.022222	b_{11}=0.667	0.13 0.15	1	1	∞	237
	b_1=0.300	b_{22}=-1.833				F>F (α,ν1,ν2)	
	b_2 =3.500	b_{112}=-1.700					
	b_{12}=0.950	b_{122}=0.6000					
2	b_0=38.8222	b_{11}=0.7667	0.11 0.14	0.99	0.99	34	19
	b_1=-0.600	b_{22}=0.6668				F>F (α,ν1,ν2)	
	b_2 =2.030	b_{112}=0.050					
	b_{12}=-0.75	b_{122}=1.7500					

All predicted values of the mathematical models can be visualized using 3-D surface chart and contour plots (Figs. 1, 2). Maximum (over 42%) and minimal (less than 37%) values of degree of crystallinity are marked on the wire frame contour charts in Fig. 2. The main effect plots (Fig.3) identify strain stress as the first factor in importance in the degree of crystallinity responses for both specimens. The values of the main effects of the strain stress for the samples 1 and 2 are ME_{S1} = 7 points and ME_{S2} = 4 points respectively.

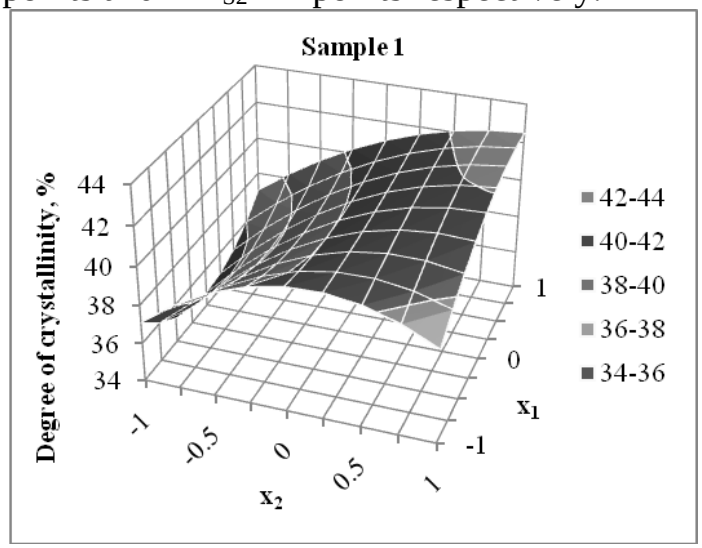

Fig. 1. 3-D response surface chart of the degree of crystallinity as a function of the processing temperature x_1 and strain stress x_2.

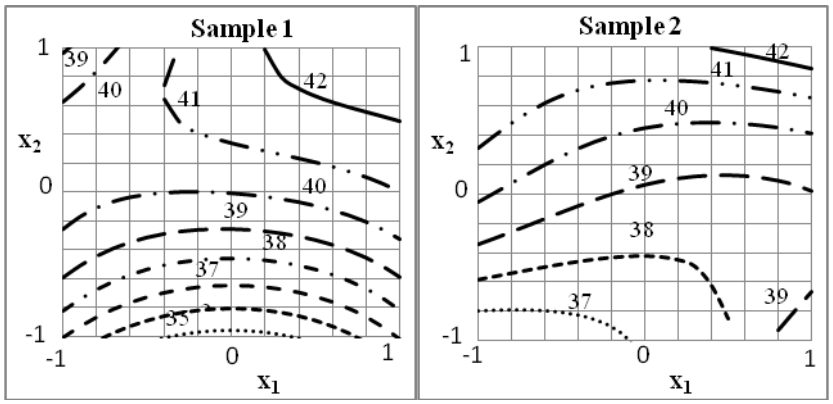

Fig. 2. Contour plots of the degree of crystallinity as a function of the processing temperature and strain stress.

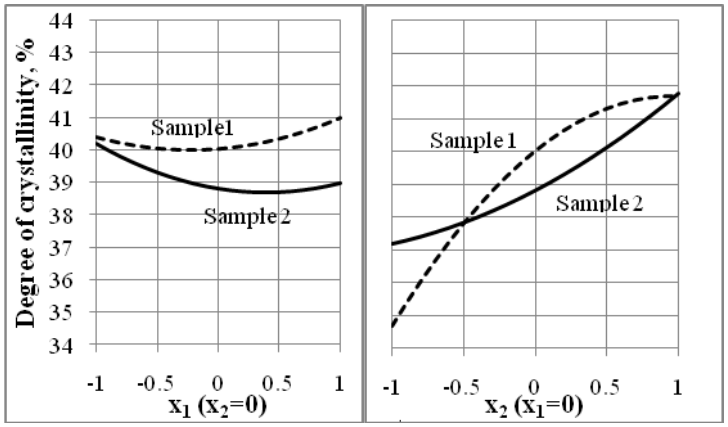

Fig. 3 Plots of the main effects

The processing temperature and strain stress have a positive effect on the responses, i.e. the degree of crystallinity increases when the values of factors increase. An exception was also observed - the processing temperature negatively influences on the degree of crystallinity in sample 2 (Fig.3).

The effect of the processing temperature – strain stress interaction on the degree of crystallinity is also significant. Its influence is positive for specimen 1, whereas it is negative for the specimen 2.

The final degree of crystallinity depends on the initial structure as well as the following heat-mechanical treatment. The contour chart of Specimen 2 shows a quick process of structural development. The initial degree of crystallinity of 28.8% rises to 39% at strain stress of
80 *MPa*. The degree of crystallinity of sample 1 increases with 3% under the same treatment conditions.

4. Conclusions

The combined influence of the tensile stress and temperature of uniaxially orientation drawing on the degree of crystallinity of partially crystalline PET fibers was investigated.

Established relationships allow determination of the dependencies between the parameter values of the heat mechanical processing and the desired degree of crystallinity of the studied PET fibers.

The obtained mathematical models for the degree of crystallinity of PET filaments are valid only for the tested samples and for the specific experimental conditions.

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