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“Sigmoidal” temperature dependence of mechanically induced birefringence in polymers

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The structural was obtained by birefringence and thermal shrinkage stress relaxation measurements. The PET filaments possess birefringence as a consequence of their formation conditions. The changes in the birefringence were measured after thermal treatment under isothermal conditions, over a large temperature range, using a polarization microscope and a CCD camera. The data were analyzed using Mocha – 1.2 (Jandel-Scientific) software. The glass transition temperature of the samples was defined by thermal shrinkage stress relaxation measurements using the specialized device “Relax-P04”. The results obtained by the two methods are in good agreement.

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1. Introduction

Polyethylene terephthalate (PET) is a widely used material in different fields, such as industry, medicine and high technologies. Many experimental investigations have been conducted with oriented PET materials, using various methods such as transmission electron microscopy (TEM), small- and wide-angle X-ray scattering (SAXS, WAXS), conventional and modulated differential scanning calorimetry (DSC, MDSC), etc. [1-4]. Nevertheless, the effect of thermal treatment of oriented PET samples on their structural development remains not completely clarified. The subject of this paper is the birefringence Δn and glass transition temperature T_g of PET fibers. The studied samples possess birefringence as a consequence of the fiber formation conditions. The birefringence $\Delta n = n_\perp - n_{II}$ after thermal annealing of the fibers in the temperature range from 25 to 81^0C is changed. Here, $n_\perp$ and n_{II} are the refraction indices for linear polarized light vibrating perpendicular and parallel to the fiber axis, respectively.

2. Experimental

2. 1. Materials

PET amorphous as-spun yarns were used as precursor samples. The filaments were produced on a industrial spinning machine under technological conditions. The initial basic characteristics were as follows:
spinning speed 1150 *m/min*;
number of spinnerets in yarn 32;
single filament diameter 44 μm.
density $\rho = 1338\ kg/m^3$;
degree of crystallinity $\alpha = 1.7$ % ;
birefringence $\Delta n = 0.008$;
coefficient of amorphous orientation $f_a = 0.0029$.

As can be seen the specimens were in fact amorphous and orientated.

2.2. Methods

The density ρ of the samples was determined using a density gradient column filled with a tetrachloromethane and n-heptane mixture. The degree of crystallinity α was calculated from this density value. The birefringence Δn of untreated PET filaments was measured using an Amplival pol D (Karl-Zeiss Jena) polarizing microscope, equipped with Bereck compensators. The coefficient of amorphous orientation f_a was estimated using Stein’s equation [5]. Thermal shrinkage stress measurements were carried out using an apparatus constructed in our laboratory [6]. Amorphous as-spun filaments in the annealing device were rapidly raised from room temperature to a temperature of interest, held there for 30 *min* and then cooled to room temperature (below the sample T_g).

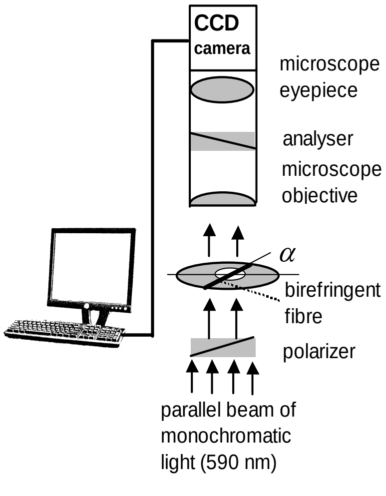

Fig. 1. Scheme of the experimental set-up.

The birefringence measurements were performed using a polarizing interference microscope and a CCD camera (Fig.1). The main element of the experimental set-up is the system of a polarizer P, analyzer A and birefringent fiber F in between the so-called “P-F-A” system [7]. The transmitting directions of the polarizers P and A are mutually perpendicular (crossed polarizers). The fiber can be rotated round the optical microscope axis. The angle α is that between the electric vector $\vec{E}$ of the linearly polarized monochromatic $(\lambda = 590nm)$ light falling on the sample and the fiber axis.

3. Results and discussion

The theory predicts that the incident light excites two linearly polarized normal waves in the fiber. The transmitted light through the P- F-A system is a result of the interference of the mutually orthogonal normal waves.

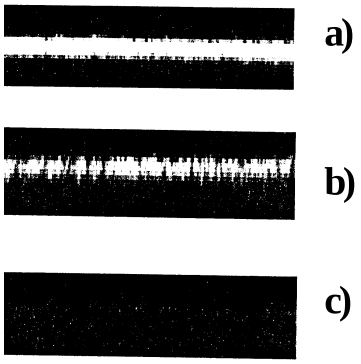

Fig. 2. Interference pictures of PET fibers annealed at temperatures as follows: a) $t_{ann} = 66^{0}C$*; b)* $t_{ann} = 72^{0}C$*; c)* $t_{ann} = 81^{0}C$*.*

The interference picture (Fig. 2) is recorded by a CCD camera and computer. This picture is converted in a digital mode by Mocha-1.2 (Jandel-Scientific) software. If $\alpha = \pi/4$, the magnitude of

$$arcsin\sqrt{\frac{I^{\perp}_{\pi/4}}{I_0}} = c\frac{\pi d}{\lambda}\Delta n = C\Delta n \qquad (1)$$

is a measure of the birefringence, where $I^{\perp}_{\pi/4}$ is the intensity of the transmitted light through the P-F-A system, and I_0 is the intensity of the incident light on the fiber. The symbol “ $\perp$ ” shows that *P* and *A* are crossed. *C* and *c* are constants.

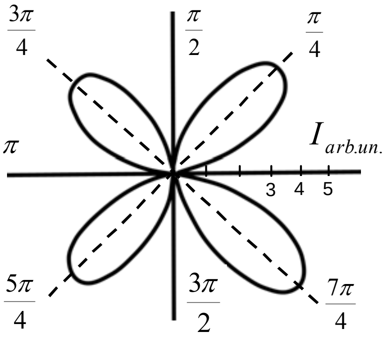

Fig. 3. Polar diagram $I^{\perp} = I^{\perp}[\alpha]$

The transmitted light intensity was measured as a function of the sample rotation angle and the obtained result is shown in Fig.3. The symmetry of the polar diagram was taken to indicate the possibility of measuring the fiber birefringence.

The value of $arcsin\sqrt{I^{\perp}_{\pi/4}/I_0}$ for different temperatures of annealing t_{ann} was measured. The studied fibers were heat-treated isothermally for 30 *min* at various temperatures as follows: $25^{0}C$, $35^{0}C$, $45^{0}C$, $66^{0}C$, $69^{0}C$, $72^{0}C$, $75^{0}C$, $78^{0}C$, $81^{0}C$. Our experiments showed that in the temperature range 25 to $66^{0}C$, Δn_{rt} is not changed within the experimental error, whereas from $69^{0}C$ to $81^{0}C$ $\Delta n(t_{ann})$ is significantly reduced (Fig.4). Here, Δn_{rt} is the birefringence in the temperature range 25 to $66^{0}C$, and $\Delta n(t_{ann})$ is that in the temperature range 69 to $81^{0}C$. The calculations show that the ratio $\Delta n(t_{ann})/\Delta n_{rt}$ as a function of the annealing temperature t_{ann} could by written in “sigmoidal” form:

$$\frac{\Delta n(t_{ann})}{\Delta n_{rt}} = \frac{1}{1+exp\left(-\frac{t_{ann}-T}{2.4}\right)} \qquad (2)$$

where T = $73.8^{0}C$. The calculations were carried out using “Table curve” software. The obtained coefficient of correlation R was 0.98.

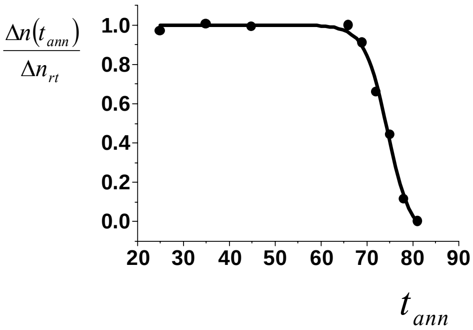

Fig. 4. ”Sigmoidal” dependence.

$$\frac{\Delta n(t_{ann})}{\Delta n_{rt}} = f(t_{ann}) \qquad (3)$$

A relationship between the annealing temperature T and the glass transition temperature T_g has been proposed. This assumption was tested by the determination of T_g by a thermal shrinkage stress relaxation measurement.

It is well known that the thermal behaviour of oriented amorphous polymeric materials strongly depends on their orientation. In the case of oriented polymeric materials, the development of a suitable method for the determination of the glass transition temperature (T_g) is very important [3]. Very often, DSC is used to study polymeric samples. However, DSC traces cannot show the relationship between the specimen's thermal behaviour and its orientation. The reason is the sample preparation for DSC analysis as a powder. On the other hand, the well-known methods for testing oriented polymeric materials, such as shrinkage in boiling water, stress-elongation diagrams, etc., do not give precise data about the T_g of the studied samples.

Therefore, the thermal shrinkage stress diagrams were applied for such a purpose. The shrinkage forces arise in the polymer filaments in the temperature region in which the glass transition occurs. The shrinkage force curve obtained at temperatures below T_g shows an increase of the shrinkage force up to maximal equilibrium value. The shrinkage force diagram obtained at temperatures above T_g, for the examined specimen shows a rapid increase in the contractile strength to a maximum value and after that a decay to the equilibrium one. Such a diagram allows one to determine the so called frozen stress in the fibers. A simple graphical method for the determination of T_g using an extrapolation to zero of the frozen stresses obtained by experiments performed at different temperatures has been suggested [8].

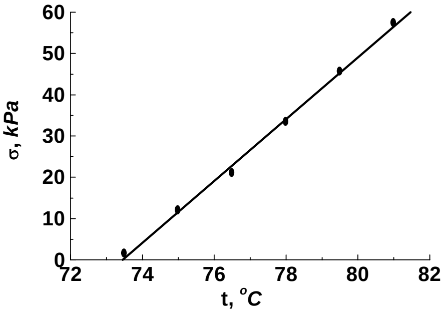

Fig. 5. Frozen stresses values as a function of temperature

It is necessary to mention that the above proposed method [8] was developed and applied to partially crystalline polymer samples. Using an apparatus constructed in our laboratory [6] the values of the frozen stresses in the PET fibers were measured at temperatures of: 73.5, 75, 76.5, 78, 79.5 and 81^0C. The resulting data are presented in Fig.5.

Following the above suggested graphical method, the glass transition temperature of the PET filaments, T_g = 73.4 ^oC, was determined. The results obtained by birefringence and frozen stresses measurements are in good agreement with the data presented in [6].

4. Conclusions

The birefringence Δn of PET fibers, after isothermal annealing for 30 *min* at temperatures from 25 to 81^0C has been measured.

A method for the determination of the glass transition temperature of partially crystalline polymer filaments was successfully applied to the amorphous PET fibers.

The calculations show that the dependence $\Delta n = f(t_{ann})$ possesses a “sigmoidal” form. The glass transition temperature determined by the shrinkage forces method is in a good agreement with the T parameter value of the sigmoidal dependence.

The obtained results afford a new opportunity for the relatively fast and precise determination of the glass transition temperature of oriented polymer materials.

It is interesting to study the influence of the annealing time of the fibres on their structural development, and such experiments are envisaged.

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