

SHRINKAGE RATE OF POLYESTER FOR MEMBRANE APPLICATIONS

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ABSTRACT

The isothermal shrinkage kinetic of PET monofilament and monofilament extracted from gray and heat treated woven fabric for membrane net is studied in the temperature range from 70°C to 200°C. The shrinkage rate curve is obtained by the using of spline smoothing with optimized smoothing parameter. The maximum shrinkage rates evaluated from these curves is used for estimation of shrinkage rate thermal sensitivity. The changes of monofilaments orientation is characterized by the measurement of acoustical waves spread.

Key Words: Shrinkage rate, industrial polyester monofilaments, membrane reinforcements, monofilament fabrics

1. INTRODUCTION

The ion exchange membranes are often reinforced with woven fabric or a net from polymeric filaments. The properties of these supporting nets have major influence on the mechanical strength, dimensional stability, and durability of membrane. The plain woven fabrics from synthetic monofilaments (usually polyesters) are often used for creation of nets. By proper drawing and heat setting the monofilaments structure and macroscopic shrinkage can be changed in wide range. Their breaking strength can vary in broad bounds depending upon manufacturing conditions as well.

It is well known that the final properties of polyethylene terephthalate (PET) fibers are a result of a number of operations taking part during their production. It is very important to find the right conditions of these operations for formation of the optimal structure and properties according to the aim of utilization [1].

During spinning, due to the take up speed, the pre-orientation of amorphous PET occurs. The speed of the molten polymer emerging from the spinneret is much less than the speed at the godet wheel and this stretching in the semi-molten state induces molecular order and orientation in the fiber. Stretching during spinning leads to the huge increase of the surface area per unit volume, which tends to reduce the chance of crystallization.

On the other hand, stretching by spinning results in a molecular orientation and therefore accelerates crystallization. It depends on the spinning conditions which effect will be dominated [2].

Thermal setting of PET fibers is mainly used for dimensional stabilization, improving of some properties and removing of internal stresses evolved during spinning and drawing. The main mechanism of setting is establishment of new conformation balances of polymeric chains in fibers deformed during their formation. In semi crystalline polymers is this process accompanied by re-crystallization leading to the more perfect crystallites with higher melting temperatures. In the loose state the chains retraction and disorientation in amorphous regions occurs. These processes are macroscopically visible as shrinkage [2]. By proper drawing and heat setting the fibers structure and macroscopic shrinkage can be changed in wide range.

Main aim of this work is investigation of the isothermal shrinkage kinetic of non stabilized and thermally stabilized PET monofilament for membranes applications in the temperature range from 70°C to 200°C. The maximum shrinkage rate is used for estimation of shrinkage rate thermal sensitivity SRTS.

2. SHRINKAGE OF POLYESTER FIBERS

Shrinkage is generally defined as an irreversible shortening of fiber length. Fibers are made to shrink by the effect of elevated temperature in the atmosphere, in water or in another medium. Shrinkage in fibers, yarns and fabrics can be determined by a great number of different methods in which the changes in length after contraction are measured under defined conditions [6].

Shrinkage or shrinkage stress is generally caused by an entropic retraction. When the internal energy of an oriented polymer is released by an increase in ambient temperature, polymer molecules tend to relax the orientation by retracting from an ordered, extended conformation to a disordered, random coil. This eventually produces a change of length or contraction force [5].

In polyester fibers two basic contraction mechanisms leading to macroscopic shrinkage can be distinguished. These are amorphous and crystalline contractions. The amorphous phase in drawn PET fibers that have not yet been thermally treated comprises more than 90% of the volume. Amorphous phase consists of a "frozen" physical network with chain entanglements forming knots in it. When heated above the glass transition temperature (for amorphous PET it is about 70°C in the dry condition and 50 °C in the wet) the mobility of the physical network is released. The result is an amorphous contraction in which the individual chains in the network take up a steric configuration which is energetically the most convenient for them. But simultaneously crystallization takes place. Oriented PET fibers have half-time of crystallization shorter than 0.01 s [4]. Complete shrinkage is therefore obtained by shock heating only.

In semicrystalline PET fibers "amorphous" shrinkage takes place only partially. The amount is determined by the orientation in the amorphous phase and the mean relative molecular mass of the polymer. Amorphous shrinkage can occur at low temperatures (less than 100°C) only. The corresponding shrinkage forces are in the region 10 to 20 mN tex⁻¹.

Excessive shrinkage of textiles containing synthetic fibers is eliminated by heat-setting. By this means the crystalline phase is "improved" by recrystallization, which is connected with conformation changes to the chain in amorphous regions under defined external geometrical proportions. When the fiber is allowed to shrink during heat-setting, there are no external constraints to structural reorganization and a significant part of the residual stresses present in the non heated drawn yarns relax. When the PET is held at constant length, a shrinkage force develops and only a part of the residual stresses is able to relax through limited structural reorganization. In oriented PET yarns shrinkage is a function of the product of amorphous volume fraction and amorphous orientation factor.

4. EXPERIMENTAL PART

PET monofilaments for technical applications with measured fineness 33.84 dtex, diameter 56 µm, tenacity 550 MPa, elongation at break 34%, glass transition temperature 81°C, crystallization temperature 214 °C and melting temperature 256 °C were used as starting material.

Because the monofilaments were produced for wide range of applications their stabilization was not so high. From these monofilaments the reinforcing planar woven net for membranes "Ulester" (see fig. 1) was produced under industrial conditions. The sett of warp was 3340 [1/m] and sett of weft was 3828 [1/m]. Measured basic characteristics were:

areal density 22 g m⁻², thickness 90 µm and porosity 67%.



Figure 1. The structure of gray Ulester fabrics

Fabric was then subjected to the heat setting in partially relaxed state on the stenter (210°C, 30 second). Due to state of setting the some changes of structure appeared as is demonstrated by changes of warp sett to the 3228 [1/m] , weft sett to the 3666 [1/m], areal density to the 25.94 g m⁻², thickness to the 95 μm and porosity to the 63%..

For shrinkage measurement the original monofilament (MONOFIL NFIX), weft monofilament extracted from fabric before heat setting (FABRIC NFIX) and weft monofilament extracted from fabric after heat setting (FABRIC FIX) were used.

Shrinkage experiments were realized on the TST2 shrinkage tester (Lenzing) under standard conditions. The pre-stress 0.7 g was selected. Measurements were realized at temperatures 70, 90, 100, 120, 140, 160, 180 and 200°C. All measurements were investigated in the time interval till 1 min which was sufficient for effective (maximum - equilibrium) shrinkage S_e reaching. For characterization of overall orientation the rate of acoustic waves spread c [km s⁻¹] measured on the Lawson Dynamic modulus Tester PPM-5R under pre strain 50MPa was used. All measurements were repeated 20 times and mean values were used for curves creation and parameters estimation.

4. RESULTS AND DISCUSSION

The mean values of acoustic waves rate c are given in the first row of the table 1.

Table 1 Characteristics of samples

Sample	MONOFIL NFIX	FABRIC NFIX	FABRIC FIX
c [km s ⁻¹]	3.82	3.54	2.36
E [GPa]	19.88	16.78	7.55
f [-]	0.87	0.84	0.65

The dynamic acoustical modulus E was calculated from acoustic waves rate c and PET density ρ by using of eqn (1)

$$E = \rho c^2 \quad (1)$$

The mean values of a dynamic acoustical modulus are given in the second row of table 1.

The acoustic waves rate can be used for evaluation of monofilaments mean orientation f by using of relation

$$f = \frac{c_u}{c} \quad (2)$$

The value $c_u = 1.4 \text{ km s}^{-1}$ was used as ideal acoustic waves rate of unoriented PET [1]. The mean values of a mean orientation are given in the third row of table 1.

The typical shrinkage kinetic curve (dependence of shrinkage on the time) of sample MONOFIL NFIX for temperature 100°C is shown in the fig. 2.

It is visible that due to weaving forces has FABRIC NFIX sample slightly lower stiffness (acoustical modulus) and is less oriented in comparison with sample MONOFIL NFIX. The great drop of stiffness (acoustical modulus) and orientation of sample FABRIC FIX is indication of stucture relaxation that takes place during heat treatment and is associated with the relaxation of internal stresses.

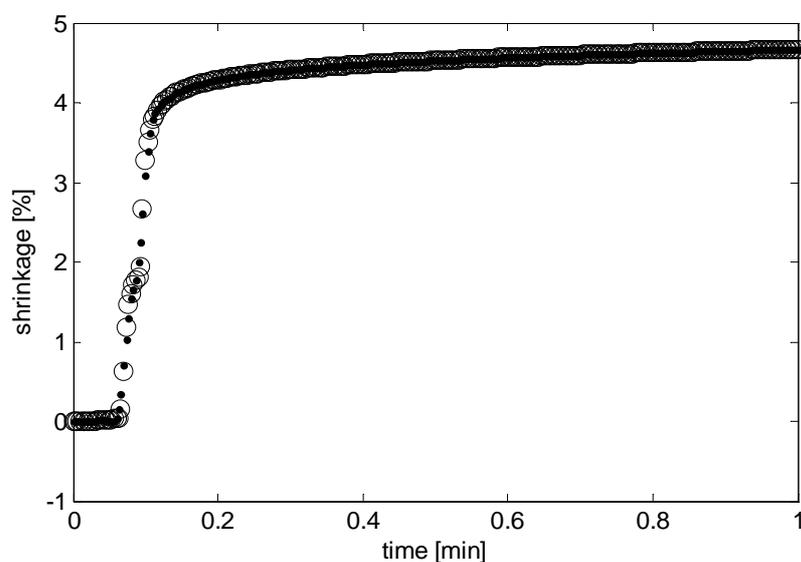


Figure 2. Time dependence of sample MONOFIL NFIX shrinkage at 100°C (empty circles are experimental points, dot are smoothed values)

The corresponding shrinkage rate curves obtained by the using of spline smoothing with optimized smoothing parameter [3] is shown in the Fig. 3.

The maximum shrinkage rate corresponding to the Fig. 3 was evaluated to be equal to the $R_s = 122.46 \text{ \% min}^{-1}$. By the same manner the values of R_s for all investigated temperatures were evaluated.

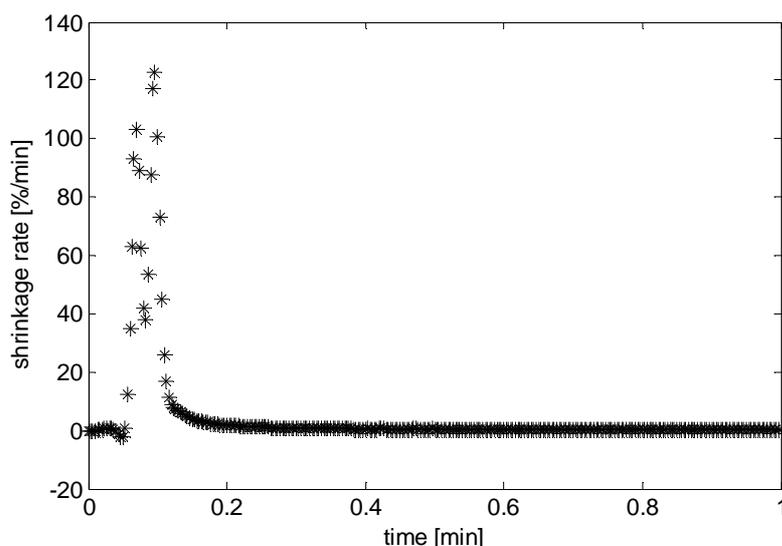


Figure 3. Time dependence of sample MONOFIL NFIX shrinkage rate at 100°C

The dependence of R_s on the temperature is shown in the Fig. 4.

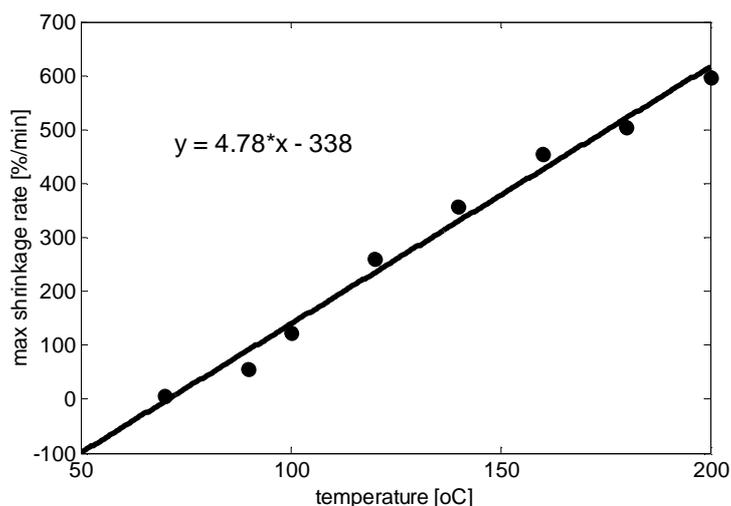


Figure 4. Temperature dependence of sample MONOFIL NFIX maximum shrinkage rate (dots) and straight line from LS regression

The approximation of this dependence by least squares (LS) straight line is very good (see Fig. 3 solid line). Coefficient of determination is $r^2 = 0.981$. Corresponding shrinkage rate thermal sensitivity coefficient SRT of MONOFIL NFIX for the range 70-200°C is then equal to the slope i.e. **SRT = 4.78 % min⁻¹ °C⁻¹**. By using of the same procedure for the sample FABRIC NFIX the shrinkage rate thermal sensitivity coefficient SRT for the range 70-200°C was **SRT = 4.84 % min⁻¹ °C⁻¹**. Corresponding coefficient of determination was $r^2 = 0.98$. It is then clear that the mechanical straining during weaving has no influence on the nature of shrinking. For the sample FABRIC NFIX the shrinkage rate thermal sensitivity coefficient SRT for the range 70-200°C was **SRT = 0.103 % min⁻¹ °C⁻¹**. Corresponding coefficient of determination was $r^2 = 0.94$. It is visible that thermal treatment suppressed thermal shrinkage extent and sensitivity (see Fig. 5).

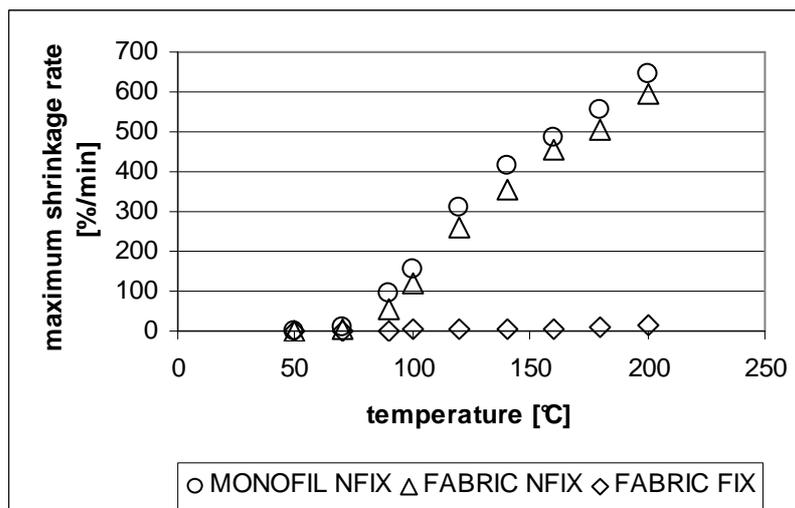


Figure 5. Shrinkage rate dependence on the shrinkage temperature for monofilament, fixed and non fixed fabric

4. CONCLUSION

The thermal shrinkage is very good tool for investigation of quality of fiber heat stabilization. It is simple to check the shrinking tendency by using of shrinkage rate thermal sensitivity coefficient SRTS. The SRTS is also the sensitive indicator of the degree of stabilization due to heat treatment. A qualitative explanation of differences between behavior of non stabilized and thermally stabilized monofilaments is to attribute the observed effects to the local relaxations of internal stresses 'unfrozen' by thermal treatment.

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