

# THE DYNAMIC-MECHANICAL STUDY OF DRAWN FIBRES OF ULTRA-HIGH MOLECULAR WEIGHT POLYETHYLENE

Jozef MURÍN, Viktor HRONSKÝ, Jozef TOPOEOVSKÝ

Department of Physics, Faculty of Electrical Engineering and Informatics, Technical University of Košice  
Park Komenského 2, 042 00 Košice, tel. 055/602 3188, E-mail: jozef.murin@tuke.sk

## SUMMARY

*This paper deals with the study of influence of drawing on structure and on molecular mobility in gel-spun fibres made of linear UHMW polyethylene by means of dynamic-mechanical method. The tensile loss modulus  $E''$  has been measured at a fixed frequency of 110 Hz as a function of temperature in the range from 115 K up to 420 K. Two relaxation processes denoted as  $\gamma$  (between 115 – 150 K) and  $\alpha$  (between 300 – 420 K) have been registered for all studied fibres. The high-temperature  $\alpha$  process has been analysed with the assumption of the distribution of relaxation times according to Davidson-Cole, with their temperature dependence according to Arrhenius relationship. Several parameters characterizing the position, maximum and shape of "loss-peaks" have been obtained by fitting experimental data according to theoretical expression for  $E''$ . The variations of these parameters in respect to draw ratio,  $\lambda = l / l_0$ , are consistent with three-stage deformation model proposed by Van Aerle and Braam as well as with the model of chain diffusion between crystalline and amorphous regions in PE, proposed by Schmidt-Rohr and Spiess.*

**Keywords:** dynamic-mechanical method, UHMW polyethylene fibres, molecular mobility, relaxation, activation energy.

## 1. INTRODUCTION

In the past 25 years several new polymer fibre processing technologies were elaborated with great improvements of their properties. Between them the "gel-spinning" method invented by Smith and Lemstra [1] plays important role in industrial production of high performance polymer fibres based mostly on linear polyethylene with ultra-high molecular weight (UHMW), with  $M_w > 10^3$  kg.mol<sup>-1</sup>. The key feature of this method is preparation of a gel fibre by spinning a dilute solution of UHMW PE into cold water, after drying, this gel fibre is drawn at higher temperatures (100 ÷ 150 °C). As a solvent may be used: paraffin, xylene, naphthalene or decalin and concentration of PE usually varies between 5 ÷ 15 % [2]. The maximum draw ratio for such conditions is normally between  $\approx 30 - 100$ . During cooling, the gel fibre forms small chain folded lamellae with a significant amount of solvent between them so that the gel fibre keeps the physical gel formation, namely, the swollen network in which crystallites form the junction. Upon drawing of the gel spun fibre, the lamellae are gradually transformed into smooth fibrils with extended-chains.

In the highly drawn fibre, there are long arrays of extended-chain crystals interrupted by disordered domains that originate from presence of topological defects, such as chain entanglements. Adjacent crystalline blocks are thought to be connected by taut tie molecules traversing the disordered domains. Therefore, this structure results in a high strength and high modulus fibre.

Investigation of the changes in the properties of the fibre at different stages of the gel-spinning and drawing is very important from theoretical as well as

practical viewpoint. In this presentation the changes caused by drawing process are investigated by means of dynamic-mechanical method, by which valuable information on structure and molecular mobility of the PE chains may be obtained.

## 2. MATERIALS AND EXPERIMENTAL TECHNIQUE

Fibres were prepared from linear UHMW-polyethylene (Hostalen GUR 412,  $M_w = 4 \times 10^3$  kg.mol<sup>-1</sup>) soluted in paraffin oil by the gel spinning method. Fibres with draw ratios  $\lambda = 6, 9, 12, 15$  were prepared at temperature of +130 °C and the fibre with maximum draw ratio ( $\lambda = 25$ ) was prepared by a two stage drawing at temperatures  $T_{d1} = 130$  °C and  $T_{d2} = 147$  °C, respectively. Fibres were prepared and tested at the Research Institute for Man Made Fibres (Svit, Slovak Republic). Some characteristic quantities of the fibres, such as density  $\rho$ , crystallinity  $X_{C RTG}$ , Young modulus  $E$ , strength  $\sigma$  and birefringence  $\Delta n$ , are listed in Tab. 1.

Dynamic-mechanical measurements were performed using RHEOVIBRON model DDV-II-C (Toyo Measuring Instruments Co., LDT, Tokyo, Japan) at the frequency of 110 Hz in the temperature range from cca -160 °C up to +150 °C. Over a temperature range from -160 °C to room temperature, temperature of the sample was regulated by using of liquid nitrogen. An electric furnace was used over a temperature range from room temperature to +150 °C. In both temperature intervals the temperature sweep  $dT/d\tau$  was  $\approx 1$ K/min. Measurements were performed on a bundle of fibres with the length approx. of 5cm.

Applying sinusoidal tensile strain on one end of sample, and evaluating the phase angle  $\delta$  of the

Quantities	PE – sample ( draw ratio $\lambda$ )					
	1	6	9	12	15	25
Density $\rho$ [kg/m <sup>3</sup> ]	944	945	951	958	956	964
Crystallinity $X_{C\text{RTG}}$ [%]	63.6	65.7	68.1	69.8	67.4	70.1
Young modulus $E$ [GPa]	2.2	4.0	9.4	10.6	18.8	43.1
Strength $\sigma$ [GPa]	0.29	0.34	0.48	0.84	1.05	1.79
Birefringence $\Delta n \times 10^3$	8.5	15.9	21.3	26.1	33.8	41.5

**Tab. 1** Basic quantities characterizing UHMW PE fibres with different drawing ratios  $\lambda = 1$  (undrawn) and drawn fibres with  $\lambda = 6, 9, 12, 15$  and  $25$ .

strain against the stress generated at the other end of the sample with direct-reading method [3], the dynamic modulus  $E'$  and the loss modulus  $E''$  were calculated from the amplitude of stress and strain, and  $\delta$  value. Assuming that sinusoidal tensile strain:  $\varepsilon = \varepsilon_0 \sin \omega t$  with amplitude  $\varepsilon_0$  is applied to the sample (fibre) of length  $L$  and cross-area,  $A$ , and the generated phase shifted sinusoidal stress,  $\sigma = \sigma_0 \sin(\omega t + \delta)$  has an amplitude  $\sigma_0$ , the absolute value of the complex modulus,  $E^* = E' + iE''$ , of this sample will be given by equation

$$|E^*| = (\sigma_0 / \varepsilon_0)(L/A) \quad (1)$$

Real part of the complex modulus (storage modulus)  $E'$  and the imaginary part (loss modulus)  $E''$  are expressed in the following form,

$$E' = |E^*| \cdot \cos \delta \quad \text{and} \quad E'' = |E^*| \cdot \sin \delta. \quad (2)$$

From measured quantities  $\tan \delta$ , and those needed for calculation of  $|E^*|$ , values of loss modulus  $E''$  with respect to temperature have been analysed in this work for a set of UHMW fibres.

In our analysis of the dependence of  $E''$  on temperature we have assumed, that in the dispersion regions it could be described by equation [4]:

$$E'' = (\delta E'') \int_{-\infty}^{+\infty} H(\tau_r) \frac{\omega \tau_r}{1 + \omega^2 \tau_r^2} d(\ln \tau_r) \quad (3)$$

where  $\delta E''$  is so called intensity of dispersion (directly proportional to the amplitude of the loss-peak),  $H(\tau_r)$  is a function characterized distribution of relaxation times  $\tau_r$  for polymer chains. Distribution of relaxation times we characterize by means of the Davidson-Cole (D-C-F) function [5, 6]:

$$H(\tau_r) = \frac{\sin \pi \varepsilon}{\pi} \left[ \frac{\tau_r}{\tau - \tau_r} \right]^\varepsilon \quad \text{for } \tau_r < \tau, \quad (4)$$

$$\text{and } H(\tau_r) = 0 \quad \text{for } \tau_r > \tau$$

where  $\tau$  represents the limit value of relaxation times  $\tau_r$  for different chains with different molecular environment. We assume, that this limit relaxation time  $\tau$ , may be expressed by the Arrhenius equation:

$$\tau = \tau_0 \exp \frac{E_a}{RT} \quad (5)$$

where  $\tau_0$  is the so-called pre-exponential factor

( $\tau = \tau_0$  at  $T \rightarrow \infty$ ),  $E_a$  is the activation energy of the corresponding molecular motion and  $R$  is the gas constant. The parameter  $\varepsilon$  ( $0 < \varepsilon \leq 1$ ) characterizes the width of this distribution.

A final expression for loss modulus  $E''$  may be then written in the form:

$$E'' = \frac{\delta E'' \cdot \sin(\varepsilon \cdot \arctan(\omega \tau))}{(1 + \omega^2 \tau^2)^{\varepsilon/2}} \quad (6)$$

where parameters  $\delta E''$ ,  $\tau_0$ ,  $E_a$  and  $\varepsilon$  may be obtained by fitting the experimental dependence of  $E''(T)$  for studied PE-fibres to the one given by eq. (6).

### 3. RESULTS AND DISCUSSION

As we can see from Tab. 1 the macroscopic quantities introduced here have tendency to grow with increasing of draw ratio  $\lambda$ .

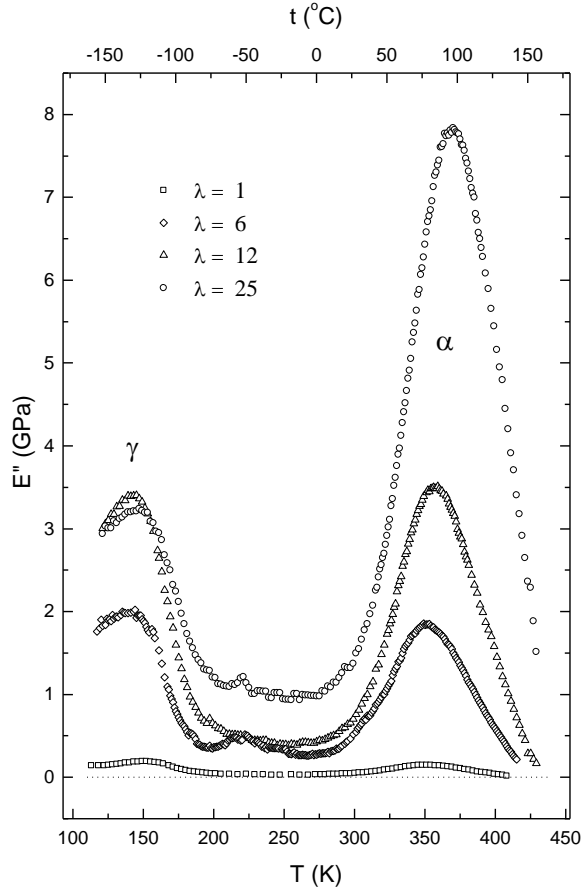
The first four quantities ( $\rho$ ,  $X_C$ ,  $E$  and  $\sigma$ ) depend on structural changes caused by deformation in a complex manner. The birefringence  $\Delta n$  is usually assumed as a measure of mean macromolecular orientation [7]. From the values of parameters listed in Tab. 1 we can conclude that the rising of strengthening and orientation take place as a result of uniaxial stretching of the fibres.

A more detailed insight into undergoing processes on macromolecular level may be obtained from dynamic-mechanical method (DMM).

We begin with the temperature dependence of the loss modulus  $E''$ , shown in Fig. 1. The two relaxation processes (denoted as  $\gamma$  and  $\alpha$ ) are clearly seen for all fibres. A small hint of another process (denoted as  $\beta$ ) was registered for some fibres at temperature between 200 – 250 K. According to a small amplitude of this  $\beta$  process we shall ignore it.

In this article we are dealing with analysis of high-temperature  $\alpha$  process. The  $\gamma$  process will be analysed together with NMR measurements in other paper.

The temperature dependencies of  $E''$  in the range from 300 K up to 420 K are shown in Fig. 2. The lines drawn through experimental points correspond to the function for  $E''$  given by expression (6) to which the experimental data have been fitted. The characteristic values:  $T_\alpha$  – the temperature of

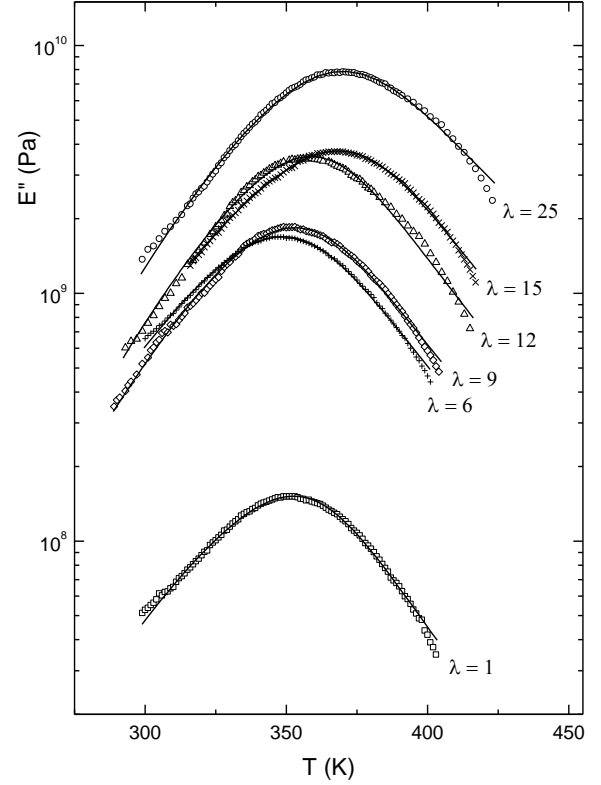


**Fig. 1** The temperature dependences of loss tensile modulus  $E''$  for some of UHMW PE fibres.

maximum value of  $E''$ ,  $\Delta T_{1/2}$  – the “half-width” of the  $\alpha$ - peak in temperature scale and the maximum  $E''_{\max}$ , have been determined directly from corresponding graph. These results are collected in Tab. 2. The final quantitative analysis of DMM, according to expression (6), are listed in Tab. 3.

From Fig. 2 and Tab. 2 it can be seen, that temperature  $T_{\alpha}$  has a tendency to shift to higher temperatures with increasing draw ratio  $\lambda$ , which is often observed for relaxation processes in polymers. The course of  $\Delta T_{1/2}$  suggests a tendency to grow the width of distribution of relaxation times,  $\tau$ , which is in correspondence with the decrease of parameter  $\varepsilon$  in Davidson-Cole distribution, represented by expression (4).

The quantities  $E''_{\max}$  and  $\delta E''$  increase with  $\lambda$ , which reflects the course of the empirical dependence of the “static” tensile modulus  $E$  in Tab. 1. The activation energy  $E_a$  and pre-exponential factor  $\tau_0$  have been introduced by means of Arrhenius formula (5) which assumes thermally activated motional process for macromolecular chains. The higher values of  $E_a$  for drawn fibres when compared to the one for undrawn fibre show that the energy needed for realization of one motional step increases with the draw ratio  $\lambda$ . As it is the pre-exponential factor  $\tau_0$  concerned, we can only



**Fig. 2** Experiment (isolated symbols) and D-C fit (solid line, param. in Tab.3) at region of  $\alpha$ -relaxation.

$\lambda$	$T_{\alpha}$ [K]	$\Delta T_{1/2}$ [K]	$E''_{\max}$ [GPa]
1	350	70	0.152
6	349	72	1.69
9	352	71	1.85
12	357	72	3.49
15	366	78	3.74
25	370	81	7.84

**Tab. 2** Main parameters of experimental  $\alpha$ - peaks:  $E''_{\max}$ ,  $T_{\alpha}$  – maximum of  $E''(T)$  and corresponding temperature,  $\Delta T_{1/2}$  – the “half-width” of spectrum.

$\lambda$	$\delta E''$ [GPa]	$E_a$ [kJ/mol]	$\varepsilon$	$\tau_0$ [ $10^{-12}$ s]
1	0.424	51.3	0.511	62.4
6	5.07	54.1	0.476	22.4
9	5.47	55.3	0.468	19.0
12	11.2	59.7	0.414	6.69
15	13.1	63.4	0.355	3.96
25	29.4	68.5	0.320	1.01

**Tab. 3** The values of parameters in Eq. (5) and (6) (see text) obtained from fitting to experim.  $E''(T)$ .

concluded that it decreases with increasing  $\lambda$ . There is not any universal expression for this quantity.

The quantities obtained from dynamic-mechanical analysis in the temperature range of  $\alpha$ -relaxation process do not provide any information on its origin. Several concepts for this have been elaborated [8]. A new concept for  $\alpha$ -relaxation in linear polyethylene (including also UHMW PE) was elaborated on the basis of 2D NMR spectroscopy [9, 10]. By these methods a longitudinal chain transport through crystallites was clearly indicated. The chain motions seems to be accomplished by a 180°-twist defect which is created at a crystallite surface and then moves through crystallite to the other side. By this mechanism macromolecular chains in noncrystalline (amorphous) zones may "diffuse" through crystallites. Hence, the both phases, amorphous and crystalline contribute to  $\alpha$ -relaxation.

As it was found out experimentally [11, 12] drawing of the gel-spun UHMW PE fibres causes a marked transformation of the original structure of undrawn fibre. Three-stage deformation process was presented in paper [11]:

1. Transformation of the lamellae into microfibrils during the initial stages of drawing.
2. Tautening of the inter- and intra- microfibrillar tie-molecules, introduced during the first stage.
3. Unfolding of microfibrillar crystallites and addition of the resulting unfolded segments to the chain-extended fractions (the original inter-microfibrillar tie-molecules).

The variations of the quantities obtained from dynamic-mechanical analysis in respect with the draw ratio  $\lambda$  are consistent with this model as well as with the model of motion of PE chains outlined above.

#### 4. CONCLUSION

Dynamic-mechanical measurements were performed on a set of drawn UHMW PE fibres in order to find some quantities characterizing the high-temperature  $\alpha$ -relaxation process. The tensile loss modulus  $E''$  vs. temperature was analysed with Davidson-Cole distribution function of relaxation times and with assumption that their temperature dependence is given by Arrhenius formula. The variations of the parameters  $E_a$ ,  $\varepsilon$ ,  $\delta E''$  (as well as  $T_a$ ,  $\Delta T_{1/2}$  and  $E''_{\max}$ ) with the drawing ratio  $\lambda$  reflect the changes in structure and molecular mobility caused by deformation.

#### REFERENCES

- [1] Smith P., Lemstra P.J.: J.Mater.Sci. 15 (1980), 505
- [2] Materials Science and Technology, Vol.12, Structure and Prop. of Polym., Vol. Ed. Edwin L.Thomas, VCH 1993, Chap.13, pp. 600-652

- [3] Rheovibron model DDV-II-instructions manual
- [4] Bartenev G.M., Frenkel S.Ja.: Fizika polimerov, Leningrad "Chimia" 1990, 205-214
- [5] Davidson D.W., Cole R.H.: J.Chem.Phys. 19 (1951), 1484
- [6] Beckmann P.A.: Phys.Reports, 171, (1988), 85
- [7] Ward I.M.(Ed.): Structure and Properties of Polymers, Appl.Sci.Ed., ISBN 0-85-334600-3 (1975), Chap.3., pp. 57-69
- [8] Alberola N., Cavaille J.Y., Perez J.: J.Polym. Sci., Part B: Polymer Phys. 28 (1990), 569 - see also Refs. here.
- [9] Schmidt-Rohr K., Spiess H.W.: Macromolecules 24 (1991), 5288
- [10] Schmidt-Rohr K., Spiess H.W.: Multidimensional Solid State NMR and Polymers, Acad. Press, ISBN 0-12-626630-1, (1994), pp. 171-180
- [11] Van Aerle N.A.J.M., Braam A.W.M.J.: J.Mater. Sci. 23 (1988), 4429
- [12] Lemstra P.J., Van Aerle N.A.J.M., Bastiaansen C.W.M.: Polymer Journal 19 (1987), 85

#### BIOGRAPHY

**Jozef Murin**, b. 1944. University study: Faculty of Natural Sciences, Comenius University, Bratislava. Ph.D. 1979, Comenius Univ., thesis: Macromolecular Orientation in Drawn Polypropylene Foils Studied by Nuclear Magnetic Resonance. Since 1980-present Associate Professor at Department of Physics, Faculty of Electrical Engineering and Informatics, Technical University of Košice. Research interests include application of solid state NMR in polymeric materials. Approx. 70 publications have been published. Pedagogical activities: lectures of Basic Physics, Solid state Physics and NMR Spectroscopy.

**Viktor Hronský**, b. 1951. University study: Faculty of Mathematics and Physics, Charles University, Praha. Ph.D. 1987, Šafarik Univ., Košice, thesis: Electron Paramagnetic Resonance Study of  $Mn^{2+}$ ,  $Cu^{2+}$  and  $VO^{2+}$  ions adsorption. Since 1975-present Assistant Professor at Department of Physics, Faculty of Electrical Engineering and Informatics, Technical University of Košice. Research interests include application of EPR and dielectric spectroscopy in solids. Approx. 30 publications have been published. Pedagogical activities: lectures of Basic Physics and Solid state Physics.

**Jozef Topol'ovský**, b. 1963. University study: Faculty of Natural Sciences, Šafarik University, Košice. RNDr. 1989. Since 1987 Assistant Professor at Department of Physics, Faculty of Electrical Engineering and Informatics, Technical University of Košice. Research interests: solid state NMR in polymeric materials.