Polymer Vol. 36 No. 18, pp. 3589-3592, 1995

0032-3861/95/$10.00+0.00

# Influence of applied stress and temperature on the deformation behaviour of high-strength poly(vinyl alcohol) fibres

**L. E. Govaert*** **and T. Peijs**
*Centre for Polymers and Composites, Eindhoven University of Technology, PO Box 513, 5600 MB Eindhoven, The Netherlands*
*(Received 15 August 1994; revised 7 September 1994)*

The deformation behaviour of poly(vinyl alcohol) (PVA) fibres is studied using dynamic mechanical analysis, stress relaxation and uniaxial tensile experiments. Results indicate that the time and temperature dependences of these fibres decrease drastically under the influence of a statically applied stress or strain. These results are discussed in an attempt to relate the deformation behaviour of high-strength PVA fibres to events occurring on a molecular scale.

**(Keywords: poly(vinyl alcohol); fibres; dynamic mechanical properties)**

## *Introduction*

The development of the so-called solution (gel) spinning process[1,2] by DSM Research at the end of the 1970s meant a major breakthrough in the development of high-performance fibres. This spinning and drawing process results in high-performance polyethylene (HP-PE) fibres with moduli of approximately 100 GPa and tenacities of about 3 GPa. Currently, commercial grades of HP-PE fibres are produced by DSM High Performance Fibres BV (Dyneema$^{TM}$) and its licensee Allied-Signal (Spectra$^{TM}$). In all these systems, the main objective was to achieve high stiffness via molecular orientation and chain extension. Typical one-dimensional structures result, with strong covalent bonds in the chain direction and weak intermolecular interactions between the chains, i.e. van der Waals in the case of polyethylene. However, given their one-dimensional character, these polyethylene fibres show relatively poor high temperature and creep resistance.

In the past decade, several attempts have been made to apply the principles of solution (gel) spinning to other, more polar, flexible polymers, such as polyamides, polyacrylonitrile and poly(vinyl alcohol). All these polymers combine a high theoretical modulus in the chain direction[3] with a higher secondary bond strength between the chains, which makes them attractive candidates for achieving high-performance fibres.

Unfortunately, the maximum attainable modulus and strength of these 'polar' polymers proved to be rather low[4-7]. However, in the case of poly(vinyl alcohol) (PVA) some interesting results have been obtained[8-13], e.g. tenacities up to 2.3 GPa and moduli of about 70 GPa. Still, these values are significantly lower than those obtained for polyethylene since the formation of hydrogen bonds within the oriented crystalline regions restricts the drawability during PVA fibre processing and, consequently, the maximum attainable properties[13]. Although the maximum attainable values for the uniaxial tensile modulus and tensile strength are not as impressive as in the case of HP-PE, specific intermolecular interactions (i.e. hydrogen bonds) in fibres produced from polar polymers might offer some advantages with respect to transverse, compressive and long-term properties. PVA fibres have, for example, a higher melting temperature (250°C), better creep performance and better adhesion to (polar) matrices[14]. One of the main disadvantages of PVA fibres is that the mechanical deformation behaviour is very sensitive to moisture[9].

In this work, the general deformation behaviour of PVA fibres is studied using static and dynamic mechanical analysis, focusing on the effect of statically applied stress (or strain) and temperature.

## *Experimental*

*Materials.* The fibres used in this study were commercial grades of solution-spun, highly drawn PVA fibres (Kuralon 5900) of 2000 dtex (1800 den), supplied by Kuraray Corp. (Japan). Fibre samples were preconditioned under standard laboratory conditions, i.e. 24 h at 50% r.h. and 21°C.

*Testing.* Tensile and stress relaxation experiments were performed on multifilament yarn of 250 mm length, provided with adhesively bonded cardboard tabs. For dynamic mechanical thermal analysis (d.m.t.a.), special samples with a reduced cross-sectional area (about 0.01 mm$^2$) and length (about 20 mm) were prepared. In the case of d.m.t.a. experiments no cardboard tabs were used.

D.m.t.a. was performed on a DMTA MK2 from Polymer Laboratories. Temperature scans were performed in uniaxial extension at a frequency of 1 Hz in the temperature range of $-50$ to 150°C. The heating rate was 1°C min$^{-1}$. To investigate the influence of stress on the thermorheological behaviour of the fibres, dynamic experiments were performed with statically applied loads in the range of 50 to 400 MPa.

---

* To whom correspondence should be addressed

Stress relaxation experiments were performed on a Frank 81565 tensile tester equipped with a thermostatically controlled oven and an extensometer. Experiments, with loading times not exceeding 3 h, were performed at strains ranging from 0.5 to 3% and temperatures of 30 to 70°C.

Tensile experiments were performed on a Zwick Rel hydraulic tensile tester, equipped with a thermostatically controlled oven. Experiments were performed at temperatures of −50, 20 and 70°C and strain rates of $10^{-3}$ and $10\,s^{-1}$.

### *Results*

*Dynamic mechanical analysis.* In order to investigate the influence of a statically applied stress on the dynamic behaviour of PVA fibres, samples were tested with static stress levels of 50, 250 and 400 MPa. The influence of stress on the loss factor ($\tan\delta$) is presented in *Figure 1*. From this graph, two observations can be made: (i) the PVA fibre displays two transitions in the temperature range from −50 to 60°C, and (ii) the loss factor decreases drastically with increasing stress level. Obviously, the fibre becomes more 'elastic' at high stress levels.

The effect of statically applied stress on the dynamic modulus is also presented in *Figure 1*, showing an increase in dynamic modulus over the entire temperature scan with increasing stress level.

The increase of the dynamic modulus, measured at a frequency of 1 Hz at 20°C, is plotted *versus* the statically applied stress in *Figure 2*. An increase of 30 GPa is observed over a stress range from 50 to 900 MPa. In repeated experiments on a single sample, the effect was found to be reversible within experimental error.

*Stress relaxation.* The effect of statically applied strain (or stress) was further studied in stress relaxation experiments. Since time dependence of viscoelastic material is indirectly related to its temperature dependence, the stress relaxation behaviour of PVA fibres will inherently be less temperature dependent at higher strain levels. This is demonstrated in *Figure 3*, where the stress relaxation behaviour of PVA fibres at 0.5, 1.0 and 2.0% strain is shown for temperatures of 30, 50 and 70°C.

To be able to compare the relaxation data at different strain levels and temperatures, the curves were approximated with a simple power law expression:

$$\sigma(t) = Ct^{-n} \qquad (1)$$

where $\sigma$ is the stress, $C$ is a constant, $t$ is time, and $n$ is the power law exponent. In the case of PVA, this exponent depends strongly on the applied strain and/or temperature. The power law exponents at 70°C for tests performed at 0.5% and 2% strain were 0.049 and 0.013, respectively. This observation is in accordance with the results of the dynamic experiments in *Figure 1*, indicating that the fibre becomes less time dependent at higher loads. Power law exponents at 30°C and 0.5% and 2% strain were 0.031 and 0.013, respectively and, especially at high load levels, are comparable with that of aramid fibres ($n = 0.01$ at room temperature)[17]. HP-PE fibres, on the other hand, show a more pronounced time-dependent behaviour with a power law exponent of about 0.07 at room temperature[17].

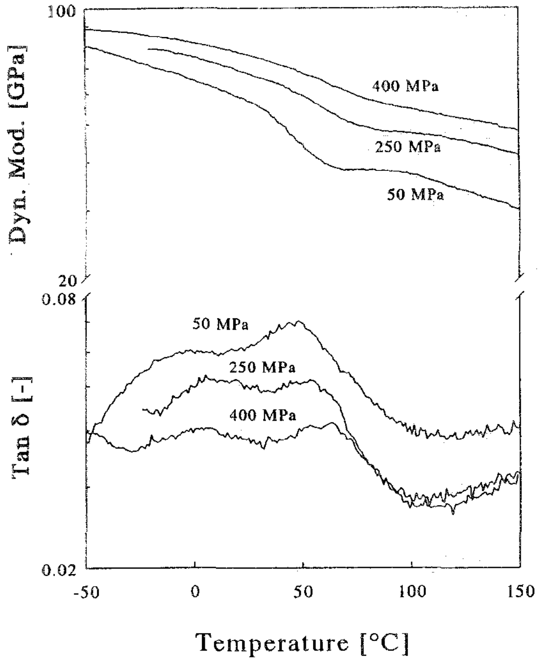

**Figure 1** The effect of statically applied stress on the temperature dependence of the dynamic modulus and loss factor ($\tan\delta$) of PVA fibres at a frequency of 1 Hz

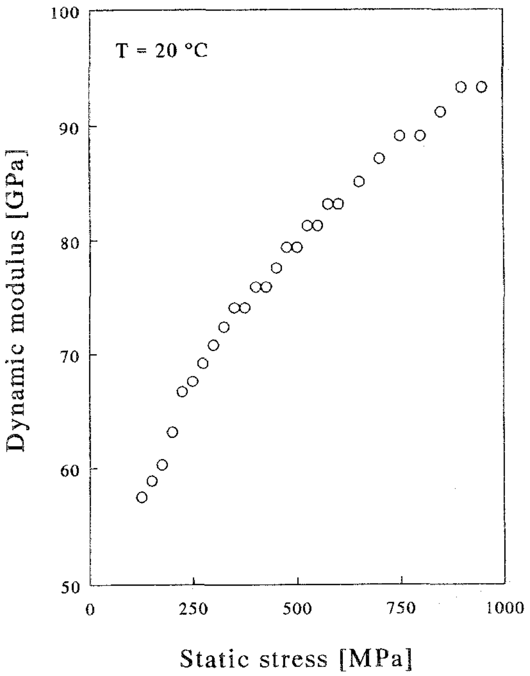

**Figure 2** The effect of statically applied stress on the dynamic modulus of PVA fibres at 1 Hz and 20°C

*Uniaxial tension.* *Figure 4* shows some stress–strain curves of PVA fibre, measured at various strain rates and temperatures. Typically, the initial modulus displays a strong dependence on strain rate and temperature, whereas at high strain levels the apparent moduli are approximately independent of the testing conditions, again indicating more 'elastic' behaviour at high stress levels.

### *Discussion*

The results of the dynamic experiments, presented in

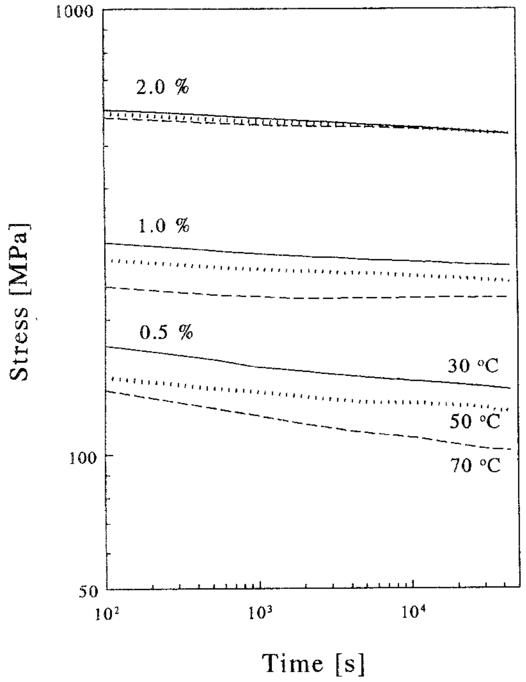

**Figure 3** Stress relaxation behaviour of PVA fibres at various temperatures and strain levels

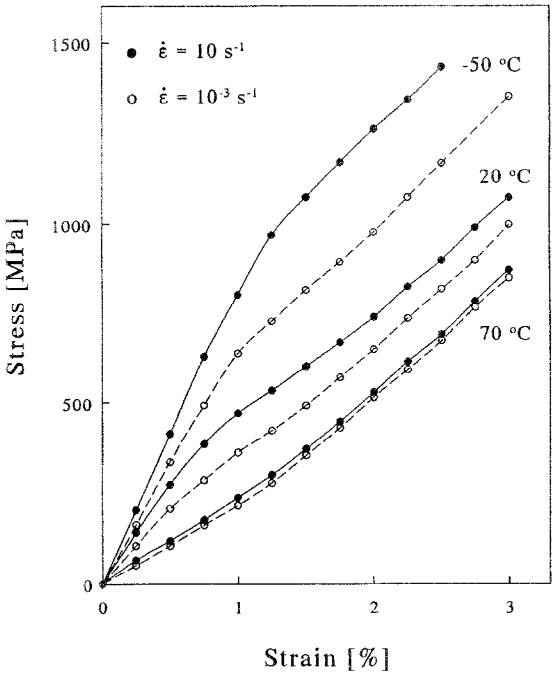

**Figure 4** Influence of temperature and strain rate on the tensile behaviour of PVA fibres

*Figure 1*, show the existence of two separate transitions in the range from −50 to 60°C. Since the crystalline ($\alpha$-)relaxation is known to shift to temperatures well over 250°C in highly oriented PVA[16], the crystalline material can be regarded as being rigid elastic in the temperature range covered in this study. Consequently, the transitions observed in *Figure 1* are most likely attributed to the amorphous phase, where the high temperature peak is related to the glass transition and the low temperature peak to a secondary transition.

The observed glass transition temperature, $T_g$ (~50°C) is rather low compared to that of isotropic PVA, which is generally reported to be in the range of 70–80°C[9,17]. However, it is well known that the $T_g$ of PVA can be influenced by water absorption and/or thermal history[9]. Moreover, the observed decrease of $T_g$ in the case of oriented PVA can easily be rationalized by a plasticizing effect due to small amounts of residual solvent from the production process, and experimental values as low as 40°C have been reported for oriented PVA samples[12]. An additional transition below $T_g$ has also been observed by Garret and Grubb[16].

At temperatures within the glass–rubber transition region, the time and strain rate dependence of the mechanical properties of the amorphous material will be most pronounced. Consequently, upon loading at room temperature, the amorphous regions in the PVA fibre will display strong viscoelastic effects leading to the strong strain rate and temperature dependence of the initial modulus that are observed in the tensile tests shown in *Figure 4*.

With increasing strain, the amorphous regions will yield under a constant level of stress, i.e. the yield stress, which depends strongly on strain rate and temperature. As a result of the breakdown of secondary bonds, an entropic strain hardening contribution of the molecular network can be activated. In the case of PVA fibres, the entropic strain hardening modulus is relatively high due to the presence of highly oriented crystalline material. Even at high stress levels this contribution will be completely reversible, since the $\alpha$-relaxation temperature is rather high for oriented PVA (>250°C) and therefore the crystalline material will be unable to deform plastically at the temperatures explored in this study[16].

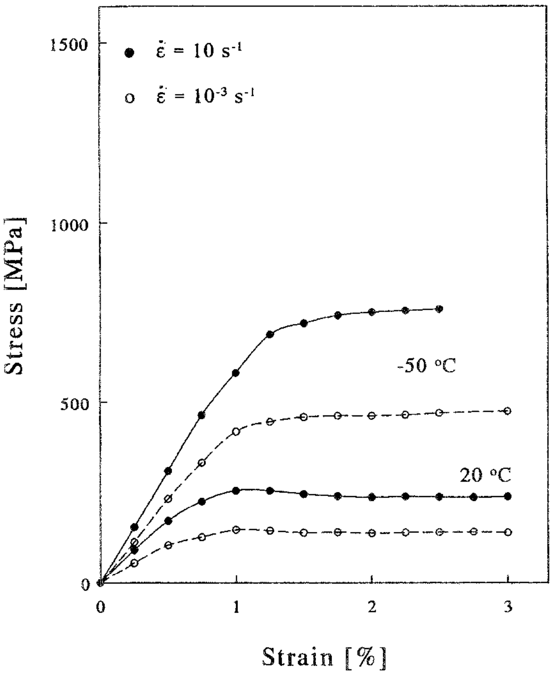

**Figure 5** The stress–strain curves of *Figure 4* at −50°C and 20°C, after subtraction of the entropic contribution to the stress

The entropic strain hardening contribution to the stress can be approximated to be independent of strain rate and temperature, which is in accordance with the observations in *Figure 4*, where at high stress levels all the curves show approximately the same apparent modulus. The observations in *Figure 2* can also be rationalized with this view.

The drastic increase of the dynamic modulus with applied static stress indicates further orientation of the crystalline material, similar to that observed in polyethylene fibres[18]. The reversibility of the effect is in complete accordance with the entropic nature suggested here.

To illustrate the interpretation suggested above, the viscoplastic contribution of the amorphous regions was constructed in *Figure 5* by subtracting the entropic contribution from the stress–strain curves depicted in *Figure 4*. To a first approximation, the entropic contribution was assumed to be equal to the stress–strain curve measured at the lowest strain rate ($10^{-3}\,s^{-1}$) and the highest temperature (70°C). By subtraction of this contribution from the total stresses, typical stress–strain curves of glassy polymers, with a distinct yield plateau, are revealed.

A similar approach, suggested by Thackray and Haward[19], is quite commonly used to describe the large strain behaviour of amorphous polymers, and might prove to be an elegant approach to develop a stress–strain relation for highly oriented PVA fibres.

## *Acknowledgements*

The authors thank Mr R. Schellekens of DSM Research for helpful discussions and valuable suggestions.

## *References*

1 Smith, P. and Lemstra, P. J. *Polymer* 1980, **26**, 1341
2 Lemstra, P. J., Kirschbaum, R., Ohta, T. and Yasuda, H. in 'Developments in Oriented Polymers - 2' (Ed. I. M. Ward), Elsevier Applied Science, New York, 1987, p. 39
3 Tashiro, K. and Tadokoro, H. *Macromolecules* 1981, **11**, 914
4 Prevorsek, D. C., Kwon, Y. D. and Sharma, R. K. *J. Mater. Sci.* 1977, **12**, 2310
5 Acierno, A., Mantia, F. P., Polzotti, G. and Cifferi, A. *J. Polym. Sci. Phys. Edn.* 1979, **17**, 1903
6 Gogolewski, S. and Pennings, A. J. *Polymer* 1985, **26**, 1394
7 Hofman, D., Goschel, U., Walenta, E., Geiss, D. and Phillips, B. *Polymer* 1989, **30**, 242
8 Kwon, Y. D., Kavesh, S. and Prevorsek, D. C. US Patent 4440771, 1984
9 Sakurada, I. 'Polyvinylalcohol Fibres', Marcel Dekker, New York, 1985
10 Schellekens, R., Rutten, H. J. and Lemstra, P. J. European Patent 212757 (awarded to DSM Stamicarbon), 1986
11 Mokveld, F. C. H. and Schellekens, R. European Patent 216407 (awarded to DSM Stamicarbon), 1986
12 Schellekens, R. and Ketels, H. *Polym. Commun.* 1990, **31**, 212
13 Schellekens, R. and Bastiaansen, C. W. M. *J. Appl. Polym. Sci.* 1991, **43**, 2311
14 Peijs, T., van Vught, R. J. M. and Govaert, L. E. *Composites* 1995, **26**(2), 83
15 Govaert, L. E., d'Hooghe, E. L. J. C. J. and Peijs, A. A. J. M. *Composites* 1991, **22**(2), 113
16 Garrett, P. D. and Grubb, D. T. *J. Polymer Sci., Polym. Phys. Edn.* 1988, **26**, 2509
17 Nagai, A. and Takayanagi, M. *Rep. Prog. Polym. Phys. Jpn* 1964, **8**, 249
18 Govaert, L. E. and Lemstra, P. J. *Colloid Polym. Sci.* 1992, **270**, 455
19 Thackray, G. and Haward, R. N. *Proc. R. Soc. London, A* 1968, **302**, 453