The effect of local distortions in the intermolecular hydrogen bond network on the lifetime of aramid yarns

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Aramids are a special class of high performance fibres. The excellent mechanical properties of this paracrystalline material are due to a combination of a high degree of molecular orientation of the rigid rod molecules and the strong hydrogen bond network between the neighbouring molecules. Northolt [1-3] has shown that the deformation behaviour of aramids during short and long time loading is primarily due to a rotation of the quasi-crystals [1-3]. This rotation requires shear and therefore the (quality of the) intermolecular hydrogen bond network between the neighbouring molecules is likely to be important for deformation behaviour. The effect of perfection of the hydrogen bond network on the time-dependent fracture behaviour of oriented polymers, however, is not known, but will be examined here for some selected PPTA copolymers with controlled distortions in the intermolecular hydrogen bond network.

Kinetic models for the lifetime of polymers under static loading have been developed by Coleman [4], using a chain slippage concept, and later by Zhurkov [5], assuming chain scission to be the dominant fracture mode. Both models assume that fracture is a thermally activated process and although they are based on quite different molecular interpretations of the fracture process the final result of their models is

mathematically identical [6]. The model of Zhurkov is the one most widely used. The lifetime t_b under constant load σ can be expressed by an exponential relationship involving three kinetic parameters:

$$t_b = t_0 \exp[(U_0 - \gamma\sigma)/kT] \quad (1)$$

The three parameters U_0 , t_0 and γ are the bond dissociation energy, the bond vibration period, and the so-called activation volume of the bond, respectively. The activation energy U_0 contains information on the breaking mechanism while the activation volume γ is supposed to contain information on the local volume leading to fracture. If misfit in the hydrogen bond network affects the time-dependent fracture behaviour of aramids the values for parameters U_0 and γ will be significantly different from those obtained for standard yarns.

Special aramid copolymers with a misfitting group have been synthesized to disturb the hydrogen bond network in a controlled manner. The copolymers studied are a PPTA-DAB copolymer (4,4'-benzanilidylene-terephthalamide) and a PPTA-NDC (naphthalene-dicarboxylic acid) copolymer. The structural misfit of the two copolymer systems is shown in Fig. 1. The NDC unit is longer than the other units in the chain. This misfit causes a disturbance in the

Figure 1 The structural misfit in PPTA copolymers containing NDC and DAB. The dashed line indicates the intermolecular hydrogen bond.

hydrogen bond network as well as in the arrangement of the phenylene groups in the crystal lattice. The DAB unit only disturbs the hydrogen bond network. Both copolymers contain 10 mol% of the misfitting group. For comparison a pure PPTA (poly(p-phenylene terephthalamide)) polymer has also been used. The molecular weight of the standard aramid and the NDC-copolymer are comparable. The DAB-copolymer has a higher molecular weight. Standard dry jet-wet spinning technology is used for the preparation of all yarns.

The yarns used were in the form of untwisted 1000 filament yarns, cut to specimens of 50 cm length. The lifetime measurements were carried out at temperatures between 250 and 400 °C in a nitrogen atmosphere to reduce oxidation of the yarn. The static load was varied between 0.1 and 1.2 GPa. At each condition 6 to 10 measurements were made. The lifetimes obtained were in the range 10 to 8000 s. During exposure of the yarn at these temperatures micro-structural changes occur. To study the effect of these micro-structural changes on the lifetime a standard aramid yarn was pre-annealed for 3 s at 600 °C at a low tension of 10 MPa, prior to further testing in the lifetime experiments.

The kinetic parameters in the Zhurkov model, U_0 , t_0 and γ , can be determined from the lifetime data by plotting $\ln t_b$ against σ and extrapolating to $\sigma=0$ yielding $(\ln t_b)_{\sigma=0}$ for each testing temperature. By plotting these data versus the reciprocal absolute temperature, both t_0 and U_0 can be determined. The activation volume γ can be determined from the slope of the $\ln t_b$ versus σ curve for each temperature separately. All kinetic parameters are determined from the lifetime data using simple linear regression analysis. The quality of the fit obtained for the determination of the kinetic parameters is shown in Figs 2 and 3 for the standard aramid yarn. Table I summarizes the values obtained for the activation energy U_0 , the reciprocal bond vibration frequency t_0 and the activation volume γ at several temperatures for the yarns investigated. From the data shown in Table I it can be concluded that the activation volume is temperature independent over this temperature range. Table I also shows large differences in U_0 and t_0 for the yarns investigated. However, these differences are due to the procedure used and are not realistic from a statistical point of view. In the procedure used t_0 and U_0 are coupled such that a high value of U_0 automatically leads to a low value of t_0 . Therefore no significance should be attached to

Figure 2 Lifetime as a function of the applied tension for various temperatures for the standard aramid yarn: $\square$ 250 °C; $\triangle$ 300 °C; $\circ$ 350 °C; $\blacksquare$ 375 °C; $\blacktriangle$ 400 °C.

Figure 3 Lifetimes at zero stress level versus the reciprocal temperature for the standard aramid yarn.

these differences in activation energy between the different yarns.

To avoid this problem in the analysis of the data the reciprocal bond vibration frequency is held constant at 10^{-12} s which is a typical bond vibration

TABLE I Experimental values of the kinetic parameters for several aramid yarns leaving all parameters free

Yarn	U_0 (kJ/mol)	t_0 (s)	γ_{250} (nm ³)	γ_{300} (nm ³)	γ_{350} (nm ³)	γ_{400} (nm ³)	Mean γ (nm ³)
Standard aramid	179	4.4×10^{-11}	0.082	0.094	0.076	0.082	0.083
DAB-copolymer	397	8.5×10^{-22}	—	0.122	0.080	0.094	0.099
NDC-copolymer	465	2.2×10^{-31}	—	0.143	0.139	0.086	0.123
Standard annealed	149	2.7×10^{-8}	0.099	0.115	0.109	0.099	0.106

period [5] and the activation volume is taken as independent of the temperature. Using this approach there are only two kinetic parameters to be determined and all lifetime data (measured at different temperatures) can be plotted in one curve of $RT \ln(t_b/t_0)$ against σ . According to the Zhurkov Equation 1 this must yield a straight line, as is shown in Fig. 4 for the data of the standard aramid yarn. The activation energy can be obtained from the intercept and the activation volume γ is obtained from the slope of the straight line. The kinetic parameters thus obtained are summarized in Table II. It is observed that the activation energy values are approximately the same for all yarns investigated. This suggests that the fracture mechanism is essentially the same and that the perfection of the hydrogen bond network has no effect on the lifetime of the yarn. The data presented in Table II compare well with the literature data for standard aramid yarns determined by Smook [7], who obtained a value for U_0 of 219 kJ/mol when t_0 was held constant at 10^{-12} s from lifetime experiments at room temperature. Vettegren [8] reported values between 168 and 189 kJ/mol, but values for t_0 are not given. Wu *et al.* [9] reported an activation energy of 335 kJ/mol and a t_0 of 6×10^{-2} s obtained from lifetime measurements on aramid filaments both at 80 °C and 130 °C. The unrealistic high value of t_0 (almost ten orders of magnitude greater than the bond vibration frequency) found by Wu indicates the unreliability of the activation energy found. It should be pointed out that these data were obtained using filaments and at longer time intervals, which might explain the difference observed.

The activation volume is an important kinetic parameter because it provides information about the structure parameters which play a role during the breaking process. Following the definition of Coleman [4] the activation volume for aramids should be equal to the product of the cross-sectional area of the polymer chain and the C-N repeat distance. This volume can be calculated from the unit cell dimensions measured by X-ray diffraction. Because there are two polymer chains in one unit cell and there are two covalent C-N bonds in one PTA repeat unit, one has to divide the cell volume by four to obtain the activation volume. This activation volume contains one covalent bond and two hydrogen bonds. The activation volumes determined with X-ray diffraction are compared to the values obtained from the lifetime experiments in Table III. The unit cell volumes determined from X-ray diffraction experiments are the same for all yarns investigated. The values obtained by X-ray diffraction are larger than those determined from lifetime measurements, except for the pre-annealed yarn. The DAB-copolymer has a surprisingly small activation volume, which is not yet understood.

Examination of filaments broken during the test showed a large variation in the (fibrillar) fracture morphology indicates that fracture is determined by micro-structural defects of dimensions considerably larger than the activation volume determined in these

Figure 4 Lifetime data measured at various temperatures versus the applied tension for the four yarns investigated ($t_0 = 10^{-12}$): $\circ$ standard aramid; --- DAB co-polymer; NDC co-polymer; — standard annealed.

TABLE II Experimental values of the kinetic parameters for several aramid yarns determined with a constant t_0 and leaving only U_0 and γ free

Yarn	U_0 (kJ/mol)	t_0 (s)	γ (nm ³)
Standard aramid	205 ± 2	10^{-12}	0.100 ± 0.003
DAB-copolymer	209 ± 2	10^{-12}	0.072 ± 0.005
NDC-copolymer	233 ± 3	10^{-12}	0.109 ± 0.008
Standard, pre-annealed	212 ± 3	10^{-12}	0.138 ± 0.009

TABLE III Unit cell dimensions of several aramid yarns measured by X-ray diffraction

Yarn	a-axis (nm)	b-axis (nm)	c-axis (nm)	$\gamma_{X\text{-ray}}$ (nm ³)	γ_{break} (nm ³)
Standard aramid	0.772	0.519	1.283	0.129	0.100
DAB-copolymer	0.770	0.521	1.282	0.129	0.072
NDC-copolymer	0.771	0.524	1.284	0.130	0.109
Standard annealed	0.783	0.516	1.283	0.130	0.138

experiments. No signs of crack blunting in the copolymer filaments were observed.

In conclusion, no effect of the perfection of the hydrogen bond network on the lifetime of aramid yarns at higher temperatures was observed. This absence of any effect suggests that fracture of aramid yarns is determined to a large extent by chain scission rather than by chain slippage.

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