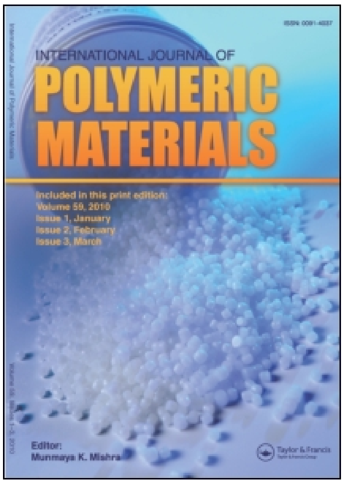

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R. A. Huijts[a]; A. J. de Vries[a]
[a] Akzo Research Laboratories Arnhem Physics of Fibre Materials Department, SB Arnhem, The Netherlands

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Mechanical Behavior of Poly(Ethylene 2,6-Naphthalene-Dicarboxylate) (PEN) Fibres near the Glass-Rubber Transition Temperature

R. A. HUIJTS and A. J. DE VRIES

Akzo Research Laboratories Arnhem Physics of Fibre Materials Department P.O. Box 9300, 6800 SB Arnhem, The Netherlands

The mechanical properties of as-spun poly(ethylene 2,6-naphthalene-dicarboxylate) (PEN) fibres were studied in order to characterize this relatively new material near its glass-rubber transition.

Tensile tests were carried out on amorphous (low-speed spun) PEN filaments. The temperature range of 90°C up to 160°C was covered using increments of 10°C. A transition from necking and cold drawing to rubber-like behavior was observed in the stress-strain relationship.

Dynamic mechanical experiments were carried out on PEN yarns spun at speeds from 500 to 4000 m min^{-1}. Both temperature and frequency were varied. The maxima in loss modulus depend on spinning speed.

Tensile behavior and dynamic mechanical behavior of PEN fibres demonstrate that the glass-rubber transition temperature of PEN is approximately 125°C.

KEY WORDS PEN, glass temperature transition, polyester fibre.

INTRODUCTION

Poly(ethylene 2,6-naphthalene-dicarboxylate) (PEN) is an interesting polyester for industrial yarn applications. Some mechanical properties of PEN yarn are better than those of the commonly applied poly(ethylene terephthalate) (PET) fibres due to the presence of the naphthalene ring. The ring introduces more stiffness in the polymer chain, see Figure 1, which leads to a better dimensional stability.

The mechanical properties of PEN fibres were studied in order to characterize this promising material near its glass-rubber transition.

EXPERIMENTAL

PEN samples were spun from the melt[1] as yarn bundles of 36 filaments. The molecular weight of the PEN polymer was about 30 000 g mol^{-1}. The winding speeds ranged between 500 and 4000 m min^{-1}. One yarn was spun under mild conditions at 700 m min^{-1} in order to obtain a highly amorphous fibre with a negligibly induced molecular orientation.

Load-elongation experiments were performed on an Instron dynamometer. Tensile tests were performed on yarn samples under ambient conditions, using a gauge length of 150 mm

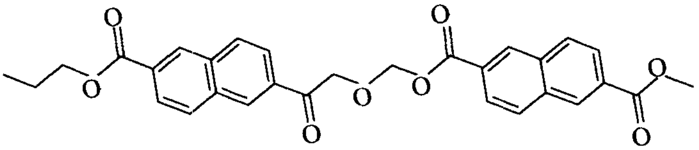

FIGURE 1 Molecular structure of poly(ethylene naphthalene-2,6-dicarboxylate).

and a strain rate of 100% per minute. Tensile tests were also carried out on amorphous, low-oriented filament samples at temperatures varying from 90 to 160°C, using increments of 10°C, a gauge length of 40 mm, and a strain rate of 1000% per minute. The tensile modulus was calculated from the slope of the initial part of the load-elongation curve at an elongation of about 2. The yield stress was taken as the observed local maximum stress at an elongation of about 5.

Dynamic mechanical tests were carried out in extension mode using a Qualimeter type Eplexor equipped with a 25 N load cell. Specially designed clamps were used to measure the properties of the as-spun yarn at a gauge length of 40 mm. In the tests a static strain of 0.5% and a dynamic strain of 0.1% were applied. The temperature dependence of the complex modulus was obtained from the 0–200°C range, the heating rate being 0.1°C per minute. The applied frequency was 10 Hz for all samples. The sample spun at 500 m min^{-1} was also measured at 0.1 and 1 Hz, and at fixed temperatures of 121, 123, and 125°C with the frequency being swept.

RESULTS

The density of the fibres was measured using a density gradient column. The density of the fibres spun at speeds up to 1000 m min^{-1} inclusive is equal to 1328 kg m^{-3}. Since the amorphous density of PEN amounts to 1325–1340 kg m^{-3}, estimated from published data,[2,3] it is clear that these low-speed spun samples are largely amorphous.

The temperature variation of the (apparent) stress-strain relation of the mildly spun PEN fibre is given in Figure 2. This figure is illustrative of the tensile behavior of the yarns spun at the speeds of 500, 700, and 1000 m min^{-1}. At the lowest temperatures the stress-strain curve shows a yield point and a subsequent decrease of the conventional stress, which means that necking and cold drawing take place. The yield stress is seen to diminish as low as 130°C. From 130°C and over the stress-strain curves display rubber-like behavior. At this stage it is clear from the change in a shape of the load-elongation curve that the glass-rubber transition temperature T_g is between 120 and 130°C.

The temperature variation of the tensile modulus is presented in Figure 3. The results of the four different PEN fibres spun at 500, 700 (two fibres), and 1000 m min^{-1} are shown in the same figure. A sharp decrease in modulus is observed between 120 and 130°C. The temperature dependence of the modulus and the decrease of about three orders of magnitude is characteristic of the glass-rubber transition. From Figure 3 one can also conclude that T_g is between 120 and 130°C.

Variation in the yield stress with temperature is shown in Figure 4 for the same four types of PEN filaments as mentioned above. It is notable that two approximately linear regions are obtained. Least-squares fit of the data to two straight lines produces an intersection at 128±2°C, which may be identified with T_g (see Reference 4). This value of T_g is in

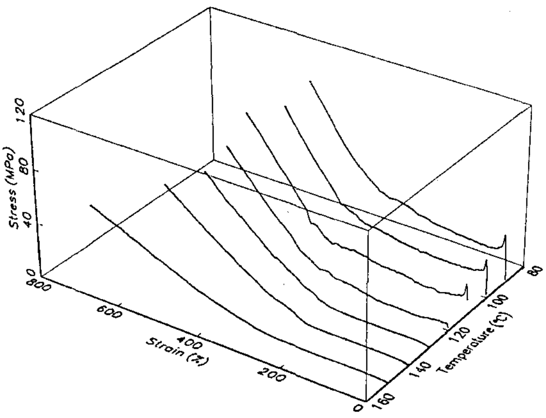

FIGURE 2 Stress-strain relations for as-spun PEN filament (spinning speed 700 m min^{-1}). Curves averaged over five samples. Stress calculated with the original cross-sectional area.

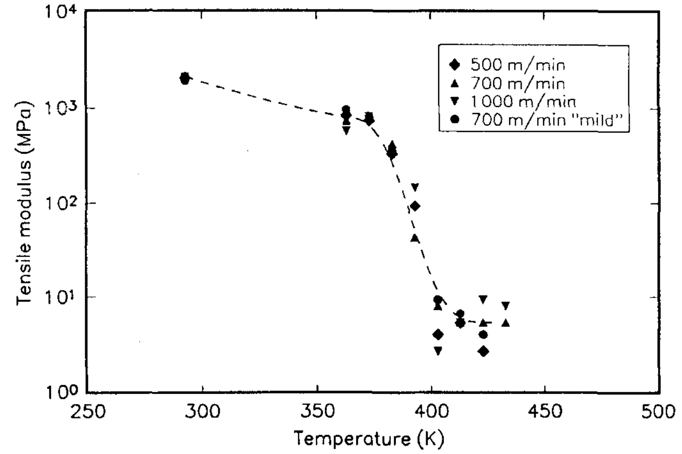

FIGURE 3 Temperature variation in the tensile modulus of amorphous as-spun PEN filament. Spinning speeds as indicated. Dashed line is a regression fit to the data of the fibre spun at 700 m min^{-1}.

perfect agreement with the one obtained from the temperature dependence of the tensile modulus.

The storage modulus measured at 10 Hz is given as a function of temperature in Figure 5. A sharp decrease is observed around 125°C for the PEN fibres spun at 500, 700, and 1000 m min^{-1}. This change in storage modulus becomes less pronounced at higher spinning speeds.

Variation in the loss modulus with temperature is shown in Figure 6. The maximum corresponding to the glass transition is observed at about 125°C. The maximum shifts towards higher temperatures with increasing spinning speed. A broader secondary transition is found at about 55°C.

The frequency dependence of T_g (i.e. the maximum in loss modulus) obtained from the dynamic mechanical measurements at constant temperature and from those at constant frequency is given in Figure 7 for the sample spun at 500 m min^{-1}. A linear relation can be observed between the logarithmic frequency and the inverse temperature.

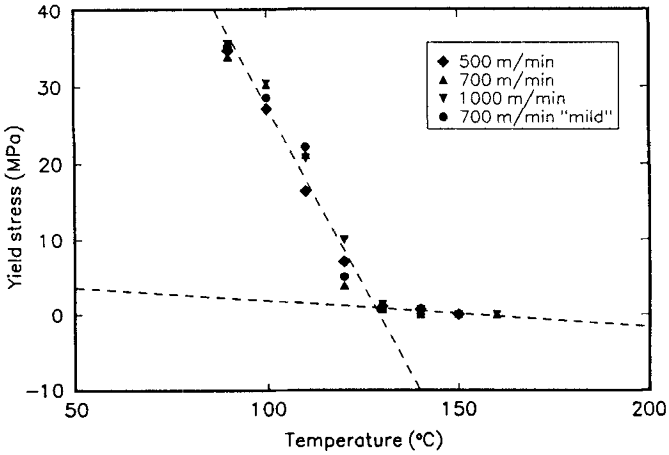

FIGURE 4 Yield stress versus temperature for amorphous as-spun PEN filament. Spinning speeds as indicated. Straight lines are least-squares fits to the data below and above 125°C.

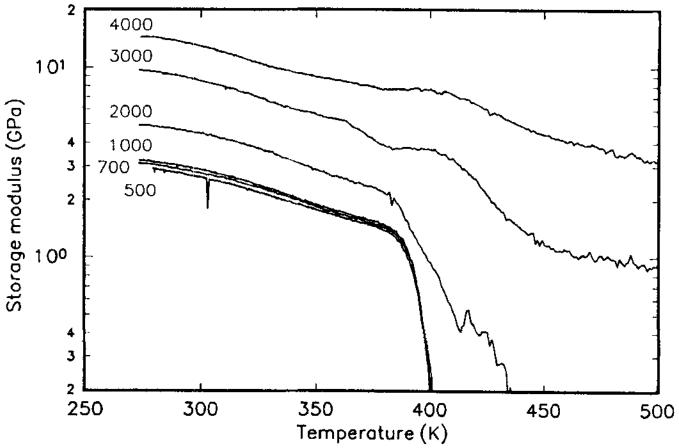

FIGURE 5 Temperature variation in storage modulus at 10 Hz of as-spun PEN filament. Spinning speeds as indicated.

DISCUSSION

The stress-strain curves illustrated in Figure 2 exhibit a clear yield point up to 120°C inclusive, which means that necking and cold drawing occur. At temperatures exceeding 120°C the local maximum is no longer visible. Consequently, no neck is formed and the filament extends uniformly with increasing load. The tensile modulus drops drastically between 110 and 130°C, see Figure 3. The decrease in modulus is about three orders of magnitude. A similar decrease is found in the storage modulus, which is illustrated in Figure 5. A distinct maximum is observed in the temperature dependence of the loss modulus for the low-speed spun yarns at 125°C, see Figure 6. These experimental results indicate that the glass-rubber transition temperature of PEN lies between 120 and 130°C. Combining the results presented in Figures 4 and 6, one can obtain a T_g value close to 125°C. This range or value for T_g is in a very good agreement with the T_g found from DSC

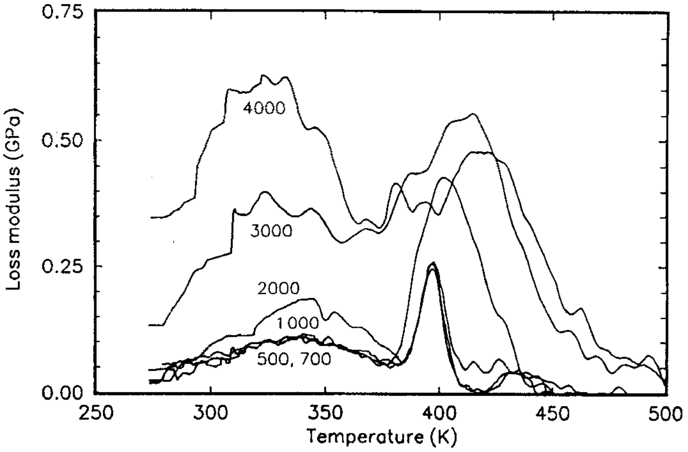

FIGURE 6 Temperature variation in loss modulus at 10 Hz of as-spun PEN filament. Spinning speeds as indicated. Drawn lines were smoothed.

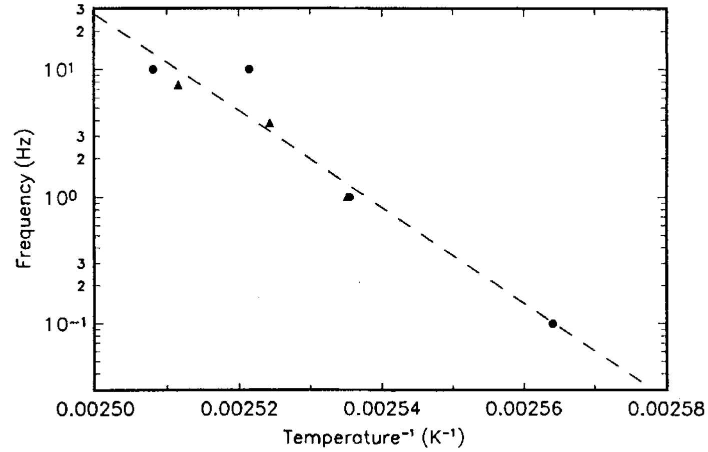

FIGURE 7 Frequency versus the reciprocal of the absolute temperature for the amorphous PEN yarn spun at 500 m min^{-1}. Results from temperature sweeps (●) and frequency sweeps (▲).

experiments,[3,5] wide angle X-ray scattering,[6] and torsional dynamic mechanical analysis.[7]

The glass transition temperature of PEN is about 40°C higher than that of PET.[8] Therefore, the thermal mechanical stability of drawn PEN fibres is expected to be better than for PET fibres. The yield stress of PEN yarn is lower than that of PET yarn.[9] The frequency of the maximum in loss modulus was found to vary linearly with the inverse temperature for amorphous PEN. The activation energy was determined from the slope of the linear regression line shown in Figure 7. An activation energy of 750 kJ mol^{-1} was obtained, which is slightly higher than the value of 600 kJ mol^{-1} for drawn PET.[10] These differences between the properties of PEN and PET fibres are manifestations of the less flexible naphthalene-2,6-dicarboxylate group in the polymer chain.

The effect of spinning speed (i.e. crystallinity or orientation) on the glass-rubber relaxation, see Figure 6, is similar to that found for PET.[11] The peak broadens, becomes asymmetrical and moves to higher temperatures. This suggests that not only the amorphous regions are involved in the process. Whether this temperature behavior is also reflected in the tensile modulus has not yet been verified by experiment.

CONCLUSION

The variation in the measured stress-strain relations of amorphous PEN filaments and in the values derived, such as yield stress and tensile modulus, and the temperature dependence of the storage and loss modulus are indicative of a glass-rubber transition of PEN at the temperature of approximately 125°C.

Acknowledgments

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