Tensile Testing Device for Measurements on Polymeric Materials Between −100 and +150°C. Mechanical Behavior of Cellulose in Liquid Media

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Synopsis

A tensile testing device for measurements on polymer samples while immersed in a liquid is described. The temperature range is approximately −100 to +150°C. The sample holder containing the immersion liquid is an all-glass container attached to a modified tensile testing device. The thermostatting and recording equipment is also described. Stress–strain curves obtained with monofilaments of regenerated cellulose immersed in *n*-pentane and liquid ammonia are shown. For filaments in *n*-pentane the variation of the modulus of elasticity with temperature down to −40°C is also reported as a further example of the applicability of the new device.

Introduction

The present paper describes an all-glass tensile testing device, intended for samples in the form of filaments or paper or plastic film strips. The stress–strain and stress–relaxation properties of the sample can be studied in a temperature range between −100 and +150°C. During the measurement, the sample may be immersed in a liquid or surrounded by a gas.

As an example, the new device makes it possible to study the behavior of cellulose or other polymeric fibers immersed in liquid ammonia or other liquids. The sample length can be varied between 1 and 10 cm.

In recent years increasing interest has been devoted to questions associated with the problem of modifying cellulose-based products in certain swelling media. There have, for instance, been several attempts to change the mechanical properties of paper and other cellulose products by treatment in liquid ammonia.[1-4] Such a treatment was shown to produce a substantial permanent shrinkage of these materials, at the same time changing the structure of the cellulose into that of cellulose III (ammonia cellulose). Despite a comparatively large amount of data relating to the behavior before and after the ammonia treatment, the behavior of the material while immersed in the liquid has not been studied, one of the reasons being difficulties associated with such measurements.[5,6]

The description given below relates to a design intended for samples consisting of comparatively thick (a few tenths of a millimeter) monofilaments of regenerated cellulose.

Description of the Sample Container

The construction of the all-glass sample container is shown schematically in Figures 1 and 2.   The container consists of an inner glass tube (G) with
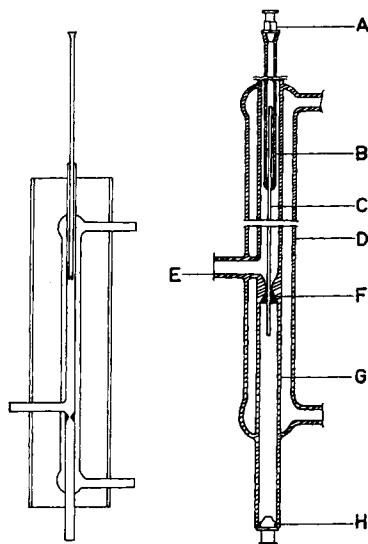

Fig. 1. Schematic diagrams: (*a*) all-glass sample holder with heat-insulating mantle; (*b*) details of the sample holder: (A, H) bayonet catch; (B) glass tube; (C) filament sample; (D) jacket; (E) inlet tube; (F) constriction; (G) inner glass tube.

a constriction (F) and an inlet tube (E).   The inner tube is fused to a jacket (D) and fixed to the moving part of the tensile apparatus by a bayonet catch (H) glued to the lower part of the glass tube.   The catch was originally a part of a hypodermic syringe with a Luer Lock grip.

The lower end of the cellulose filament (C) is glued into the inner tube at the constriction.   Its upper end is similarly fitted to the glass tube (B) which is free to move in the glass tube G and which, at its upper end, is attached to the stress-sensing element of the tensile device.   The attachment is effected by the bayonet catch (A) and the adjustable rod (M) suspended on a knife edge at (L).

The liquid in the Dewar flask (S) is under constant pressure applied through the connection (O) and just sufficient to raise the liquid level in the inner tube to the same level as the rim of the jacket.   The pressure, indicated by an open manometer (R) filled with carbon tetrachloride, is kept constant by a needle valve (P).

Gluing of the Filaments

One end of the filament was placed in the tube (B) and the glue (Araldite) is applied with a hypodermic syringe.   After the hardening, accelerated with the use of an infrared lamp, was completed, the tube with the filament
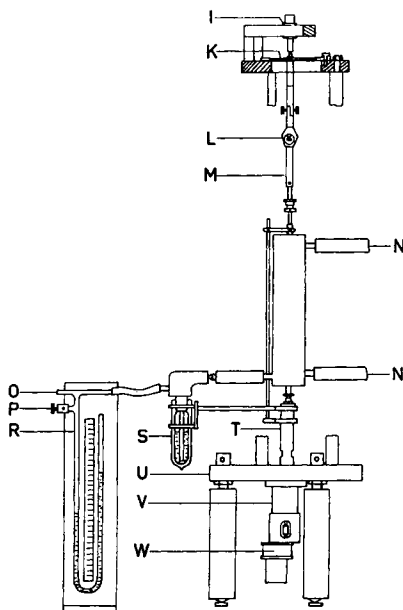
Fig. 2. The complete measuring arrangement: (I) differential transformer; (K) stress sensing steel membrane; (L) knife edge; (M) adjustable rod; (N) connections to thermostat; (O) connection to a cylinder with compressed nitrogen; (P) needle valve; (R) open manometer; (S) Dewar flask; (T) attachment to the straining device; (U) straining device, supporting plate; (V) straining device; (W) synchronous motor.

was placed in the inner tube (G) and glue applied in such a manner that the lower part of the constriction (F) was completely filled.

The glue was hardened overnight at 50°C, whereupon the tubes were stored over P_2O_5 at least 48 hr before the measurement.

Due to the shape of the constriction, the contact area between the glue and the liquid surrounding the sample is small. No swelling or softening of the glue could be seen in the liquids studied, i.e., low-boiling paraffins, alcohols, liquid ammonia, and liquid sulfur dioxide, nor was there any slipping of the filaments during measurement. A rack for simultaneous gluing of 20 samples was used in order to reduce the delay in the gluing procedure.

Temperature of the Immersion Liquid

The temperature of the liquid surrounding the sample was measured with a thermocouple (1 mm diameter) and a galvanometer. The equipment was calibrated against a standard thermometer. The temperature in the jacket was determined similarly.

Equipment for Measurement and Recording of Stress and Strain

The glass equipment for the immersion of the sample during measurement was attached to a modified stress–strain and stress-relaxation device described earlier.[7]

The main components of this device are shown in Figure 2. The stress-sensing element consists of a spring-steel membrane (K) of suitable thickness acting on a differential transformer. The membrane is deflected by the tension exerted by the sample, this deflection being proportional to the tension. The maximum movement of the upper sample attachment due to the deflection of the membrane is less than 1 μ. The stress-recording equipment consists of an amplitude-modulated carrier frequency bridge (8 kHz, Vibrometer, Type 8ATR 1/S) connected to a recorder with a full-scale response time of about 20 msec (Sanborn, Model 320). The straining is produced by a micrometer screw-based device driven by a synchronous motor (W), with about 10 msec response time. The maximum movement of the lower sample end is about 30 mm.

Errors of Measurement

The modulus of elasticity is calculated from the load–elongation curves as follows

$$E = Fl/A \, \Delta l \, \psi \tag{1}$$

The precision in E thus depends on the accuracy of the determination of the force F, the elongation Δl, the initial length of the filament l, and finally the cross-sectional area A of the fiber ψ.

In general terms, the variance of E is

$$\sigma^2 = \Sigma(\partial E/\partial x_i)^2 \sigma_i^2 \tag{2}$$

where x_i represents F, A, Δl, and l in eq. (1) and σ_i the corresponding variance. Equation (2) can be simplified if fractional errors are used. Division by E gives

$$(\sigma/E)^2 = \Sigma(\sigma_i/x_i)^2 \tag{3}$$

The error in the force F, calculated from a number of calibrations, is less than 1%, and the error in the elongation Δl is also calculated to be less than 1%.

The diameter of the filament was determined by means of a calibrated measuring microscope, and the length by a cathetometer. The error in determining the diameter was 3×10^{-3} mm, i.e., less than 1%. The error in l was 0.2 mm and could be neglected if filaments with a length greater than 50 mm were used. Consequently, the sum of the squared fractional errors was 3×10^{-4}, and the error in E was $E \times 2 \times 10^{-2}$. As seen from Figure 3, where E of a rayon filament is determined at 70 different temperatures, only four values are outside the range $E(1 \pm 0.02)$ indicated by the broken lines.

Measurements of Viscose Filaments in n-Pentane and Liquid Ammonia

In this concluding section a few examples of the results obtained with the device described above will be given. The stress–strain behavior of monofilaments of regenerated cellulose is illustrated in Figure 4. The
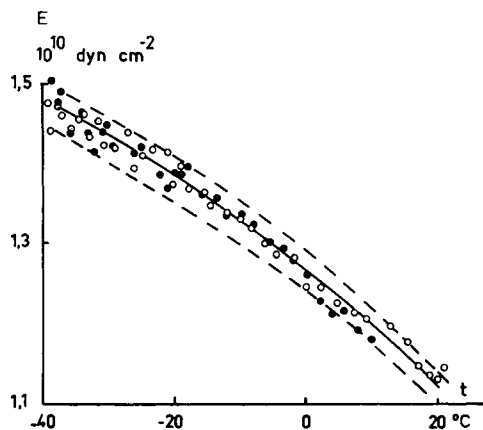
Fig. 3. Temperature dependence of the modulus of elasticity for a regenerated cellulose filament (length 96.3 mm, diameter 0.34 mm; immersion liquid, n-pentane; strain rate, 0.042% Q, 0.042%/sec): calculated scatter; (O) cooling; (●) heating of the sample. Thermostatting time at each temperature 15 min.
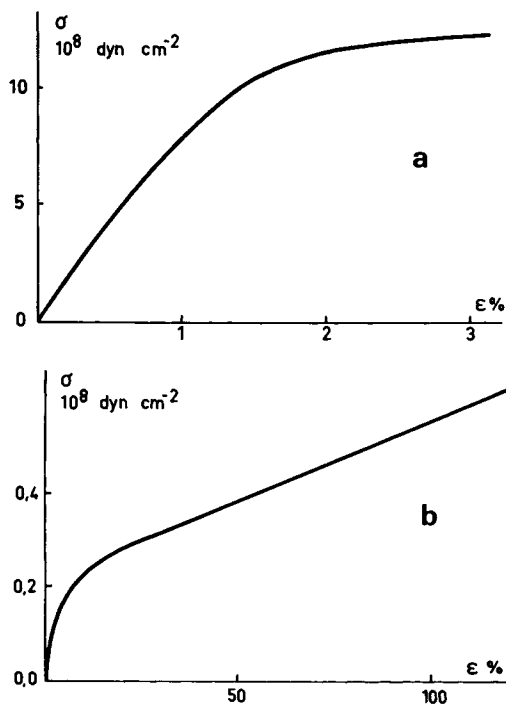

Fig. 4. Stress–strain curves for monofilaments of regenerated cellulose immersed in (a) n-pentane at 22.0°C and (b) in liquid ammonia at −43.8°C. Strain rate 0.042%/sec. Sample length 100.0 mm (a), 50.8 mm (b), diameter 0.275 mm (a) 0.345 mm (b). Curve b shows no rupture.

curves of this figure relate to measurements on filaments immersed in n-pentane at 22.0°C and liquid ammonia at −43.8°C. The weakening action of the latter agent on cellulose is clearly evident. On the one hand, it is reflected in the low stress level within the whole extension range. At an extension of 120%, where still no rupture occurred, the stress was about 20 times lower than the value recorded at about 3% breaking strain with a similar sample immersed in n-pentane. The difference in the extensibility is even larger. While with n-pentane a value of about 3% was recorded for the breaking extension, immersion in liquid ammonia produced an extensibility of over 100%, as shown in curve b, which relates to a deformation process where rupture was not achieved even at an extension of about 120%. Measurements on short samples indicated that the extension at rupture has values in the vicinity of 250%, without any local contraction of the sample taking place in this deformation range.

There are pronounced differences in the shape of the stress–strain curves. For the sample immersed in liquid ammonia, the plastic range of the curve is far larger than the initial elastic region. The values of the modulus of elasticity calculated from the initial slope of the curves were 7.77×10^{10} for n-pentane and 1.12×10^{10} dyn cm^{-2} for liquid ammonia.

The variation of the modulus of elasticity with temperature in n-pentane follows from Figure 3. In this case also the modulus was determined from the initial slope of the stress–strain curves. The values lie along a smooth curve, there being no indication of any transition, such as that in the vicinity of −30°C reported earlier.[8] There is, on the other hand, an increase in the scatter of the experimental points at about −20°C. All the points were obtained with the same filament sample. The agreement between the results obtained on cooling the sample from +20° to −40°C and those on heating it in the opposite direction is, as follows from Figure 3, very good. There is further good agreement between the observed scatter and that calculated above from the different sources of experimental error.

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