

# Effect of Temperature on Creep Fracture of Polypropylene Fibers

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## Synopsis

The tensile strength and ultimate strain of polypropylene fibers were measured by the creep fracture method at various temperatures. The tensile strength against time-to-break curves at various temperatures, which were plotted on log-log scales, were superposed by shifting the curves along the logarithmic time-to-break axis, and the composite curve of the tensile strength as a function of a reduced time to break was obtained. On the other hand, to construct the composite curve of ultimate strain from the ultimate strain against time-to-break curves at various temperatures, shifting the curves along the logarithmic ultimate strain axis was required in combination with shifting along the logarithmic time-to-break axis. The temperature dependence of the shift factor  $a_T$  followed an equation of the Williams-Landel-Ferry (WLF) form. The volume fraction of free volume at the glass transition temperature and the coefficient of thermal volume expansion, which were calculated from the WLF coefficients determined for the polypropylene fibers, are almost the same as those known as "universal values" for amorphous polymers.

## INTRODUCTION

It is known that the tensile strength and ultimate strain of textile fibers change depending on experimental conditions such as strain rate and temperature.<sup>1</sup> For elastomers, Smith<sup>2,3</sup> has found that the time-temperature superposition principle applied to their linear viscoelastic properties is also applicable to the ultimate properties, although the viscoelastic properties are no longer linear at large strains near fracture. The time-temperature superposition technique is extremely useful to predict the behavior of materials over a wide range of time scale from the experiments on a limited time scale at various temperatures. Hall<sup>4</sup> has shown for oriented isotactic polypropylene fibers, which have a glass transition temperature below room temperature, that the stress-strain behavior of the polypropylene fibers are sensitive to changes in temperature and experimental time scale. Hall<sup>5</sup> studied the possibility of applying the time-temperature superposition to the stress-strain behavior of the polypropylene fibers and suggested that the time-temperature superposition would be applicable to the entire stress-strain curve up to fracture, although sufficient data to prove applicability were not available.

In this article the temperature dependence of creep fracture of isotactic polypropylene fibers, obtained by assuming the time-temperature superposition, is reported.

## MATERIAL

Isotactic polypropylene fibers in the form of continuous filament yarn, prepared by conventional melt spinning and drawing processes, were used in this study. The polypropylene fibers were annealed at 130°C for 1 hr in the freely shrinkable state before use. The linear density of the polypropylene fibers after annealing was 6.37 tex per 24 filaments. The intrinsic viscosity determined at 135°C in tetralin was 1.05 dl/g. The birefringence on a polarizing microscope with a Berek compensator was  $31.7 \times 10^{-3}$ . The density measured in an isopropyl alcohol-water density gradient column at 30°C was 0.9060 g/cm<sup>3</sup>.

## EXPERIMENTAL

The creep fracture experiments were carried out by putting a static tensile load on the lower end of a specimen hung in an oven. The time required after the application of a load to a specimen until the specimen broke and the elongation at break were measured. The original specimen length used was 5 cm. The temperature in the oven was controlled at the desired temperatures with a precision of  $\pm 0.5^\circ\text{C}$ .

In this article the tensile strength is given by the load per unit area of the original cross section of a specimen before the application of the load, where the original cross-sectional area was calculated from the linear density and density of the fibers.

## RESULTS AND DISCUSSION

### Creep Fracture at Various Temperatures

The relationships of the tensile strength  $\sigma_b$  and the ultimate strain  $\epsilon_b$  with the time to break  $t_b$  at eight different temperatures are shown on the log-log scales in Figures 1 and 2, respectively. The tensile strength decreases with increasing time to break and temperature. The ultimate strain below about 96°C

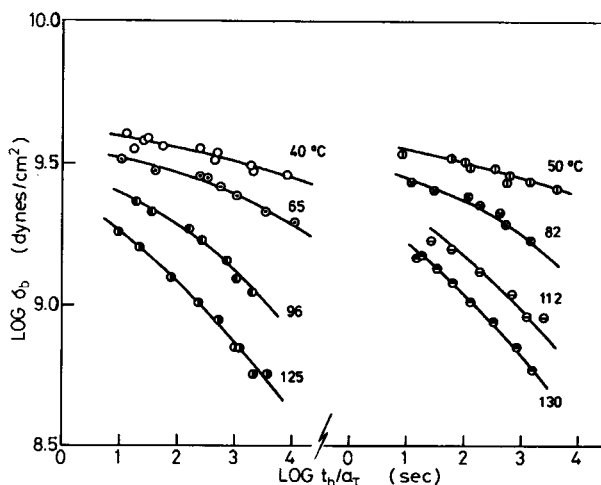


Fig. 1. Variation of tensile strength  $\sigma_b$  with time to break  $t_b$  at eight temperatures as indicated.

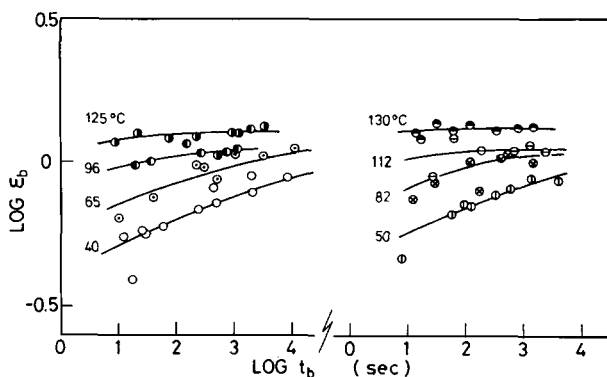


Fig. 2. Variation of ultimate strain  $\epsilon_b$  with time to break  $t_b$  at eight temperatures as indicated.

increases with increasing time-to-break and temperature. At temperatures above about 112°C the ultimate strain increases with increasing temperature but seems to take a constant value independent of the time to break if temperature is constant.

### Time-Temperature Superposition

The tensile strength curves in Figure 1 suggest they might be combined to yield a composite plot by assuming the time-temperature superposition as follows:

$$t_{b,T} = a_T t_{b,T_0} \tag{1}$$

where  $a_T$  is a shift factor, and  $T$  and  $T_0$  denote experimental and reference temperatures, respectively. The composite curve of the tensile strength against the time to break, obtained by applying the time-temperature superposition in eq. (1), is shown in Figure 3, where the reference temperature is chosen at 40°C.

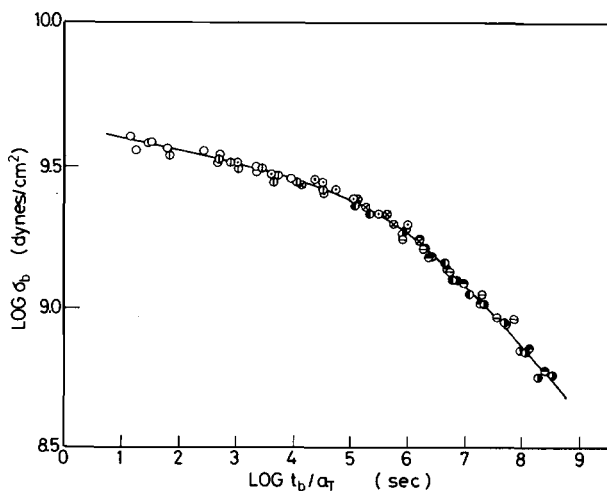


Fig. 3. Composite curve of tensile strength against time to break, where a reference temperature is chosen at 40°C. Temperature (°C): (O) 40, (◐) 50, (◑) 65, (⊗) 82, (◓) 96, (⊖) 112, (◕) 125, (◔) 130.

Nagamatsu<sup>6</sup> has shown that to apply time-temperature superposition to the stress relaxation of semicrystalline polymers a correction related to changes in the degree of crystallinity with temperature should be made to the relaxation modulus. The degree of crystallinity of isotactic polypropylene changes with temperature<sup>7</sup> in the temperature range adopted for the measurements in the present work. However, any correction regarding the effect of changes in the degree of crystallinity with temperature on the tensile strength has not been taken into account.

It is seen in Figure 3 that the tensile strength against time-to-break curves at the different temperatures are well superposed. The values of the shift factor  $a_T$  used to construct the composite curve are shown in Figure 4.

Superposing the ultimate strain against time-to-break curves allows a well-superposed curve to be constructed from the ultimate strain data obtained at temperatures below about 112°C. However, between the curves obtained by shifting the ultimate strain data from temperatures above 112°C, systematic gaps appear in the direction along the  $\log \epsilon_b$  axis, and the curves cannot be superposed to a single composite curve. Therefore, in order to construct a composite curve from all the ultimate strain data obtained at the different temperatures, shifting is required of curves along the  $\log \epsilon_b$  and the  $\log t_b$  axis. That is, between the ultimate strains at temperatures  $T$  and  $T_0$  the following conversion rule is assumed:

$$\epsilon_{b,T}(t_b) = b_T \epsilon_{b,T_0}(t_b/a_T) \quad (2)$$

where  $b_T$  is a factor dependent only on temperature. In Figure 5 the composite curve of the ultimate strain, which was constructed using the conversion rule in eq. (2), is shown. The actual procedure of the superposition was as follows. The ultimate strain curves in Figure 2 were shifted along the  $\log t_b$  axis by using the same values of  $\log a_T$  adopted for the superposition of the tensile strength, and the resulting curves were then superposed by shifting them along the  $\log \epsilon_b$  axis. The values of the shift factor  $b_T$  used are shown in Figure 4.

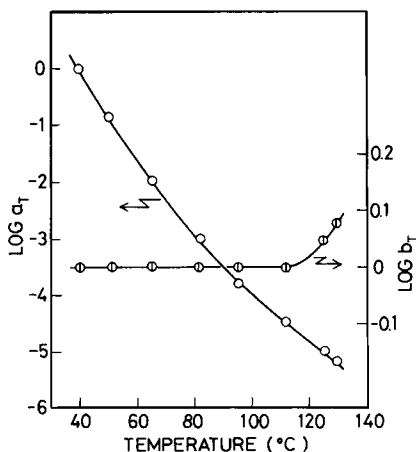


Fig. 4. Relation of the shift factors  $a_T$  and  $b_T$  with temperature, used in superposition procedures.

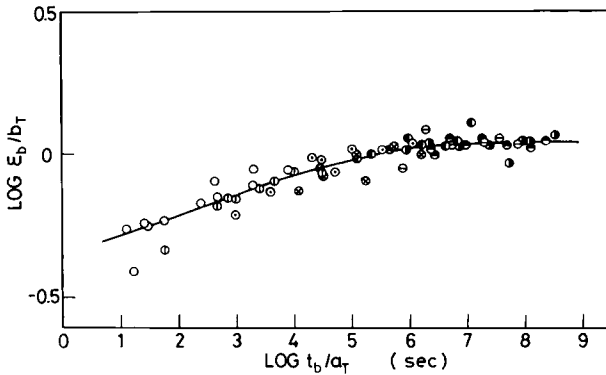


Fig. 5. Composite curve of ultimate strain against time to break, where a reference temperature is chosen at 40°C. Symbols as in Fig. 3.

**Temperature Dependence of the Shift Factor  $a_T$**

It has been proved that the temperature dependence of the shift factor  $a_T$  for amorphous polymers is expressed by the Williams-Landel-Ferry (WLF) equation<sup>8</sup>

$$\log a_T = -C_1(T - T_0)/(C_2 + T - T_0) \tag{3}$$

where  $C_1$  and  $C_2$  are constants depending on the choice of the reference temperature  $T_0$ . In order to check whether or not the values of  $\log a_T$  for the polypropylene fibers fit eq. (3), the values of  $\log a_T$  in Figure 4 are replotted in the form of  $(T - T_0)/\log a_T$  against  $(T - T_0)$  in Figure 6. The plots in Figure 6 lie on a straight line, and this diagram indicates that the plots are well approximated by eq. (3). Calculating the values of  $C_1$  and  $C_2$  from the slope and intercept at  $T - T_0 = 0$  of the straight line in Figure 6 gives  $C_1 = 13.64$  and  $C_2 = 146.8^\circ$ .

The WLF coefficients  $C_1$  and  $C_2$  are converted to the values  $C_1^g$  and  $C_2^g$  corresponding to the glass transition temperature  $T_g$  by the following equations:

$$\begin{aligned} C_1^g &= C_1 C_2 / (C_2 + T_g - T_0) \\ C_2^g &= C_2 + T_g - T_0 \end{aligned} \tag{4}$$

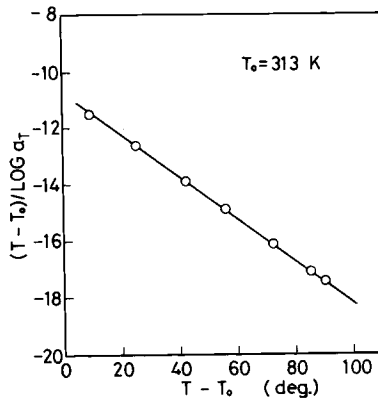


Fig. 6. Plots of  $(T - T_0)/\log a_T$  against  $T - T_0$ .

Those coefficients can be related to the volume fraction of free volume  $f_g$  at  $T_g$  and to the coefficient of thermal expansion  $\alpha_f$  as follows<sup>8</sup>:

$$\begin{aligned} f_g &= 1/2.303 C_1^{\frac{1}{2}} \\ \alpha_f &= 1/2.303 C_1^{\frac{1}{2}} C_2^{\frac{1}{2}} \end{aligned} \quad (5)$$

Assuming the  $T_g$  of the polypropylene fibers as 265 K,<sup>9</sup> and calculating the values of  $f_g$  and  $\alpha_f$  by using eqs. (4) and (5) with the values of  $C_1$ ,  $C_2$ ,  $T_g$ , and  $T_0$ , we get  $f_g = 0.021$  and  $\alpha_f = 2.2 \times 10^{-4} \text{ deg}^{-1}$ . These values of  $f_g$  and  $\alpha_f$  are almost the same as the values  $f_g = 0.025$  and  $\alpha_f = 4.8 \times 10^{-4} \text{ deg}^{-1}$ , known as the "universal values" for amorphous polymers.<sup>8</sup>

In this article the temperature dependence of creep fracture of isotactic polypropylene fibers, obtained by assuming the time-temperature superposition, is reported. The tensile strength against time-to-break curves, which are plotted on log-log scales, can be superposed by shifting the curves along the logarithmic time to break. It is noted that the WLF equation describes well the temperature dependence of the shift factor  $a_T$ .

This work was done by the author at the Central Research Laboratory of Mitsubishi Rayon Co. Ltd., and was released under agreement with the company.

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