Creep Birefringence in Cellulose Nitrate and Cellulose Acetate under Superimposed Tensile and Hydrostatic Stresses

INTRODUCTION

The mechanical behavior of polymers in plastic deformation has been seen to be influenced by the hydrostatic pressure (or hydrostatic stress).[1,2] The creep behavior of a cellulose nitrate is also found to be significantly influenced by the hydrostatic stress,[3] unlike most metals. The creep birefringence, in particular, under superimposed tensile and hydrostatic stresses in polymer solids may be different from that under uniaxial stress.

In the previous note,[4] the experimental birefringence under the uniaxial tensile stress was qualitatively investigated for plastically deforming polymer solid by using the cellulose nitrate at 65°C. In this note, as a continuation of the previous note,[4] the experimental birefringence in creep tests under various combinations of superimposed axial tensile stress and hydrostatic stress is investigated using the cellulose nitrate and cellulose acetate. Moreover, comparison of the experimental results with the optical relation deduced in the previous note[4] is discussed to ascertain the validity of the optical relation. As a result, although the instantaneous elastic–plastic birefringence at the instant of loading was not particularly influenced by the hydrostatic stress, the creep birefringence was remarkably influenced by the hydrostatic stress. Such a phenomenon cannot be predicted by the ordinary concepts which apply under uniaxial stress. The optical relation proposed in the previous note[4] gives good agreement with the actual birefringence obtained for the cellulose nitrate and the cellulose acetate under the superimposed axial tensile and hydrostatic stresses.

SUMMARY OF OPTICAL RELATION

The electric induction **D** and the electric field strength **B** are related by the symmetrical index tensor $\boldsymbol{\eta}$ as follows[4–6]:

$$\mathbf{B} = \boldsymbol{\eta}\mathbf{D} \tag{1}$$

The isochromatic fringe order per unit thickness in photomechanics is given by[4,6]

$$N = \omega\left(\frac{1}{V_2} - \frac{1}{V_1}\right) = \frac{\omega}{c}\left(\frac{1}{\sqrt{\eta_2}} - \frac{1}{\sqrt{\eta_1}}\right) \tag{2}$$

where ω, c, and $V_i = c\sqrt{\eta_i}$ ($i = 1,2$) are the frequency, the light velocity under vacuum, and the velocities of the polarized light, respectively. η_1 and η_2 in eq. (2) are the principal values of $\boldsymbol{\eta}$.

Assuming that the solid is optically isotropic before deformation, the index tensor is rewritten as[4]

$$\boldsymbol{\eta} = \eta_0\mathbf{I} + \tilde{\boldsymbol{\eta}}$$

or

$$\eta_1 = \eta_0 + \tilde{\eta}_1, \quad \eta_2 = \eta_0 + \tilde{\eta}_2, \tag{3}$$

where η_0 and **I** are the index coefficient and the unit tensor, respectively.[4] Equation (2) is approximately expressed for the principal values $\tilde{\eta}_1$ and $\tilde{\eta}_2$ as follows:

$$N = A(\tilde{\eta}_1 - \tilde{\eta}_2) \tag{4}$$

where $A = \omega/(2c\eta_0^{3/2})$.

The anisotropy that replaces the original optical isotropy is assumed to consist of the following two parts as mentioned in the previous note.[4] One part corresponds to the elastic strain tensor $\mathbf{E}_e$ with regard to the change of orientation of molecular chains. Another part corresponds to the inelastic strain tensor $\mathbf{E}_i$ with regard to the permanent change of orientation of molecular chains ap-

pearing in the inelastic deformation such as creep or plastic one.   When the axes of two tensors $\mathbf{E}_e$ and $\mathbf{E}_i$ coincide with each other, the index tensor $\tilde{\bar{\eta}}$ is proposed as a function of the two tensors.[4]   The index tensor of the first-order approximation is given as[4,7,8]

$$\tilde{\bar{\eta}} = \mathbf{F}(\mathbf{E}_e, \mathbf{E}_i) = a_0\mathbf{I} + a_1\mathbf{E}_e + a_2\mathbf{E}_i$$

or

$$\tilde{\eta}_1 = a_0 + a_1E_{e1} + a_2E_{i1}, \quad \tilde{\eta}_2 = a_0 + a_1E_{e2} + a_2E_{i2} \tag{5}$$

where the subscripts 1 and 2 of the strain components denote the principal values of the strain tensor. The fringe order per unit thickness for the first-order approximation is derived from eq. (4) as follows[4]:

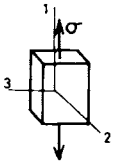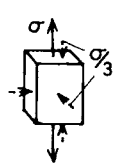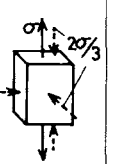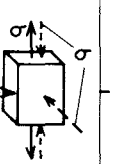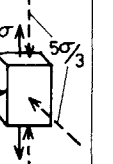$$N = C_1(\Delta\sigma) + C_2(\Delta E_i) \tag{6}$$

where C_1 and C_2 are optical coefficients, $\Delta\sigma = \sigma_1 - \sigma_2$ is the difference of principal stresses, and $\Delta E_i = E_{i1} - E_{i2}$, as shown in the previous note.[4]

EXPERIMENTS

The uniaxial specimens were made of the same cellulose nitrate as in the previous note[4] and of cellulose acetate, 6 mm thick, which were initially isotropic.   The experimental apparatus consists of three major parts, namely, a high pressure generator associated oil vessel with heater, a loading system, and instruments to record the load and deformation.   On a surface of each specimen, a square gauge mark was cut in a region of uniform stress.   The detailed descriptions of the specimen, and the apparatus are shown in Ref. 9.   Axial elongation and cross contraction over the distance between the gauge marks were measured to within 0.005 mm by using a magnifying projector with the same procedure as in the previous note.[4]   The difference of principal strains $\Delta E = E_1 - E_2$ was calculated in Green's strain system[4,10] $E_\alpha = \epsilon_\alpha + (\epsilon_\alpha)^2/2$, where ϵ_α ($\alpha = 1,2$) is the conventional engineering strain. The fringe order of creep birefringence was measured by Tardy's method.[11]

The creep tests were performed under the superimposed axial tensile stress and hydrostatic stress, as shown in Table I, at each test temperature for both cellulosic polymers.   Table I shows the stress states of an element of the specimen for various values of $A = \sigma_{ii}/\Delta\sigma$, where A is the dimensionless first invariant of the stress tensor, and $\sigma_{ii} = \sigma_1 + \sigma_2 + \sigma_3$ is the first invariant of the stress tensor,[12] and $\Delta\sigma = \sigma_1 - \sigma_2$ corresponds to the equivalent stress.[12]   For example, $A = 1$ corresponds to the uniaxial tensile stress state ($\sigma_2 = \sigma_3 = 0$), and $A = -4$ corresponds to the case of the superimposed axial tensile stress σ and hydrostatic stress $5\sigma/3$.

TABLE I
Stress States of an Element of the Specimen for Various Values of A

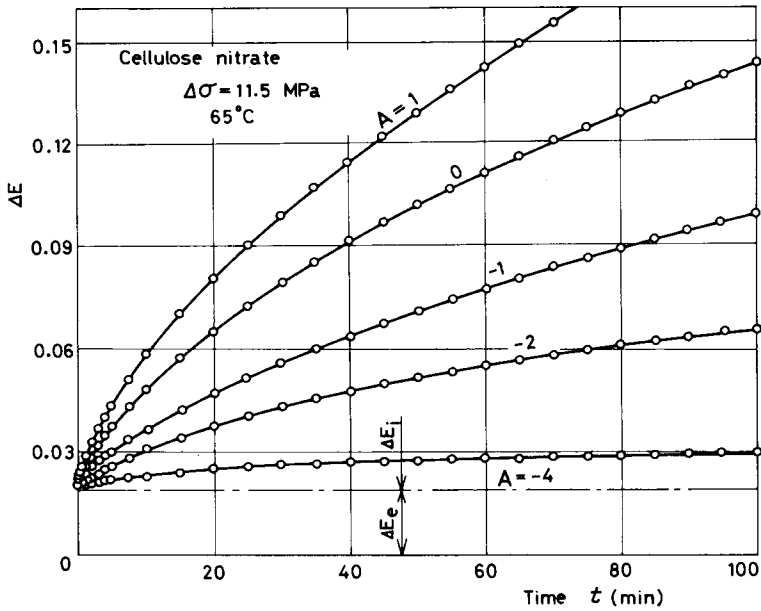| $A = \dfrac{\sigma_{ii}}{\Delta\sigma}$	1	0	1	-2	-4
Stress state					
— Axial tensile stress, - - - Hydrostatic stress					
σ_1	σ	$2\sigma/3$	$\sigma/3$	0	$-2\sigma/3$
$\sigma_2 = \sigma_3$	0	$-\sigma/3$	$-2\sigma/3$	$-\sigma$	$-5\sigma/3$
$\Delta\sigma = \sigma_1 - \sigma_2$	σ	σ	σ	σ	σ
$\sigma_{ii} = \sigma_1 + \sigma_2 + \sigma_3$	σ	0	$-\sigma$	-2σ	-4σ

Fig. 1. Experimental creep relation between ΔE and time of the cellulose nitrate at 65°C for various values of A with $\Delta\sigma = 11.5$ MPa.

Cellulose Nitrate

Each load was applied so as to obtain constant values of $\Delta\sigma$ of 4, 6, 8, 10, and 11.5 MPa for each value of A with the cellulose nitrate at 65°C. Figure 1 shows the experimental creep relation between the total strain $\Delta E = \Delta E_e + \Delta E_i$ and time for each value of A at $\Delta\sigma = 11.5$ MPa, as an example, where the subscripts e and i denote the elastic and the inelastic (or plastic-creep) parts. Each symbol is plotted using the average values of three tests results. The circle symbol and solid curve in Figure 2 shows the relation between the experimental fringe order per unit thickness N and time corresponding to the results shown in Figure 1.
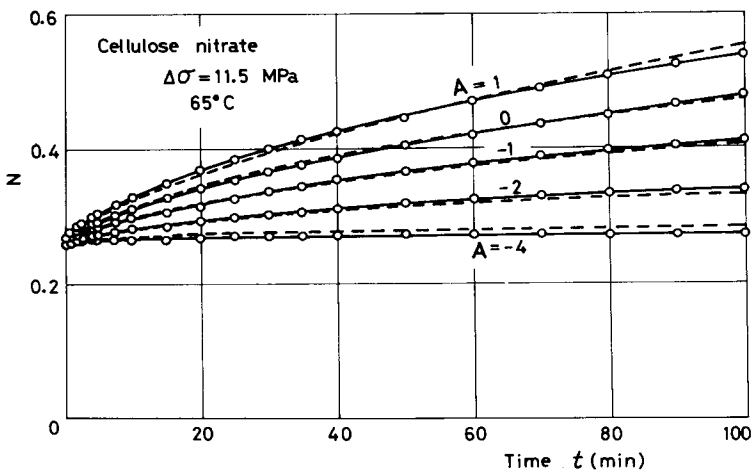

Fig. 2. Relation between fringe order per unit thickness N and time of the cellulose nitrate for various values of A with $\Delta\sigma = 11.5$ MPa in creep tests: (—○—) experiment; (- - -) eq. (6).
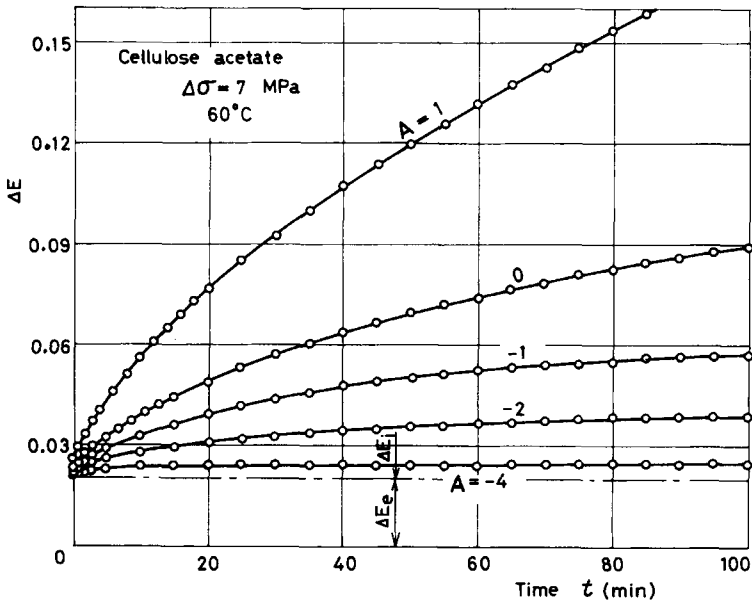
Fig. 3. Experimental creep relation between ΔE and time of the cellulose acetate at 60°C for various values of A with $\Delta\sigma = 7$ MPa.

Cellulose Acetate

Each load was applied so as to obtain constant values of $\Delta\sigma$ of 7, 6, 5, and 4 MPa for each value of A with the cellulose acetate at 60°C. Figure 3 shows the experimental creep relation between $\Delta E = \Delta E_e + \Delta E_i$ and time for each value of A at $\Delta\sigma = 7$ MPa with the cellulose acetate, as an example. Each symbol is plotted using the average values of three test results. The circle symbol and solid curve in Figure 4 show the relation between the experimental fringe order per unit thickness N and time corresponding the results shown in Figure 3.

For comparison, Figure 5 shows the experimental creep relation between ΔE and time at lower value of $\Delta\sigma$ for each cellulosic polymer. The circle symbol and solid curve in Figure 6 show the
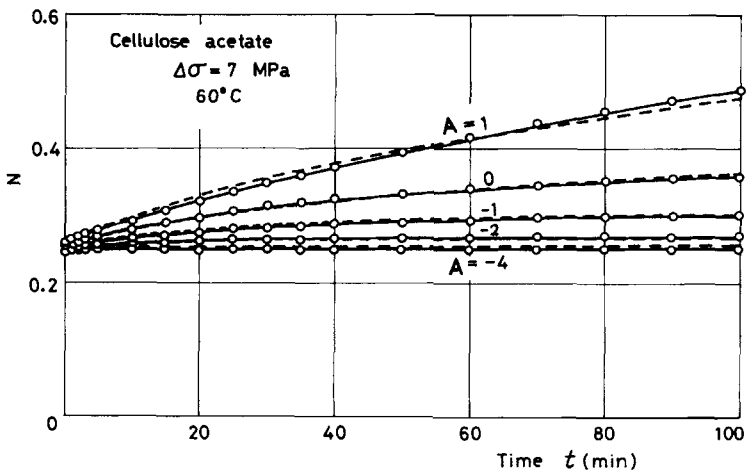

Fig. 4. Relation between N and time of the cellulose acetate for various values of A with $\Delta\sigma = 7$ MPa in creep tests: (—O—) experiment; (- - -) eq. (6).
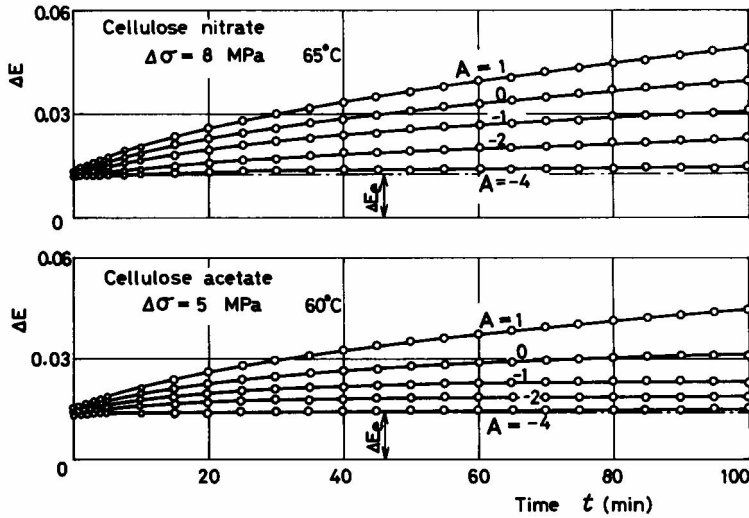
Fig. 5. Experimental creep relation between ΔE and time of each cellulosic polymer for various values of A.

relation between N and time corresponding the results shown in Figure 5 for both cellulosic polymers.

DISCUSSIONS AND CONCLUDING REMARKS

As shown in Figures 1, 3, and 5, although the instantaneous elastic–plastic strain at the instant of loading ($t = 0$) is not so significantly influenced by the value of A, the creep strain is remarkably influenced by that for both cellulosic polymers. Such as trend appears in the experimental creep birefringence as shown in Figures 2, 4, and 6. Though the instantaneous elastic–plastic birefringence at the instant of loading is scarcely affected by the value of A, the creep birefringence is remarkably influenced with lapse of time after loading by the hydrostatic stress as shown in Figures 2, 4, and
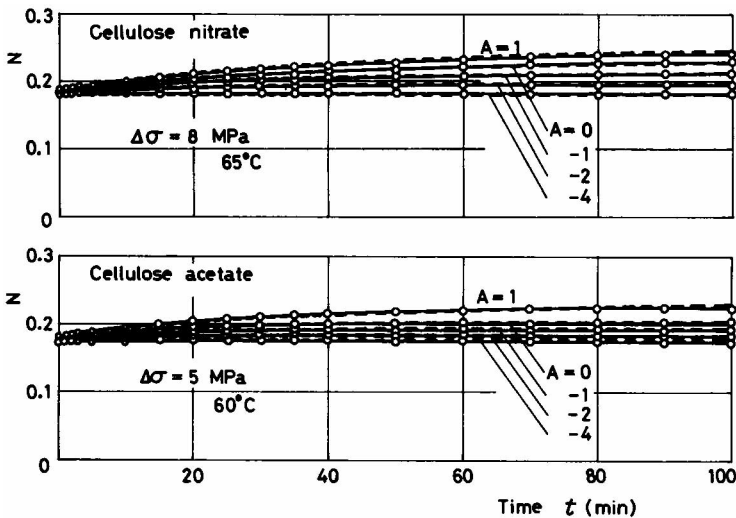

Fig. 6. Relation between N and time of each cellulosic polymer for various values of A in creep tests: (—O—) experiment; (- - -) eq. (6).

6. Furthermore, taking the extremes $A = 1$ and $A = -4$ in Figures 2, 4, and 6, the curves for $A = 1$ indicate that the creep birefringence is sensitive to the stress level $\Delta\sigma$, but those for $A = -4$ show little variation of creep birefringence. The creep birefringence tends to zero with decreasing value of A. These phenomena may not be expected in the uniaxial tensile creep birefringence as shown in the previous note.[4]

The coefficients in eq. (6) were determined from the experimental results for each polymer by using the procedure mentioned in the previous note.[4] They are as $C_1 = 0.023$ (MPa)$^{-1}$ (mm)$^{-1}$ and $C_2 = 1.7$ (mm)$^{-1}$ for the cellulose nitrate at 65°C, and $C_1 = 0.036$ (MPa)$^{-1}$ (mm)$^{-1}$ and $C_2 = 1.5$ (mm)$^{-1}$ for the cellulose acetate at 60°C. In Figures 1, 3, and 5, the difference of principal strains ΔE is divided by the chain line into the elastic part ΔE_e and the inelastic part ΔE_i, where ΔE_e is calculated from $\Delta E_e = \Delta\sigma/(2G)$ by using the value of $2G$ for each cellulosic polymer. The procedure to determine the value of $2G$ is described in the previous note[4] in detail, and they were obtained as $G = 315$ MPa for the cellulose nitrate at 65°C and as $G = 172$ MPa for the cellulose acetate at 60°C. The broken curves in Figure 2 were calculated from eq. (6) by using of C_1 and C_2 for the cellulose nitrate mentioned above and the corresponding values of ΔE_i shown in Figure 1 for each value of A. The broken curves in Figure 4 were calculated from eq. (6) by using C_1 and C_2 for the cellulose acetate and the corresponding values of ΔE_i shown in Figure 3 for each value of A. The broken curves in Figure 6 were calculated by the same procedure as mentioned above for each polymer. They agree fairly well with the corresponding experimental results expressed by the solid curve, independent of the values of A and of $\Delta\sigma$.

From foregoing discussions, neglecting the small amount of error, it is concluded that the deduced optical relation (6) of the first-order approximation gives good agreement with the actual observations in creep tests under the superimposed axial tensile stress and hydrostatic stress for the cellulose nitrate and the cellulose acetate. The creep birefringence in the cellulosic polymers is remarkably influenced by the hydrostatic stress.

Although the features of creep birefringence mentioned above are obtained for two specific cellulosic polymers, it may be considered that similar phenomena may appear in the creep birefringence for many polymer solids.

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