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Mechanical behaviour and formulation of stress–strain relation for non-linear viscoelastic cellulose nitrate under cyclic loadings

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The cyclic deformations under various repeated stresses are quantitatively investigated using non-linear viscoelastic cellulose nitrate heated to 60° C. The non-elastic strain or creep-plastic strain is remarkably influenced by the repeated stress and the stress rate. The cyclic deformations corresponding to the repeated stress less than a certain stress level attain the saturated state called the "shake down" after some cycles. The stress–strain relations of the non-linear viscoelastic media in the loading and unloading processes are deduced from the invariant theory using an hypothesis of creep potential. The non-linear viscoelastic observations obtained on the cellulose nitrate at 60° C under cyclic loadings are found to fit the deduced relations for the loading and unloading processes independent of the repeated stress and the stress rate.

1. Introduction

The mechanical behaviour of polymers has been widely investigated because of the large advances in the utilization of polymers. A number of previous papers are concerned with the deformation behaviour in loading of polymers at initial cycles and not the unloading process [1–5]. The deformation behaviour in the unloading process of non-linear viscoelastic polymer is remarkably different from that in the loading process and is known to be more complicated than metals [6, 7]. Moreover, the deformation behaviour of non-linear viscoelastic polymers subjected to cyclic loadings deviate from that at the initial cycle with increases in the number of cycles, and is also affected by stress rate. The difference of deformation behaviour due to the number of cycles becomes more remarkable for larger values of repeated stress level.

In this paper, the deformation behaviour in the loading and unloading processes under cyclic loadings are quantitatively investigated using non-linear viscoelastic cellulose nitrate heated at 60° C under various repeated stresses and various stress rates. Moreover, the stress–strain relations of the non-linear viscoelastic media in the loading and unloading processes are deduced from the invariant theory with an hypothesis of creep potential considering the distinctive features of the deformation behaviour. The deduced relations are compared with the experimental results in the loading and unloading processes under the cyclic loadings. The deduced relations in the loading and unloading processes give fairly good agreement with the actual observations under the cyclic loadings independent of stress rate and repeated stress level.

2. Formulation of stress–strain relations

2.1. Loading process

When the stress increases slowly, the strain rate of an element of a polymer is considered to consist of the creep strain rate and the instantaneous elastic–plastic strain rate. When the time hardening theory is adopted for convenience of analysis, the creep strain rate is proposed by using the second invariant of the deviatoric stress tensor as follows [8]

$$(\dot{\varepsilon}_{ij})_c = B(t+s)^{\alpha} \exp(bJ_2^{1/2})(\partial J_2/\partial\sigma_{ij}) \quad (1)$$

where ε_{ij} are the components of strain tensor, the dot represents differentiation with respect to time. B, α and b are material constants. t and s denote current time and material constant time introduced by the author [8]. $J_2 = S_{ij}S_{ij}/2$ is the second invariant of the deviatoric stress tensor [8, 9]. σ_{ij} and $S_{ij} = \sigma_{ij} - \frac{1}{3}\sigma_{ii}\delta_{ij}$ are components of stress tensor and deviatoric stress tensor of σ_{ij}. Hence $\partial J_2/\partial\sigma_{ij}$ in Equation 1 becomes S_{ij}.

The instantaneous elastic–plastic strain rate may be given as [10]

$$(\dot{\varepsilon}_{ij})_0 = \frac{1}{2G}\dot{S}_{ij} + \frac{2n+1}{4G}\left(\frac{J_2}{k^2}\right)^n \frac{\dot{J}_2}{J_2} S_{ij} \quad (2)$$

which is Ramberg–Osgood's relation of rate type, and is good approximation of the non-linear stress–strain relation. G, n and k in Equation 2 are material constants. Therefore, from the above mentioned two parts, the component of strain rate is expressed as follows

$$\dot{\varepsilon}_{ij} = (\dot{\varepsilon}_{ij})_c + (\dot{\varepsilon}_{ij})_0 \quad (3)$$

With the components of principal stress σ_1, σ_2 and σ_3, J_2 is expressed as follows [8, 9]

$$J_2 = \tfrac{1}{6}[(\sigma_1-\sigma_2)^2 + (\sigma_2-\sigma_3)^2 + (\sigma_3-\sigma_1)^2] \quad (4)$$

In the present tests, the axial tensile stress σ_1 is applied to the uniaxial specimen (i.e. $\sigma_2 = \sigma_3 = 0$)

$$J_2 = \sigma_1^2/3, \quad \dot{J}_2 = 2\sigma_1\dot{\sigma}_1/3 \quad (5)$$

is obtained from Equation 4. By substituting Equation 5 into Equation 3, the axial strain rate is expressed as

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follows

$$\dot{\varepsilon}_1 = \frac{\dot{\sigma}_1}{3G} + \frac{(2n+1)}{3G}\left(\frac{\sigma_1}{(3)^{1/2}k}\right)^{2n}\dot{\sigma}_1 + \tfrac{2}{3}B(t+s)^{\alpha}\exp\left[\frac{b\sigma_1}{(3)^{1/2}}\right]\sigma_1 \qquad (6)$$

When it is necessary to calculate the total strain ε_1, the following procedure may be adopted [8]. Time is subdivided into small invervals, $0 \sim t_1,\ t_1 \sim t_2, \ldots, t_{m-1} \sim t_m, \ldots, t$, in which the magnitude $\dot{\varepsilon}_1$ may be considered to be approximately constant. For example, $\varepsilon_1(t_m)$ at arbitrary time t_m in the period $t_{m-1} \sim t_m$ is approximated as

$$\varepsilon_1(t_m) = \varepsilon_1(t_{m-1}) + \dot{\varepsilon}_1(t_{m-1})(t_m - t_{m-1}) \qquad (7)$$

2.2. Unloading process

An unloading co-ordinate whose axes are directed in the opposite directions to those in the preceding loading co-ordinate is considered as a new loading process beginning at the instant t^* of the beginning of unloading as shown in Fig. 1. The measures corresponding to the unloading co-ordinate are distinguished with the bar over symbols. In Fig. 1, the strain ε_1 in the loading process is divided into the elastic strain ε_e and the creep-plastic strain ε_{cp} by the broken line. In the non-linear viscoelastic deformation, the strain in the unloading process is proposed to consist of the three major strains, namely, an elastic strain $\bar{\varepsilon}_E$, a creep recovery strain $\bar{\varepsilon}_U$ in the unloading process, and an additional creep strain $\bar{\varepsilon}_L$ as shown in Fig. 1 [7]. The additional creep deformation corresponding to $\bar{\varepsilon}_L$ continues to appear in the early stage of unloading process for the operating load even in the unloading process. That is, it may be considered that the additional creep strain which could not sufficiently appear for the stress state of the loading process continues to appear for the operating stress in the early stage of unloading process. As the amount of creep strain which has appeared in the loading process has been counted already in the loading process, it is only necessary to take into account such a strain from the beginning of unloading to the considered instant during unloading. Therefore, H is used instead of B in Equation 6 as shown in Equation 8.

In the unloading process which is considered as a new loading beginning at the origin of the unloading co-ordinate, the plastic deformation may be neglected and the components of strain rate may be expressed in the following form by means of the same manner as in the loading process [7].

$$\dot{\bar{\varepsilon}}_1 = \dot{\bar{\varepsilon}}_E + \dot{\bar{\varepsilon}}_U - \dot{\bar{\varepsilon}}_L = \frac{\dot{\bar{\sigma}}_1}{3F} + \tfrac{2}{3}D(\bar{t}+s)^{\beta}\exp\,[g\bar{\sigma}_1/(3)^{1/2}]\bar{\sigma}_1 - \tfrac{2}{3}H(t+s)^{\alpha}\exp\,[b\sigma_1/(3)^{1/2}]\sigma_1 \qquad (8)$$

where F, D, β and g are material constants in the unloading process. In Equation 8, time, stress and strain are expressed as $\bar{t} = t - t^*$, $\bar{\sigma}_1(\bar{t}) = \sigma_1(t^*) - \sigma_1(t)$ and $\bar{\varepsilon}_1(\bar{t}) = \varepsilon_1(t^*) - \varepsilon_1(t)$. The total strain $\bar{\varepsilon}_1$ is calculated from Equation 8 by the same manner as in the loading process. Time in the unloading process is subdivided into small intervals, $0 \sim \bar{t}_1,\ \bar{t}_1 \sim \bar{t}_2, \ldots, \bar{t}_{m-1} \sim \bar{t}_m, \ldots, \bar{t}$. $\bar{\varepsilon}_1(\bar{t}_m)$ at arbitary time $\bar{t}_m$ in the period $\bar{t}_{m-1} \sim \bar{t}_m$ is approximated as

$$\bar{\varepsilon}_1(\bar{t}_m) = \bar{\varepsilon}_1(\bar{t}_{m-1}) + \dot{\bar{\varepsilon}}_1(\bar{t}_{m-1})(\bar{t}_m - \bar{t}_{m-1}) \qquad (9)$$

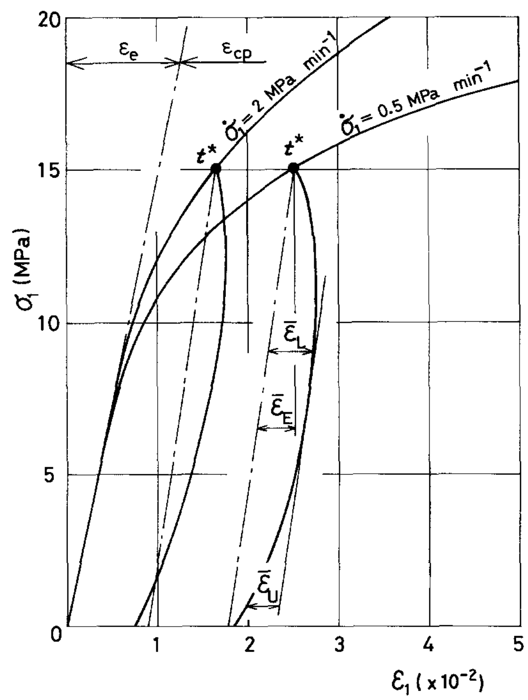

Figure 1 Relationships between stress σ_1 and strain ε_1 in loading and unloading processes obtained from experiments for $\dot{\sigma}_1 = 0.5$ and $2\,\mathrm{MPa\,min^{-1}}$ at 60° C.

2.3. Determination of values of material constants

The material constants in Equations 6 and 8 at the first cycle can be approximately determined from the experiments of creep test (σ_1 = constant) and proportional loading ($\dot{\sigma}_1$ = constant) by using uniaxial specimens subjected to axial tension. The material constants in Equations 6 and 8 at the second cycle and after the second cycle are empirically determined from the experimental results by trial and error method. We show the procedure for determining the material constants in the unloading process is almost same as in the loading process.

In the case of creep test $\sigma_1 = c$(const), or $\dot{\sigma}_1 = 0$

$$\dot{\varepsilon}_1 = \tfrac{2}{3}B(t+s)^{\alpha}\exp\,[b(c/(3)^{1/2}](c) \qquad (10)$$

is obtained from Equation 6, and taking logarithms of both sides, the following form is obtained

$$\log\,(\dot{\varepsilon}_1/c) = \log\,(\tfrac{2}{3}B) + \alpha\log\,(t+s) + 0.434bc/(3)^{1/2} \qquad (11)$$

As the values of $\bar{\varepsilon}_1$ and t are known from the experimental results, the values of B, α, s and b are approximately determined by the experiments for more than two different values of c.

For the case of proportional loading (namely, uniform rate of stress increase with time) $\dot{\sigma}_1 = d$(constant) or $\sigma_1 = dt$, the following equation is obtained from Equation 6

$$\dot{\varepsilon}_1 = \tfrac{2}{3}B(t + s)^{\alpha} \exp [b(\sigma_1/(3)^{1/2}](\sigma_1) + \frac{\dot{\sigma}_1}{3G}$$

$$+ \frac{2n + 1}{3G}\left[\frac{\sigma_1}{(3)^{1/2}k}\right]^{2n} d \qquad (12)$$

Unknown values in Equation 12 are G, k and n. As the quantity

$$\dot{\varepsilon}_1 = \dot{\sigma}_1/(3G)$$

is predominant while the value of σ_1 is small, we can determine G in the early state of loading process. By denoting the known terms in Equation 12 with $A(t)$ as

$$A(t) = \dot{\varepsilon}_1 - \frac{\dot{\sigma}_1}{3G} - \tfrac{2}{3}B(t + s)^{\alpha} \exp [b(\sigma_1/(3)^{1/2}]\sigma_1$$

Equation 12 becomes

$$A(t) = \frac{2n + 1}{3G}\left(\frac{\sigma_1}{(3)^{1/2}k}\right)^{2n} d \qquad (13)$$

Taking logarithms of both sides, the above relation becomes

$$\log A(t) = (2n) \log \sigma_1 + \log (2n + 1)d - \log 3G[(3)^{1/2}k]^{2n} \qquad (14)$$

As the values of G, $A(t)$ and σ_1 are known already, the values of k and n can be found from the experiment in which σ_1 increases linearly with time. The material constants in the unloading process can be determined by the almost same procedure as in the loading process.

3. Experiments in cyclic loadings

The uniaxial specimens were made of initially isotropic cellulose nitrate, 6 mm thick. On a surface of each specimen, a square gauge mark was cut in a region of sufficiently uniform state. The experimental apparatus is same as in the previous papers [7, 8] and consists of three major systems, namely: a heated oil vessel, loading and unloading equipment with a load cell, and instruments to record the load and deformation. Detailed description of the shape of the specimen and of the apparatus is given in reference [10].

The tests of cyclic loadings were performed under the axial tensile stress σ_1 at 60° C. The stress increases linearly with time in the loading process and decreases with time in the unloading process as the proportional loading. Each load was applied so as to obtain the constant rates of change of $\dot{\sigma}_1 = 0.5$, 1 and 2 MPa min^{-1}, and the repeated stresses (maximum stress of cyclic loading) was adopted as the conditions of $\sigma_m = 15$, 14, 12 and 10 MPa for each value of $\dot{\sigma}_1$. The experiments were performed during 10 cycles, or $\varepsilon_1 = 0.08$ for various values of σ_m and $\dot{\sigma}_1$.

The gauge mark in each instant during the cyclic loadings was photographed, and the relative change of the distance of the gauge mark was precisely measured to within 0.005 mm by using a magnifying projector [7, 8]. The accuracy of strain thus obtained is within about 2×10^{-4}. The strain was calculated in the natural strain system $\varepsilon_1 = \ln (1 + e_1)$, where e_1 is the conventional engineering strain [7, 8].

4. Experimental results and discussion

The solid curves in Figs 2 and 3 show the stress–strain relation obtained from the experiments of cyclic loadings for the repeated stress $\sigma_m = 15$ MPa with $\dot{\sigma}_1 = 0.5$ and 2 MPa min^{-1}, respectively, as examples. The solid curves in Figs 4 and 5 show those for the repeated stress $\sigma_m = 10$ MPa with $\dot{\sigma}_1 = 0.5$ and 2 MPa min^{-1}, as examples. Each curve in these figures is plotted using the average values of three test results.

In Figs 2 to 5, the strain ε_1 at the first cycle is divided into the elastic and creep-plastic (non-elastic) strains by the thin chain line. From Figs 2 and 3, it is confirmed that the creep-plastic strains are substantially influenced by the values of the stress rate $\dot{\sigma}_1$ and they become larger for smaller value of $\dot{\sigma}_1$ in the loading and unloading processes. The reason is due to the effect of viscosity of material.

The modes of stress–strain relation in the loading process are fairly affected by the number of cycles N, and those in the unloading process are not so influenced as shown in these figures. The cyclic deformations at the tenth cycle in Fig. 4 and the sixth cycle in Fig. 5 may be considered to attain to the saturated state, and this effect is called the "shake down" due to work-hardening of material [11]. In Figs 4 and 5, the cyclic

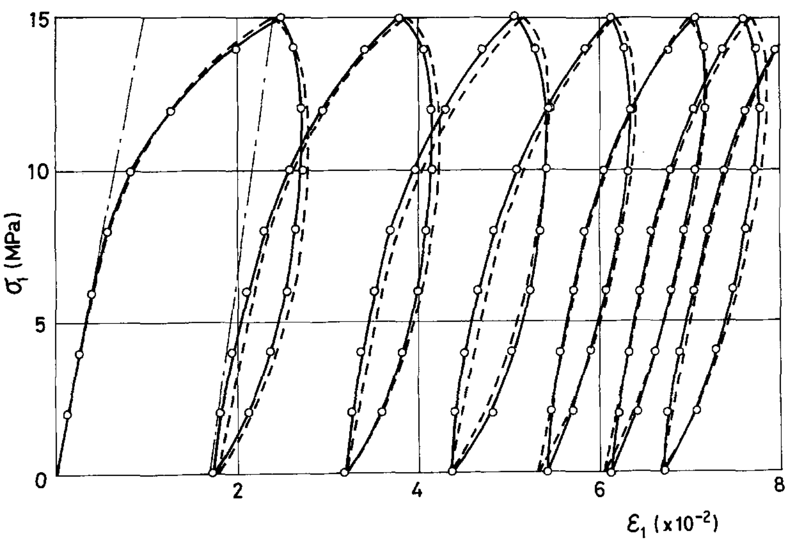

Figure 2 Stress–strain relations for cyclic deformation of repeated stress $\sigma_m = 15$ MPa with $\dot{\sigma}_1 = 0.5$ MPa min^{-1}. (–o–) experiment, (– – –) calculation.

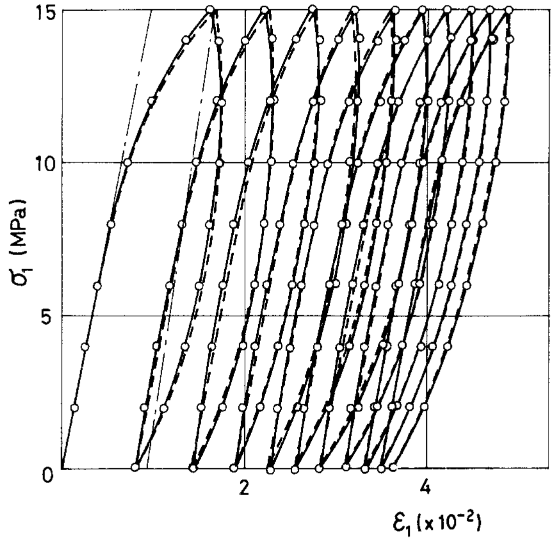

Figure 3 Stress–strain relations for cyclic deformation of repeated stress $\sigma_m = 15\,\mathrm{MPa}$ with $\dot{\sigma}_1 = 2\,\mathrm{MPa\,min^{-1}}$.

deformation for $\dot{\sigma}_1 = 2\,\mathrm{MPa\,min^{-1}}$ attains to the saturated state at smaller cycle than that for $\dot{\sigma}_1 = 0.5\,\mathrm{MPa\,min^{-1}}$. It is worth noting that the effect of shake down under the cyclic loadings appears at smaller cycle for larger value of stress rate $\dot{\sigma}_1$.

The values of material constants in Equations 6 and 8 were determined according to the procedure mentioned in Section 2.3 from the experimental results shown in Fig. 2 and from the creep test results as shown in the previous paper [8]. Fig. 6 shows the relations between the values of material constants and the number of cycles N in the loading process. The

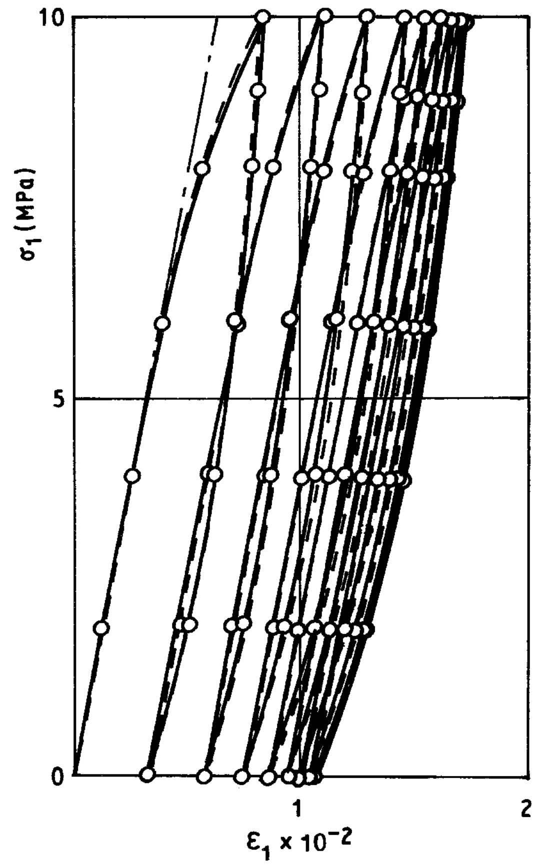

Figure 4 Stress–strain relations for cyclic deformation of repeated stress $\sigma_m = 10\,\mathrm{MPa}$ with $\dot{\sigma}_1 = 0.5\,\mathrm{MPa\,min^{-1}}$.

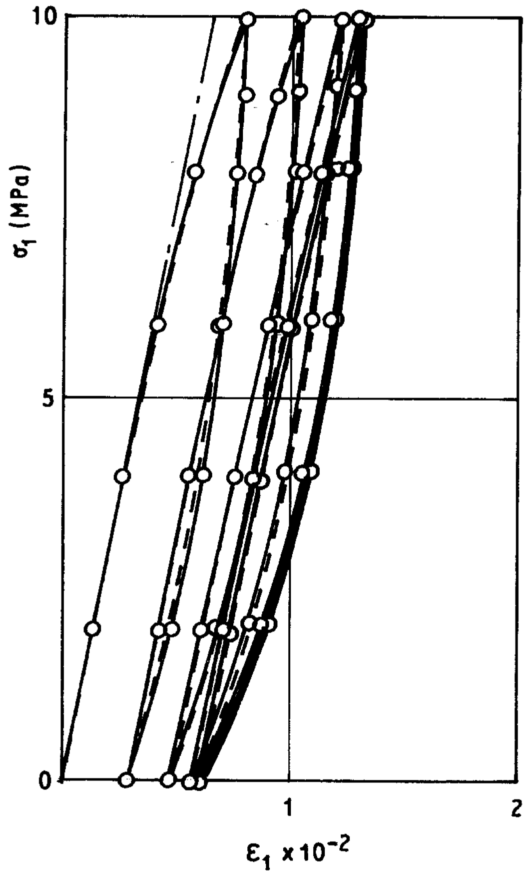

Figure 5 Stress–strain relations for cyclic deformation of repeated stress $\sigma_m = 10\,\mathrm{MPa}$ with $\dot{\sigma}_1 = 2\,\mathrm{MPa\,min^{-1}}$.

material constants except for H in the unloading process are not almost affected by the cycle N, and the constant H is shown in Fig. 6. The value of s is 1.0 min in the loading and unloading process. The values of material constant in the unloading process are as $F = 680\,\mathrm{MPa}$, $D = 5.7 \times 10^{-7}\,\mathrm{MPa^{-1}\,min^{-(\beta+1)}}$, $\beta = -0.65$, $g = 0.65\,\mathrm{MPa^{-1}}$. As shown in Figs 2 to 5, the broken curves calculated from Equations 7 and 9 using the corresponding material constants for each cycle fairly agree well with the corresponding experimental results shown by the solid curves for each value of stress rate $\dot{\sigma}_1$ and for each value of repeated stress σ_m. The above mentioned calculation were performed for several time increments: 1 min for $\dot{\sigma}_1 = 0.5$ and $1\,\mathrm{MPa\,min^{-1}}$, 0.5 min for $\dot{\sigma}_1 = 2\,\mathrm{MPa\,min^{-1}}$. In these calculations, the co-ordinate of loading process for the second cycle has its origin at the final point of unloading process of the first cycle. The time for the second cycle is adopted as $t = 0$ at the origin of the loading process of the second cycle. In the same manner, the origin for every cycle in the loading process is considered as the final point of unloading process for the preceding process.

In Fig. 6, the value of k corresponding to yield stress becomes large with increase of cycles N, and hence the plastic strain becomes small with increase of cycles N. The values of b and B also become small with increase of cycles N.

5. Concluding remarks

The main results are:

1. The creep-plastic strain is remarkably influenced

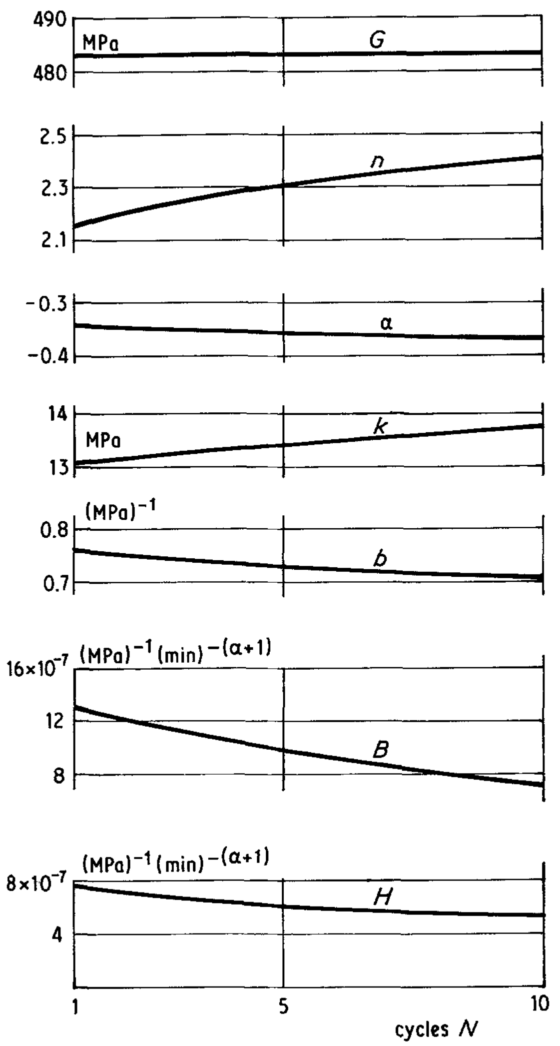

Figure 6 Relationships between number of cycles N and various material constants.

by the effect of viscosity of material due to the stress rate. The creep-plastic strain decreases with increase of the stress rate.

2. The creep-plastic strain in the loading process is fairly affected by the number of cycles, and that in the unloading process is not so influenced as in the loading process.

3. The modes of stress–strain relation obtained from experiments are fairly affected by the value of repeated stress. The cyclic deformations corresponding for the repeated stress less than a certain stress level attain to the saturated state which is called as the shake down after some cycles. Moreover, this shake down attains at smaller cycle for larger value of stress rate.

4. The material constants in the loading process are affected by the number of cycles and may be approximately considered as a linear function of the number of cycles. However, the many material constants in the unloading process are not so affected by the number of cycles and may be approximately considered to be kept unchanged.

5. The additional creep strain $\bar{\varepsilon}_L$ continues to appear in every early stage of the unloading process of cyclic loadings of non-linear viscoelastic deformation.

6. The proposed stress–strain relations based on the invariant theory give good agreement with the actual observations in the loading and unloading processes for non-linear viscoelastic polymer under cyclic loadings independent of the stress rate and repeated stress.

7. Although the features of non-linear viscoelastic behaviour mentioned above are obtained for the cellulose nitrate, it may be considred that the similar phenomena may appear in the non-linear viscoelastic behaviour for other polymers.

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