Viscoelastic Properties of Cellulose Acetate-Plasticizer Systems (Supplement) Elastic Behavior

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One second- and sixty second-modulus of cellulose acetate - plasticizer systems were determined by means of the tensile creep test at temperature of 20° to 50°C. The measurements were carried out on film strips which had been initially oriented slightly by applying a small amount of stretch. In the range of our experimental conditions, the modulus of cellulose acetate decreased to some extent by the addition of plasticizers, though the amount of this decrease was not so large as to change the order. These plasticized cellulose acetates were still insensitive to temperature as in the case of unplasticized acetate. The modulus of cellulose acetate - plasticizer systems decreased as the amount of plasticizer increased, and almost ceased after the amount of plasticizer was over a critical value. This value was in the neighbourhood of 0.1–0.2 expressed in mole ratio of plasticizer to the polymer unit molecule.

Introduction

In our previous paper[1] the viscoelastic behavior of cellulose acetate–plasticizer systems was studied at temperature of 20–50°C. over a wide range of time by means of the tensile creep test. Plasticizers used here were butyl–, amyl– and octyl–borate (BB, AB and OB, respectively), dimethylphthalate (DMP) and triphenylphosphate (TPP). The measurements were carried out on film strips which had been initially oriented to some extent by applying a small amount of stretch. In the description of these results, we referred all creep curves to a unit stress, *i. e.*, plot strain divided by stress (instead of strain itself), as a function of log time (instead of time itself) for a few convenient reasons which had been pointed out by Aiken and his coworkers.[2] Tensile strain γ was calculated from:

$$\gamma = (L_z - L_0)/L_0 ,$$

here, L_0 is the length of the strip just before the additional large weight was applied, and L_z is the elongation at time z (min.) after application of the additional large weight.

Since the change of cross-sectional area with creep was corrected at each points in all the curves, assuming that the Poisson's ratio was 0.3, the stresses S (g./cm^2.) have been calculated for the actual area.

As all γ/S–$\log z$ curves was analogous in type and considerably flat in the early period, the modulus of elasticity may be approximately determined by extrapolating those curves. Thus, we obtained the one second modulus (ε_1) from the extrapolated value of γ/S at period of 1/60 min., and the sixty second modulus (ε_{60}) from the value observed at period of 1 min.

Results

The values of γ/S at periods of 1/60 and 1 min. are shown in Figures 1–5, which were determined by means of the above-mentioned procedure.

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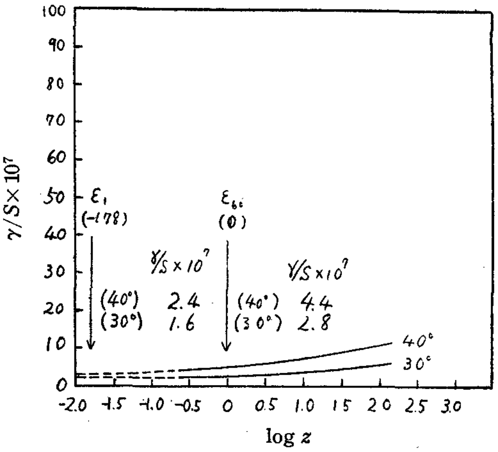


Fig. 1. No plasticizer.

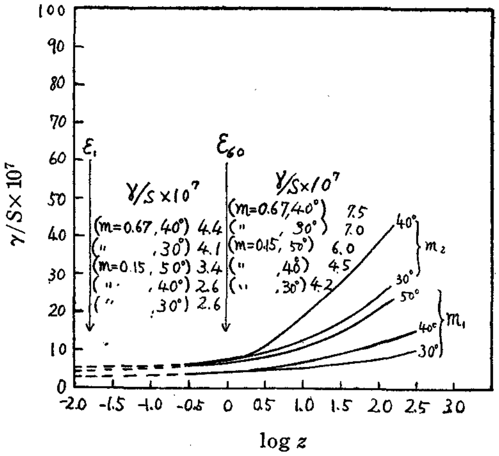


Fig. 2. *AB* (m_1=0.15, m_2=0.67)

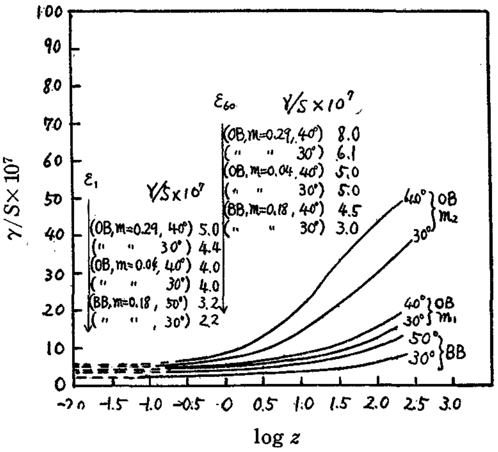


Fig. 3. *BB* (m=0.18),
OB (m_1=0.04, m_2=0.29).

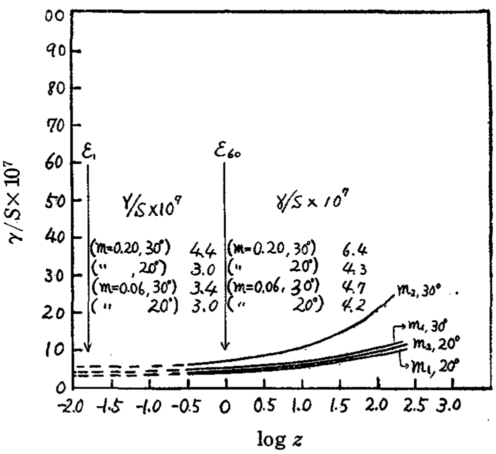


Fig. 4. *DMP* (m_1=0.06, m_2=0.20).

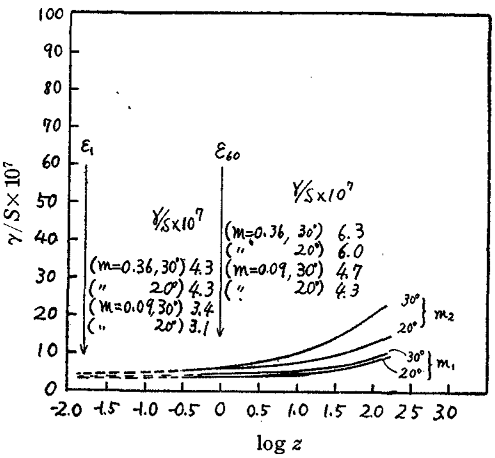
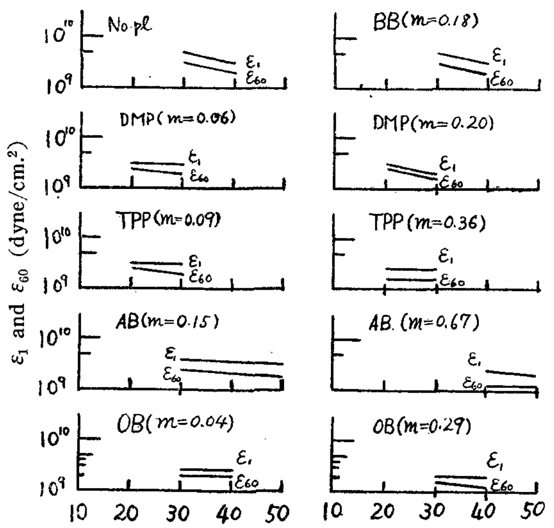


Fig. 5. *TPP* (m_1=0.09, m_2=0.36).



t (°C.)

Fig. 6.

Young's modulus ε (g./cm.^{2}) was defined as follows:

$$\varepsilon=(P/A)\{(L_z-L_0)/L_0\}\,, \quad (1)$$

where, P is the tensile force (g.), and A is the corrected cross-sectional area (cm.^{2}).

Also,

$$\gamma/S=\{(L_z-L_0)/L_0\}(P/A)^{-1}\,, \quad (2)$$

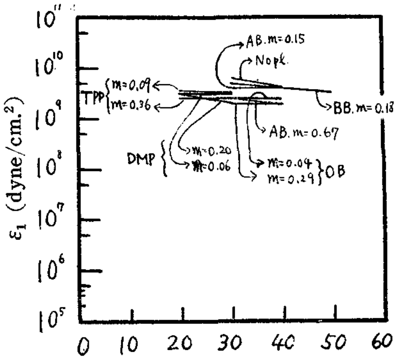
From the equations (1) and (2), we obtained the equation:

$$\varepsilon=1/(\gamma/S)\,, \quad (3)$$

Therefore, ε_1 (dyne/cm.^{2}) and ε_{60} (dyne/cm.^{2}) were calculated from the values of γ/S in Figures 1–5 by means of the equation (3), and these values are shown in Figure 6.

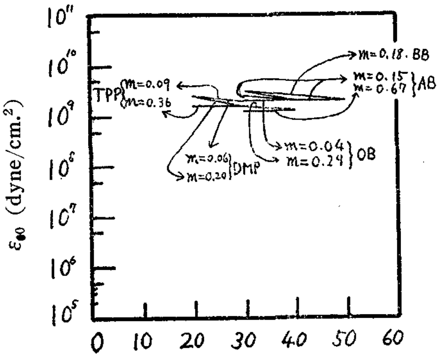
Discussion

It was found in Figure 6 that each value of ε_1 was slightly larger than the corresponding value of ε_{60}. All of ε_1 and ε_{60} are plotted in Figures 7 and 8.



t (°C.)

Fig. 7.



t (°C.)

Fig. 8.

These simple figures showed that the moduli of cellulose acetate–plasticizer systems were comparatively insensitive to temperature. This tendency was not varied by means of the addition of plasticizer, and the very flat curves of $\log\varepsilon-t$ relation were slightly lowered maintaining nearly the same slope. Valko[3] determined the modulus of cellulose acetate at the temperature of liquid air (−195°C.) and found the value of ca. 5×10^{10} to 5×10^{11} dyne/cm.^{2} Figure 7 shows that the moduli of cellulose acetate at the temperatures of 30° and 40°C. were 5 and 3×10^9 dyne/cm.^{2}, respectively. It can be seen from a direct comparison of these values that the modulus was comparatively insensitive at temperatures below the second-order transition point (68.6°C.[4]), though it decreased to some extent with elevation of temperature.

The effect of the addition of plasticizer on the modulus of cellulose acetate are shown in Figures 9–12. The amount of plasticizer (m) is expressed in unit of mole ratio of plasticizer to polymer unit molecule.

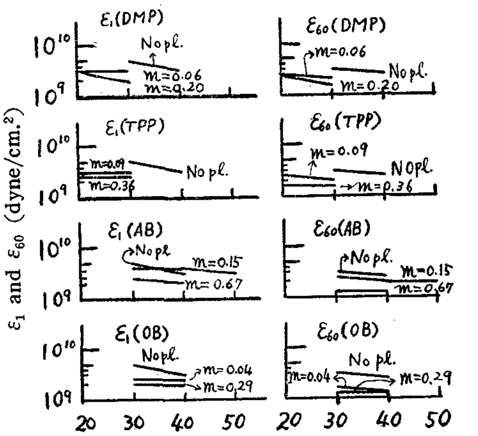


Fig. 9.

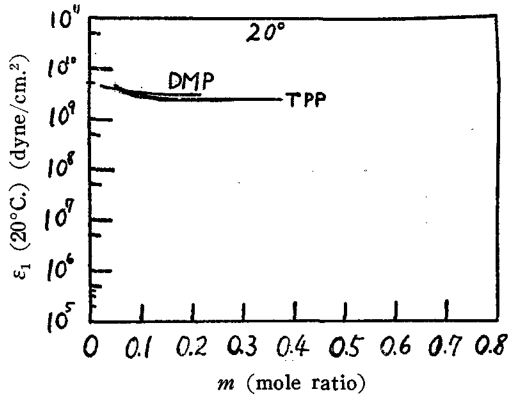


Fig. 10. [P]: DMP=415, TPP=711.

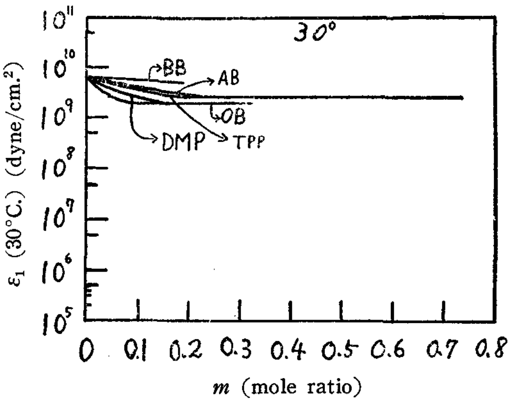


Fig. 11. [P]: BB=596, AB=713, OB=1,064, DMP=415, TPP=711.

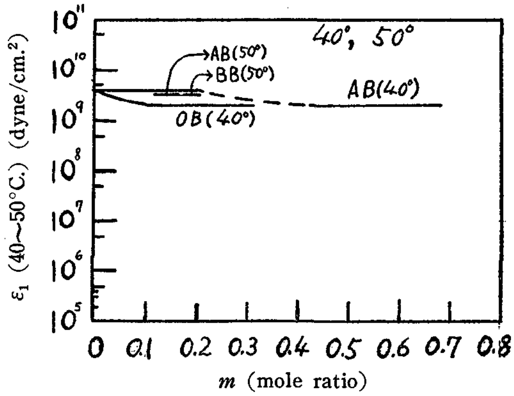


Fig. 12. [P]: BB=596, AB=713, OB=1,064.

It was found in the range of our experimental conditions that the effect of the addition of plasticizer on the modulus of cellulose acetate was not so sensitive as to change its order. The modulus of the cellulose acetate–plasticizer systems decreased to some extent as the amount of plasticizer increased. However, it almost ceased to decrease after the addition of plasticizer was larger than a critical amount. This amount was in the neighbourhood of 0.1–0.2 in m (mole ratio) and was not sensitive to temperature in all our samples.

It would require more data to discuss the effect of the type of plasticizer on modulus in general. As regards to the case of our alkyl borate plasticizers, the modulus decreased as the bulk of plasticizer increased, and this would be particularly true when the amount of plasticizer was small. Where, as in our previous paper,[1] the molecular parachor $[P]$ was used as an approximate measure of the bulk of the plasticizer with inflexible structure.

Summary

One second- and sixty second–modulus of cellulose acetate–plasticizer systems were determined by means of the tensile creep test at temperature of 20° to 50°C. In the range of our experimental conditions, the modulus was comparatively insensitive to temperature. The modulus of cellulose acetate decreased to some extent by the addition of plasticizers, though the amount of this decrease was not so large as to change the order. These plasticized cellulose acetates were still insensitive to temperature as in the case of unplasticized acetate. The modulus of cellulose acetate–plasticizer systems decreased as the amount of plasticizer increased, and almost ceased after the amount of plasticizer was over a critical value.

References

1) M. Tanaka, M. Hattori and O. Kamiike, Bulletin of Naniwa University, Series A, **2**, 141 (1954).
2) W. Aiken, T. Alfrey, A. Janssen and H. Mark, J. Polymer Sci., **2**, 178 (1947).
3) *Taken from* R. Houwink, Elasticity, Plasticity and Structure of Matter, Cambridge University Press (1937), p. 248.
4) R. F. Boyer and R. S. Spencer, Advances in Colloid Science, **2**, 1 (1946).