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Author(s)	Tanaka, Masami; Hattori, Makoto; Kamike, Osamu
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Viscoelastic Properties of Cellulose Acetate-Plasticizer Systems*

By

Masami TANAKA,** Makoto HATTORI** and Osamu KAMIKE**

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Abstract

The viscoelastic behaviors of cellulose acetate-plasticizer system were studied at temperature of 20°-50°C. over a wide range of time by means of the tensile creep test. The measurements were carried out on film strips which had been initially orientated equally by applying a small amount of stretch. The effects of the addition of several plasticizers on creep behavior was discussed from the standpoint of activation energies for viscoelastic elongation and the viscosity coefficients for viscous flow, calculated from these data. From these results, the following molecular mechanism concerning the effects of the addition of plasticizer of bulky structure on viscoelastic behavior in the neighbourhood of 20°-50°C. was advanced. That is, tensile creep behavior is more concerned with the "Masking Efficiency" of a plasticizer, which makes the fairly strong polar attraction of polymer chain inactive rather than the diffusion ability of the plasticizer. Hence, the interaction between chain segments decreases and also the activation energy for viscoelastic deformation decreases as the amount or bulk of plasticizer increases. It seems convenient to adopt the "Molecular Parachor" for the approximate measurement of the relative value of molecular bulk of plasticizers. The effects of plasticizer on viscous flow was also discussed.

Introduction

Gearhart and Kennedy¹⁾ by means of a parallel plate plastometer measured the viscosity of cellulose acetate butyrate as a function of the nature and amount of plasticizer, and of temperature. They analysed the data by the use of a four-element mechanical model consisting of springs and viscous dashpots and showed that all constants of this system decrease with rise in temperature or with increase in the plasticizer content.

We have determined the complete deformation- and recovery-time curve for cellulose acetate-plasticizer system by means of the constant-load creep test. In order to remove the differences in orientation, these film strips were previously stretched by applying a small constant weight before the measurements were started. We studied the effects of the type and amount of plasticizers added, referring to the data obtained by these measurements.

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** Department of Applied Chemistry, College of Engineering.

Experimental Procedure

Film strips for creep tests were prepared in the following manner: Cellulose acetate (Degree of Acetylation=ca. 2.5) was dissolved in acetone and a 18% solution was prepared. The plasticizer was added to this solution with constant stirring. Plasticizers used here were butyl-, amyl-, and octylborate (BB, AB, and OB, respectively), dimethylphthalate (DMP), and triphenylphosphate (TPP). The solution was allowed to stand for 24 hours to remove the foams formed, and was poured over a flat horizontal surface of a glass plate. The solvent was allowed to evaporate gradually in a desiccator for about 2 hours, then the film was stripped from the plate and dried in vacuum. Suitable test strips were cut from the films. The plasticizer content was expressed in units of mole ratio of plasticizer to polymer unit molecule.

All the measurements were carried out in a constant temperature box under temperatures ranging from 20° to 50°C., the air in which being stirred constantly with a fan. The temperature was kept constant with a thermo-regulator within $\pm 1/100^\circ\text{C}$.

The tensile creep apparatus used is illustrated schematically in Figure 1.

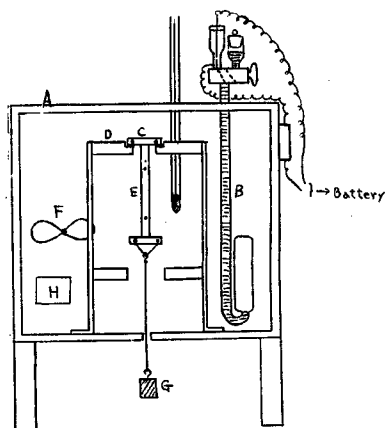


Fig. 1

- A: Constant temperature box.
- B: Thermoregulator
- C: Clamp
- D: Supporter
- E: Test strip
- F: Fan
- G: Lead weight
- H: Heater

The thickness of the strip was measured with a micrometer and width with a reading microscope, both were measured at several points and their average values were computed. In our experiments, the thickness and the width were about 0.05 mm. and 5 mm., respectively. Two light clamps were attached to both ends of the strip, the upper being fixed to the supporter. At the start of the measurement, lead weight was hung onto the lower clamp. Two marks were pointed separately on the middle part of the strip. The length was taken as the distance between these points which was measured with a reading microscope and was about 5 cm. When the data were analyzed, all the initial lengths were converted to 10 cm.

It seems probable that each sample had a different degree of orientation which resulting from the strain produced in the film during the drying process, which was undesirable to neglect. A small weight, 100 g., was applied for about 120 minutes initially in order to maintain the orientation of each sample equal. Thereafter, an additional large weight, 300 g., was added and the creep behavior was observed over a period of 120-240 minutes. Finally, the 300 g. weight was removed to study the relation between creep and its recovery. The change of cross-sectional area with creep was corrected at every point of the creep curve, assuming that the Poisson's ratio was 0.3. Therefore,

the stress, S (g./cm.²), was computed by dividing 300 g. by the corrected cross-sectional area.

The tensile strain, γ , was calculated from:

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

where L_0 is the length of the strip, reached before the additional large weight was applied, and L_t is the elongation at time t after the additional weight was applied. γ/S obtained in the manner mentioned above were plotted against $\log t$.

Experimental Results

The tensile creep curves of cellulose acetate-plasticizer systems which were obtained by means of the above-mentioned procedure are shown in Figure 2 to Figure 9.

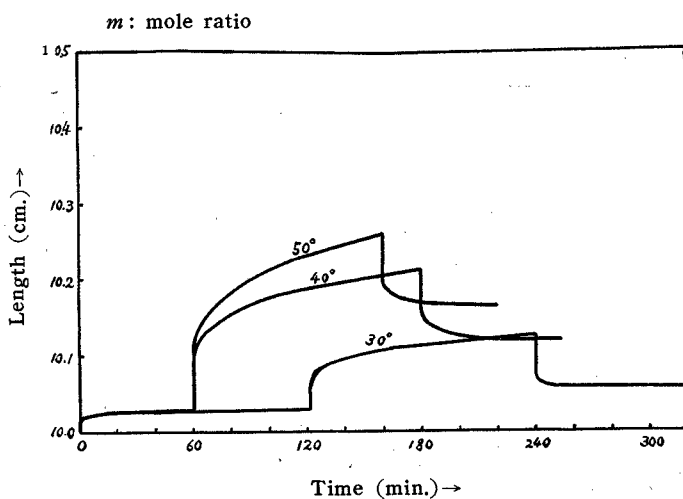


Fig 2 No plasticizer

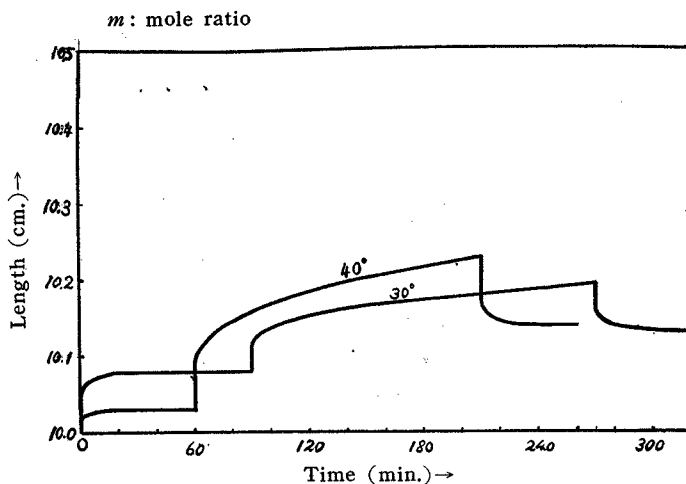
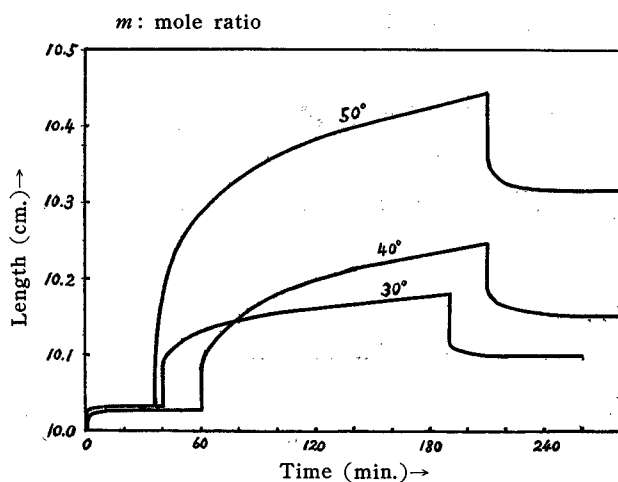
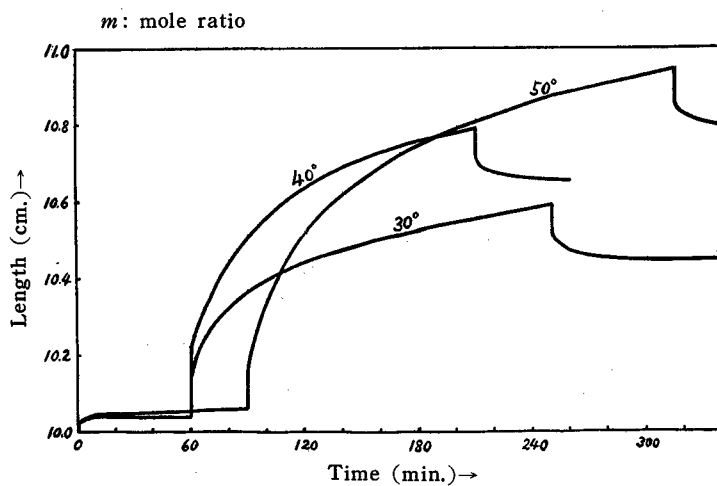
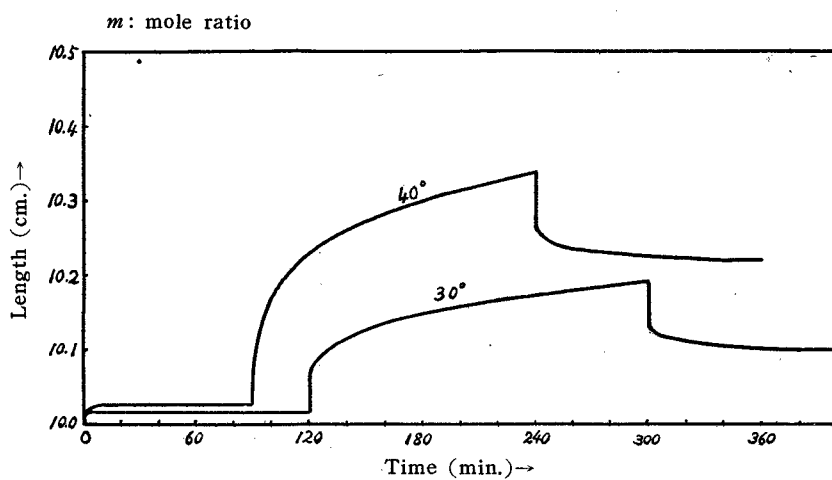


Fig 3 BB. $m=0.18$

Fig. 4 AB. $m=0.15$ Fig. 5 AB. $m=0.67$ Fig. 6 OB. $m=0.04$

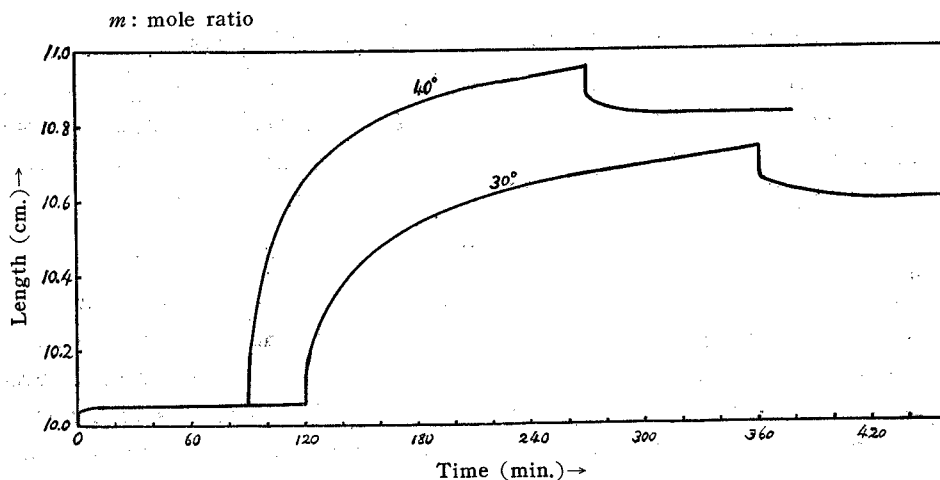


Fig. 7 OB. $m=0.29$

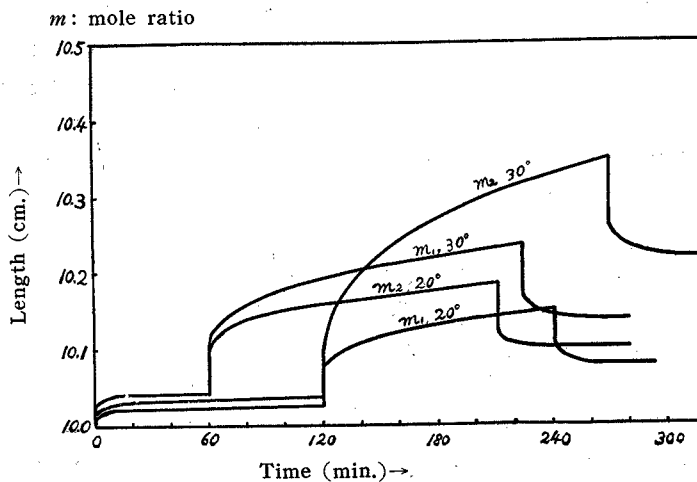


Fig. 8 DMP. $m_1=0.06$, $m_2=0.20$

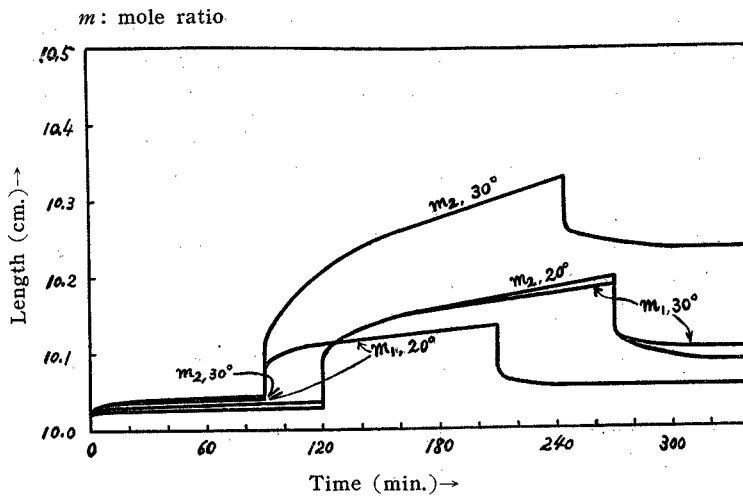


Fig. 9 TPP. $m_1=0.09$, $m_2=0.36$

Analysis of Creep Curves and Discussion of Results

Viscoelastic behavior. Taylor and his coworkers^{2) 3) 4)} measured the elongation of sodium silicate glasses with time (creep) under tensile load near the annealing temperature, and resolved the total deformation into three components—(1) instantaneous elastic elongation: (2) delayed elastic elongation: (3) viscous flow—as follows:

$$E_t = I + L_1(1 - e^{-kt}) + vt,$$

where E_t is the over-all elongation at time t ; I the instantaneous elastic elongation; L_1 the total delayed elastic elongation; e the base of natural logarithms; k the rate constant for the delayed elastic process; v the constant rate of viscous flow; and t time. Previously, we have assumed that the viscoelastic deformation of plasticized cellulose acetate could be approximately represented by a single mean rate constant and analyzed the creep curves. The average value of various rate constants over the range between 10 and 50 minutes after loading was taken as the mean rate constant. Under the above assumption, the elongation curves which we obtained were analyzed by the method used by Taylor and his coworkers in their treatment in the case of glass. The values changing from 20 to 1 kcal./mole were obtained as the activation energies for viscoelastic deformation of cellulose acetate-plasticizer systems, and these activation energies, calculated from our data over the range of 20°–50°C. decreased as plasticizer content increased. Moreover, in concern with the type of plasticizers the larger molar volume or Parachor of a bulky plasticizer is associated with the activation energy for slow creep behavior. It was pointed out by Ichitaro Uematsu, Tokyo Inst. Technol., Japan (at the 4th Annual Lecture-Meeting, Chem. Soc. Japan, April 7, 1951), and the referee of Jour. Polymer Sci. (Sept. 18, 1952) that activation energies of 1–20 kcal./mole seems extremely small for a viscoelastic process. According to letter of the latter usually viscous flow processes involve activation energies of 10–20 kcal./mole, while that of elastic processes are in the range of 50–100 kcal./mole.

We considered that such low energy values resulted from the following two assumptions: (1) Only a mean rate constant was applied over the wide range of viscoelastic deformation. Generally, in the creep behavior of polymer-plasticizer systems which includes plasticized cellulose acetate, the range of continuous change in the rate constants for the stress relaxation processes is much wider than in the Taylor's case of sodium or potassium silicate glass. Dahlquist and his coworkers⁵⁾ in their paper on the constant-stress elongation tests for several soft polymers reported that several terms for delayed elasticity are required to fit an empirical equation to the elongation time curves, and it seems probable that these terms are only an approximation of a very large number of delayed elastic processes having different relaxation times. (2) The viscoelastic deformation for the first 10 minutes after the additional loading was not properly considered, otherwise a definite rate constant could not be obtained. As in the discussion mentioned below, it appears at least in cellulose acetate that the plasticizer has much more influence on the viscoelastic process with shorter relaxation time rather than with one so large.

Similar to the methods used by Aiken and his coworkers⁶⁾ instead of strain itself, all creep curves due to the additional larger load were referred to a unit stress, i. e., plot strain γ divided by stress S (g./cm^2), as a function of common logarithms of time t . Figures 10-15 show the γ/S - $\log t$ relation for the samples.

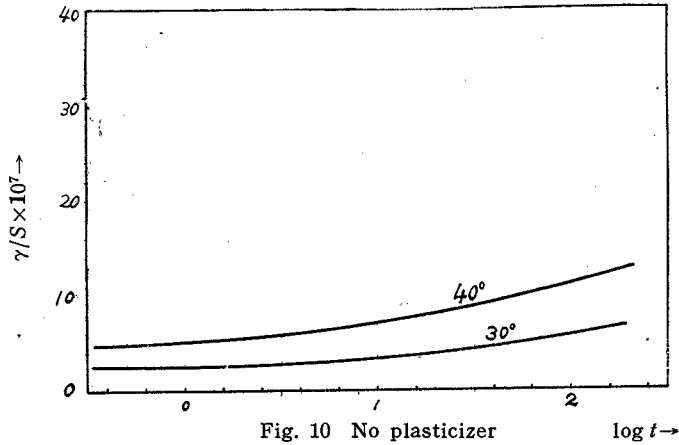


Fig. 10 No plasticizer

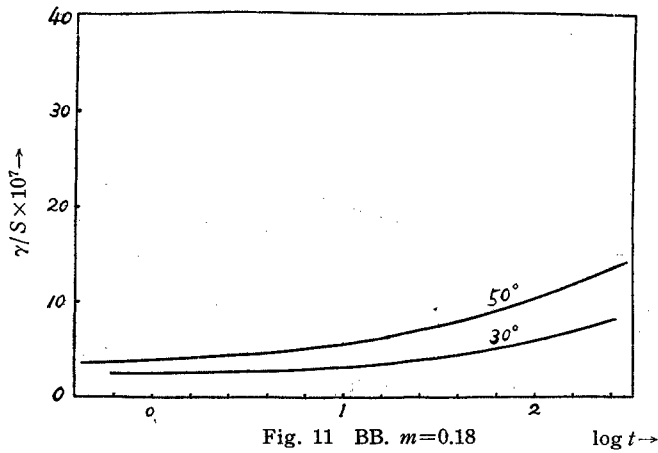


Fig. 11 BB. $m=0.18$

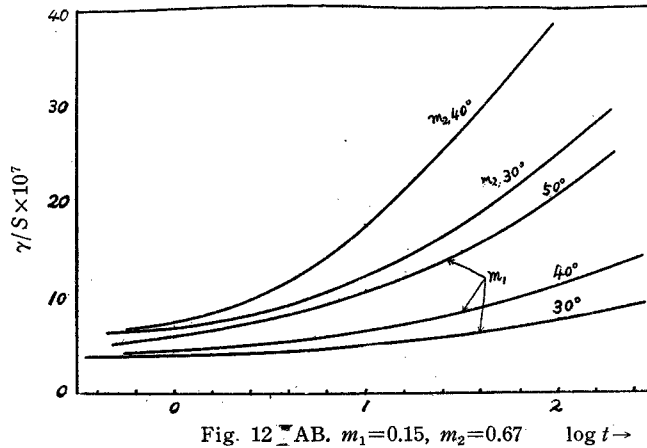


Fig. 12 AB. $m_1=0.15, m_2=0.67$

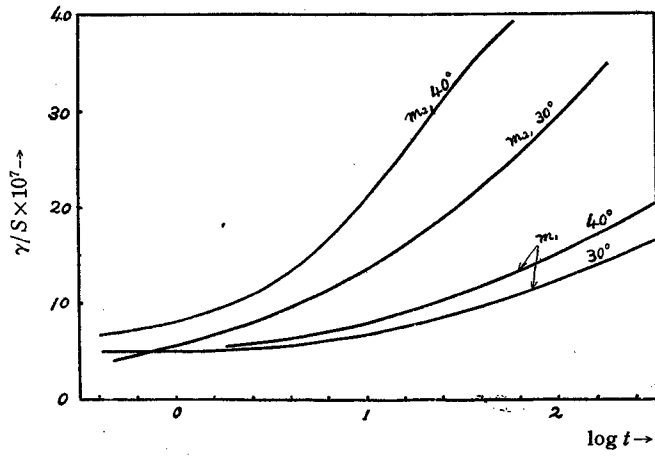


Fig. 13 OB. $m_1=0.04, m_2=0.29$

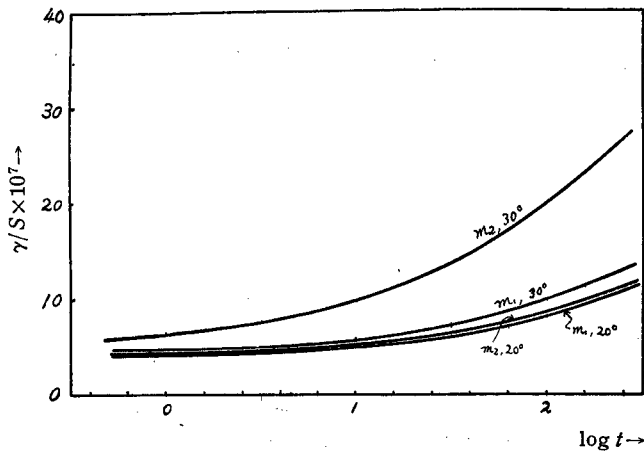


Fig. 14 DMP. $m_1=0.06, m_2=0.20$

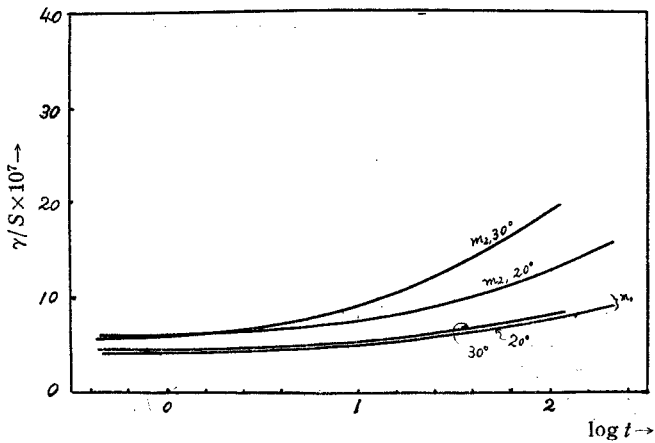


Fig. 15 TPP. $m_1=0.09, m_2=0.36$

The time t_{10} required to reach a γ/S value of 10×10^{-7} was obtained from the each of these curves. Figures 16–21 show how t_{10} vary with the reciprocal of absolute temperature for each sample.

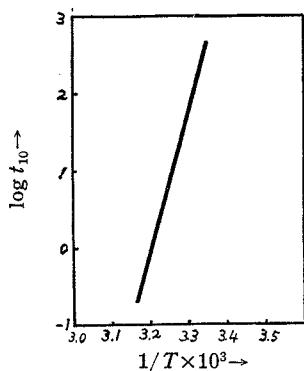


Fig. 16 No plasticizer

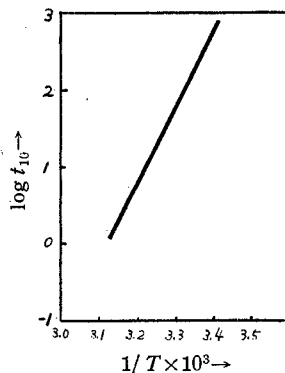


Fig. 17 BB.

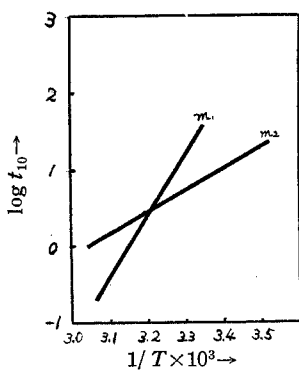


Fig. 18 AB.

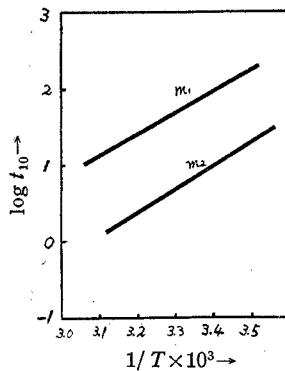


Fig. 19 OB.

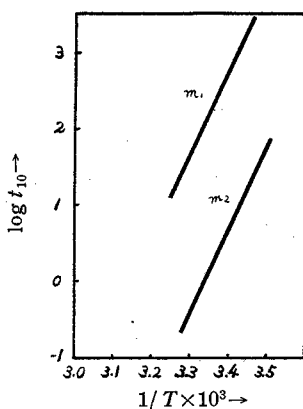


Fig. 20 DMP.

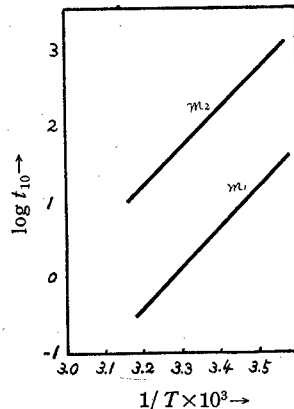


Fig. 21 TPP.

Aiken and his coworkers said in their study of "Creep Behavior of Plasticized Vinylite VYNW", "If the various molecular processes which contribute to the viscoelastic compliance of a plasticized polymer all have the same activation energy, then an increase

in temperature will cause the same relative increase in the rates of all the creep processes. Under these conditions, the creep curves will be rigidly shifted along the log time axis with no change in shape". In our case of cellulose acetate-plasticizer systems, as such shift has been also found approximately true, we can conclude that a single activation energy governs the viscoelastic behavior. As will be shown below, the experimental error was relatively large. The activation energy for viscoelastic elongation (ΔE) can be determined from the slope of the curve obtained by plotting logarithm of t_{10} against the reciprocal of absolute temperature, in the same fashion as in an ordinary kinetic study. The activation energies calculated in this way are shown in following Figure 22. Where, the maximum error of about 5 kcal./mole would result from our experimental and calculating methods.

Obviously in Figure 22 the activation energy decreased as the amount or the molecular Parachor or bulky plasticizer increased. Larger molecular Parachor would, in turn,

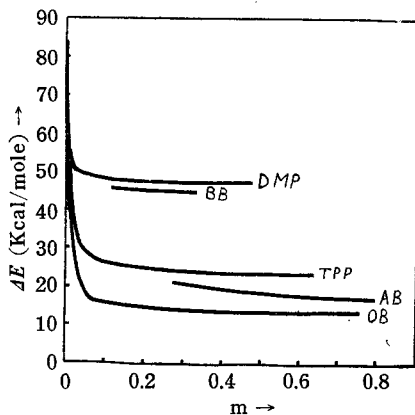


Fig. 22

be associated with larger molar volume for plasticizers in the state of equal surface tension, and also, larger molar volume with higher molecular weight for plasticizers in the state of equal density. We believe that it is convenient to adopt the molecular Parachor rather than the molar volume for the approximate determination of the relative bulk of plasticizers. This molecular Parachor value of a plasticizer is simply obtained by the summation of the atomic and structural Parachor.

Here, it may be reasonable to consider the above behavior as follows. The brittle point test is a fast deformation test, while the tensile creep test used on the cellulose acetate by us is a slow test. Boyer⁷⁾ believed that tensile strength represents the average number of groups inactivated by a plasticizer molecule, whereas the brittle point depends on the ability of the plasticizer molecule to diffuse to points where it is most needed, and from this point of view he accounted clearly for the data obtained by Rider, Sumner, and Myers⁸⁾ on the relation of tensile strength to brittle point for plasticized Vinylite VYNW.

It would appear that the effect of the addition of a plasticizer on tensile creep behavior of cellulose acetate was concerned with the masking action of the plasticizer, which made the polar attraction of polymer chain inactive, rather than its diffusion ability. The motion of chain segments in cellulose acetate is hindered by fairly strong polar attraction. When a plasticizer is mixed in cellulose acetate, the polar groups of the latter cannot approach each other as they will be masked by the plasticizer. Consequently, the reduced interaction between chain segments permits considerable freedom of motion, and the activation energy for creep behavior is decreased. Therefore, it seems

reasonable that this masking efficiency of plasticizer would be proportional to its bulk in the case of plasticizers of bulky and inflexible structure. This is in accordance with our experimental data. These activation energy values for viscoelastic deformation decreased from 100–50 kcal./mole to 20–10 kcal./mole as the molecular Parachor and the amount of plasticizer increased.

Small⁹⁾ ascribed the abnormal diffusion behavior of butyl acetyl ricinoleate relative to the other bulky plasticizer molecules to the difference in molecular shape, and Park¹⁰⁾ showed more recently that not only molar volume but shape is important in determining diffusion rate. It would appear from data for our plasticized polyvinyl chloride¹¹⁾ that the masking efficiency of a plasticizer is also concerned with the shape of its molecule in the case of thin, long, and flexible plasticizers.

Viscous flow. As Dahlquist and his coworkers pointed out in their constant-stress elongation test of soft polymers, the tensile creep method is not a practical tool for measurement of viscosity separated from delayed elasticity in solid state.

It can be seen in Figures 2–9 that the relation between the respective viscoelastic elongation and its recovery, obtained by the application and removal of the larger load, was reversible for unplasticized polymer, but irreversible for plasticized one.

During stretching of polymers, intermolecular attraction and therefore viscosity may gradually increase as a result of orientation, and this gradual change, though extremely small, may occur in tensile creep curve. The final creep of our data may be a viscoelastic process with a relaxation time so great which is nearly equal to viscous flow. Hence, it may be approximately regarded as a viscous flow process. Thus the viscosity coefficients obtained from the slopes of the latter portion of the creep curves, which is almost linear, are given in Figure 23.

It seems that in Figure 23 the viscosity coefficient decreases to some extent with elevation of temperature, while the effect of the difference in the type or the amount of plasticizers was within the experimental error.

Thus, it seems reasonable to consider that the plasticizer is effective in viscoelastic processes with short relaxation time rather than on creep with very long relaxation time which resembles or equals viscous flow in the neighbourhood of 20°–50°C,

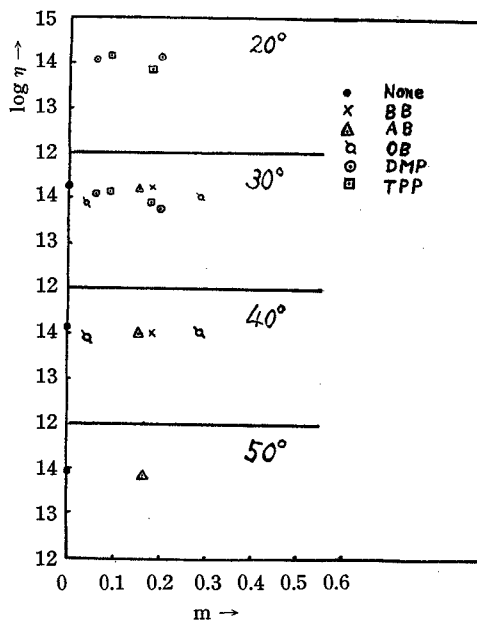


Fig. 23

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