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Elastico-Viscous Properties of Polyvinyl Chloride- and Polyvinyl Acetate- Plasticizer Systems*

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Elastico-viscous behaviors of polyvinyl chloride- and polyvinyl acetate-plasticizer systems at temperatures near the second-order transition point were studied in order to compare with those of glass (*inorganic oxide glass*) which show both elasticity and plasticity remarkably in the transformation range of temperature. The measurements were carried on film strips which had been initially oriented slightly by applying a small amount of stretch. It was found that the creep curves over a wide range of time for the PVC- and PVAc- plasticizer systems were very different in shapes. The effects of the addition of plasticizers on creep behavior was discussed from the standpoints of elastic-, viscoelastic- and viscous flow-behaviors calculated from these data. The modulus of elasticity, activation energy for viscoelastic behavior and viscosity coefficient (or activation energy for viscous flow) were decreased as the amount of plasticizer increased. However, these values almost ceased to decrease when the content of plasticizer became larger than a critical amount, which was in the neighbourhood of 0.05-0.1 expressed in mole ratio of plasticizer to the polymer unit molecule. These results were reported in detail.

Introduction

Elastico-viscous behaviors of polyvinyl chloride- and polyvinyl acetate-plasticizer systems have been studied in the same manner as our previous reports^{1), 2)} on cellulose acetate-plasticizer systems in order to compare with those of glass (*inorganic oxide glass*) which showed both elasticity and plasticity remarkably in the neighbourhood of transformation temperature.

The measurements of creep behavior of polyvinyl chloride- and polyvinyl acetateplasticizer systems were carried out in the neighbourhood of second-order transition temperature. The results observed by Aiken and his coworkers³) mainly at lower temperatures than in our experiment indicated that different plasticizers impart different shapes to the creep curves. In our case at about second-order transition temperature, all plasticizers used gave creep curves of nearly the same shape. The elastic-, viscoelasticand viscous flow-behaviors were analyzed from these results, respectively. Their structural interpretation will be reported later.

I. Experimental procedure and creep curves obtained

Polyvinyl chloride (PVC) (the average degree of polymerization=1,500) was dissolved in cyclohexanon at about 50°C. to prepare a 20% solution; then the plasticizer was added. Plasticizers used for polyvinyl chloride were triacetin (TA), butyl phthalyl butyl glycollate (BPBG), tricresylphosphate (TCP), dioctylsebacate (DOS), diethyl-,

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dibutyl-, diamyl- and dioctyl-adipates (DEA, DBA, DAA and DOA, respectively).

For polyvinyl acetate (PVAc) (the average degree of polymerization=1,300), acetone was preferred as the solvent, and following plasticizers were used: TA, BPBG and TCP.

From these solutions film strips of ca. 0.2 mm. thick and ca. 5 mm. wide were prepared for the creep tests.

Measurements of creep behaviors were carried out under temperatures ranging from 10° to 50° C. by the same method as described previously in our paper¹⁾ where the apparatus and measuring procedures were reported in details. During the early part of the present work, comparatively large loads were applied, *i. e.*, a small weight of 50 g. and additional large weight of 150 g. were applied to the TA-, BPBG- and TCP-PVC systems. On the other hand, 30 g, and then 50 g. weights were applied for DOS- and dialkyl adipates-PVC systems and 10 g. and then 20 g. for PVAc-plasticizer systems in order to subject these systems to moderate deformations.

The elongation-time curves for a few typical samples are shown in Figures 1-3: the creep- and recovery-curves for PVC-plasticizer systems in Figures 1 and 2, and the creep curves for PVAc-plasticizer systems in Figure 3.



Fig. 3. PVAc-Plasticizer.

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Since the change in cross-sectional area of film with creep was corrected at each points in all the curves, assuming that the Poisson's ratio of these polymers was 0.3, the stresses S (g./cm.²) have been calculated for the actual area. All creep curves due to the additional larger load were referred to a unit stress, *i.e.*, plot strain γ divided by stress, as a function of common logarithms of time t.³⁾

These results are shown in Figures 4-11 for PVC-plasticizer systems and for PVAcplasticizer systems in Figures 12-15. One second- and sixty second-moduli written in these figures would be mentioned in the next part.

The almost analogous and almost flat shapes were obtained for all creep curves of PVC-plasticizer systems in the temperature range of 10° to 50°C. This tendency was remarkable in the early periods of creep. And these curves became somewhat steep, though gradually, as the temperature was elevated and the amount of plasticizer increased.



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In our creep curves, a formulation consisting of PVC plus 0.138 mole ratio-TA partially exhibited less creep at temperature of 30°C. than a formulation containing only 0.053 mole ratio-TA. It had been reported by Alfrey, Jr. and his coworkers⁴⁾ that a particular formulation was stiffer than would be expected from the properties of other similar formulations and these anomalous mechanical properties occured infrequently. They concluded that the structural origin of the unusual stiffness lies in the excessively large extent of crystallization, although the reasons why certain samples exhibited this effect is not known.

In the case of PVAc-plasticizer systems, almost similar shapes of creep curves were obtained in the temperature range of 10° to 20°C. These curves were very flat in the region of initial creep. However, they became extremely steep curves after a certain time. This inflexion region of creep curve shifted with elevation of temperature and addition of plasticizer. It seems that these differences in creep curves between PVC- and PVAc-plasticizer systems should be discussed from the standpoint of their characteristics in isogel structure.

II. Elastic Behavior Results

Very flat shapes were obtained for the early periods of creep curves of the PVCplasticizer systems within the temperature range of 10–50°C. This tendency of flat shape for the early period was also true for the creep curves of PVAc-plasticizer systems at temperatures from 10° to 20°C. Therefore, it would be possible to determine a reliable modulus of elasticity by extrapolation of these curves toward the initial period of creep.

In the manner similar to the case of our cellulose acetate-plasticizer systems,²⁾ the one second modulus (ε_1) was calculated from the extrapolated value of γ/S at period of 1/60 min. by the use of following equation:

 $\varepsilon = 1/(\gamma/S)$.

The sixty second modulus was also obtained from the observed value of γ/S at period of 1 min. These results are shown in Figures 16-26. The values of PVC-plasticizer systems are given in Figures 16-22, and those of PVAc-plasticizer systems in Figures 23-26.



Discussion

Elastic behavior of PVC-plasticizer systems. It is natural that the values of one second moduli obtained by the tensile creep test were somewhat higher than sixty second moduli. By extrapolating the $\log \varepsilon_1 - t$ (temperature in degree Cersius) curve of unplas-







ticized PVC to lower temperature side, we obtained 2.5- 1.3×10^{10} dyne/cm.² as values of ε_1 at 25-30°C., which showed good agreement with the value obtained by Walter⁵⁾ in compression test. In Figures 27-30, the tendency of the dependence of ε_1 and $\varepsilon_{\varepsilon_0}$ on temperature is shown for each system containing different types and varying of plasticizers. As a whole $\log \varepsilon - t$ curves for PVC were lowered along the $\log \varepsilon$ axis by addition of plasticizers. Increasing the amount of plasticizers at first

> caused the shapes of curves to flatten at the side of the higher temperature, and then, with further increase such changes also extended toward the region of lower temperature. Of course, the above mentioned behavior of $\log \epsilon - t$ curves differed according to the type of plasticizers used. Especially, the differences in behavior were very characteristic between plasticizers having bulky, inflexible structures such as BPBG and TCP, and plasticizers having comparatively long, flexible structures such as dialkyladipates. This phenomenon seems to be closely associated with transition temperature of solid **PVC-plasticizer** systems. For the discussion of these relations, it is necessary to consider the effect of the amount of plasticizer on the modulus of solid PVC-plasticizer systems.

It is obvious from Figures 31–34 that the modulus decreases with increase in the amount of plasticizer. It may be understood, however, from the correlations of ε and m shown in Figures 32-34, that there are limits to the decrease of modulus, *i.e.*, modulus was considerably lowered until the amount of plasticizer was increased to m=ca. 0.1, but it no longer decreased when the amount of plasticizer became larger than m=ca. 0.1. The critical amount of plasticizer at various temperatures, where a almost flat $\log \varepsilon - m$ curves are obtained, were different for each plasticizers and the range of this critical amount was m=ca. 0.05 to 0.1 in our experiments.

From such observations, it may be considered that at temperatures above the second-order transition temperature, Tm, the amount of plasticizer has no appreciable effect upon the variation of modulus, while at temperatures lower than Tm, modulus decreases with increase in the amount of plasticizer. For example, Tm of unplasticized PVC is 75°C.6) and it is lowered by addition of plasticizer; Tm are 23°C.7) and 12°C.7) for the PVC containing of 33.3% and 0.1 mole fraction of TCP, respectively. These facts agree with the results we obtained and are shown in Figure 27 (log $\varepsilon - t$ relation) and Figure 32 (log $\varepsilon - m$ relation). The moduli of PVCplasticizer systems are gradually lowered until the amount of plasticizer reached the critical value mentioned above. Under the conditions of our experiments, plasticizers having inflexible, bulky structures are more effective than those having linear structures, and molecules of larger bulk (represented by molecular parachor, [P], here) are more effective in both types of plasticizers. At higher temperatures, however, such difference becomes inappreciable. These behaviors may be associated with the softening effect of plasticizers.

Elastic behavior of PVAc-plasticizer systems. One second-modulus was larger than sixty second-modulus in each system similar to the case of PVC-plasticizer systems. We have only obtained a few data for these systems. The relations of $\log \varepsilon - t$ for all specimens are shown in Figures 35 and 36. As seen in these figures, the $\log \varepsilon - t$ curves are considerably steep, and it is obvious that the temperature dependence of unplasticized PVAc and especially that of plasticized PVAc are remarkably great. That is, at about

 10° C., all the specimens were neither too soft nor ε too small. At about 20° C., however, modulus decreased rapidly and at temperatures above 20° C. the sample became too soft to measure the modulus by the tensile creep test.

Figures 37-39 shows the effect of the amount of plasticizer on the modulus. At temperatures about 20°C. lower than the Tm for unplasticized PVAc, *i. e.*, at *ca.* 10°C, the effect of the amount of plasticizer on the modulus seems to be inappreciable, but at temperatures about 10°C. lower than Tm, *i. e.*, at about 20°C, the variation of modulus becomes sensitive to changes in the amount of plasticizer. The temperature at which the value of modulus varies sensibly is different for each plasticizer. For example, the sensible changes occurred at about 15°C. and 20°C. for BPBG and TCP, respectively.

For solid PVC-plasticizer systems, we came to the conclusion that, among the series of plasticizers having similar structures, the plasticizer of large molecular bulk had greater effect in decreasing the modulus. For solid PVAc-plasticizer systems, although the moduli of the systems of PVAc-BPBG and PVAc-TCP at about 15°C. were inconsistent with those observed in PVC-plasticizer systems, at higher temperatures (*ca.* 20°C.) tendency similar to the systems of PVC-plasticizer were observed. This conclusion must be restricted to those plasticizers which we have studied.

III. Viscoelastic- and Viscous Flow-Behaviors Results

Viscoelastic behavior. In order to determine the activation energy (ΔE_v) for the

viscoelastic behavior of PVC-plasticizer systems, the time z'_{20} required to reach a γ/S value of 20×10^{-6} obtained from almost all of the curves in Figures 4-11 was generally used. The time required to reach smaller or larger γ/S value was respectively obtained

only in a few cases of the creep curves with very small or large elongation. For the determination of activation energy for the viscoelastic behavior of PVAc-plasticizer systems, the time z_{10}^{n} required to reach a γ/S value of 10 $\times 10^{-5}$ obtained from Figures 12-15 was used and the time required to reach a value smaller than 10×10^{-5} was obtained only in a few cases of extremely small elongation curves. Relation of z_{20}^{n} (or z_{10}^{n}) vs. the reciprocal of absolute temperature are shown in Figures 40-42.

We have seen that the creep curve for materials of PVC- and PVAc-plasticizer systems

were rigidly shifted along the log time axis with little change in slope. Therefore, we can conclude that the various moleclar processes which contribute to the viscoelastic compliance of these materials have the same activation energy,³⁾ and then roughly determined ΔE_v of each material from the slope of the curves obtained by plotting log z'_{20} (or z''_{10}) against the reciprocal of the

Fig. 40. PVC-Plasticizer.

Time (after the application of the large weight) (min.) Fig. 44. PVC-Plasticizer.

Fig. 45. PVC-Plasticizer.

absolute temperature. ΔE_v calculated in this way are shown in Figure 43.

A somewhat large error of about 5 Kcal./mole would be contained generally in the activation energy for viscoelastic behavior at the above-mentioned point $(z'_{20} \text{ or } z''_{10})$, and the maximum error of about 10 Kcal./mole may occur though very seldom.

Viscous flow. It can be seen in a few typical Figures 1 and 2 of the PVC-plasticizer systems that the relation between the respective viscoelastic elongation and its recovery, obtained by the application and removal of the larger load, was irreversible except for unplasticized PVC at temperature of 30° C. The final creep of our data may be a viscoelastic process with a relaxation time so great being nearly equal to a viscous flow, and it may be approximately regarded as a viscous flow process. Thus, the viscosity coefficient (η) for viscous flow of PVC-plasticizer systems was obtained from the slope of the later portion of the creep curve, which was almost linear as shown in Figures 44-46, by the use of following equation:

$$\eta = (20 MgL)/(A_V),$$

where M is the total weight applied to strip (gr.); g the acceleration of gravity; L the length of strip (cm.); A the corrected cross-sectional area (cm.²); and $_V$ the velocity of elongation (cm./min.).

The results are given in Figure 47.

The viscosity coefficient for viscous flow of PVAc-plasticizer systems was also found from the later portion of creep curve shown in Figure 48. As these values were sensitive

Fig. 48. PVAc-Plasticizer.

Table	
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to temperature, the activation energy $(4E\eta)$ for viscous flow of these systems was determined from log η vs. 1/T curves.

The results obtained are shown in Table 1.

Discussion

Plasticizer	<i>m</i> (mole ratio)	$\eta \times 10^{-10}$ (poise)			ΔE_{η}
		10°	15°	2 0°	(Kcal./mole)
None	0	2×10^2	_	5	6×10
TA	0.05	5	-	2	2×10
BPBG	0.04	—	3	2	2 ×10
TCP	0.04	—	3	2	2×10
	1	1	1		

The values of 78 and 48 Kcal./mole were obtained for the activation energy for viscoelastic behavior of unplasticized PVC and PVAc, respectively. Obviously in Figure 43 the activation energy ΔE_v of both plasticized PVC and PVAc decreased as the amount of plasticizer increased. However, the activation energy almost ceased to decrease when the amount of plasticizer became larger than a critical amount, which was in neighbourhood of 0.05-0.1 in mole ratio. These minimum values of activation energies were about 20-40 and 10-20 Kcal./mole for plasticized PVC and PVAc, respectively.

It was found in the case of plasticizers of bulky structure type such as TA, BPBG and TCP that the activation energy ΔE_v of PVC-plasticizer systems decreased as the bulk of the plasticizer increased. This was also true in the case of PVAc-plasticizer systems. Here, the molecular Parachor [P] of plasticizer was used for the comparison of their relative bulk. The effect of the addition of long chain type plasticizers such as DOS or dialkyl adipates on the activation energy ΔE_v was more complicated and was considerably different from that of plasticizer with bulky structure. In the same manner as shown by Park⁸ in determining the diffusion rate of plasticizer molecule, not only molar volume but shape of plasticizer molecule would be concerned with decreasing the ΔE_v of plastics.

It can be seen in Figure 47 that the viscosity coefficient of PVC-plasticizer systems decreased to some extent (in the range of 10^{12} to 10^{13} *poise*) as the amount of plasticizer was increased and the temperature elevated.

The effect of the difference in type of plasticizer on the viscosity coefficient of PVCplasticizer systems was within experimental error. The temperature dependency of viscosity coefficient η was so small within the temperature range of 10° to 50°C. that we could hardly determine the activation energy $\Delta E\eta$ for viscous flow.

On the other hand, the temperature dependency of viscosity coefficient for PVAcplasticizer systems was remarkable at temperatures from 10° to 20°C., where the value of viscosity coefficient varied within the range of 10¹⁰ to 10¹² poise as shown in Table 1. From these values of viscosity coefficient, the activation energy for viscous flow $\Delta E \eta$ of ca. 60 Kcal./mole was obtained for unplasticized PVAc and ca. 20 Kcal./mole for three kinds of plasticized PVAc. However, as regards the plasticized PVAc in our experimental conditions, the effect of difference in type of plasticizer on the activation energy for viscous flow $(\Delta E\eta)$ was not found. Since ΔE_v for PVC-plasticizer systems were larger than those for PVAc-plasticizer systems in the same temperature region, it may be seen that PVC-plasticizer systems have viscoelastic structures stronger than the latter. As previously described, ΔE_v and ΔE_η for unplasticized PVAc were ca. 50 and 60 Kcal./mole, respectively, and for plasticized PVAc (m=0.04-0.05) both were ca. 20 Kcal./mole. It is interesting that the values of ΔE_v computed from relatively earlier parts of the creep curves were comparable with the values of $\Delta E\eta$ which were computed from later parts of the creep curves, where each sample was subjected to a large elongation. That is, if assumed that the error resulted from the difference in the manner of computation for ΔE_v and ΔE_η is not so large, it may be said that the deformations at both parts of creep curves take place under approximately the same molecular process.

Discussion on the molecular mechanism of these elastico-viscous behaviors shall be reported in another paper.

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