

Viscoelastic Properties of Plasticized Amylose Triacetate Films

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Synopsis

The viscoelastic properties of amylose triacetate films plasticized with diisobutyl phthalate were studied. The modulus-temperature curves of diisobutyl-phthalate-plasticized amylose triacetate are typical for amorphous polymers with the decrease of amylose triacetate content. The glassy modulus is not affected by the incorporation of diisobutyl phthalate, but the rubbery modulus and glass transition temperature are depressed with increased diisobutyl phthalate. The rubbery modulus appears at first to maintain for a wide temperature range, then disappears with increased diisobutyl phthalate. From the results of modulus-time measurements and x-ray diffraction patterns: in a system of amylose triacetate-diisobutyl phthalate, amylose triacetate exists as an amorphous polymer at all concentrations of amylose triacetate and it acts intermediately between semicrystalline and amorphous polymers at lower concentrations below about 90%.

INTRODUCTION

Amylose triacetate is similar to cellulose triacetate in that both contain substituted D-glucopyranose rings; but in the former these rings are jointed by α -D-(1 \rightarrow 4) linkages, while in the latter the linkage is β -D-(1 \rightarrow 4). Because of this difference, amylose triacetate exhibits different physical and chemical properties.

X-ray diffraction patterns of amylose triacetate in the solid state give typical amorphous patterns.¹ Moreover, the crystal structure of amylose triacetate is a nonintegral helix² as determined by x-ray diffraction of an oriented film sample.

It is reported that amylose triacetate changes to a more crystalline form when it is heated at 185°C¹ and that amylose triacetate films upon stretching become birefringent and increase in tensile strength. This is evidence that a molecular orientation occurs within the film during stretching.³

Some studies have been reported on the mechanical properties of amylose triacetate films;^{1,4} and the viscosity properties of amylose triacetate in dilute solution⁵ has been reported. In this paper we report same data of the viscoelasticity of amylose triacetate films plasticized with diisobutyl phthalate.

EXPERIMENTAL

Materials

The amylose sample used in this experiment was supplied by the AVEBE Co., Ltd., of Poland. This sample has an iodine absorption number of 16 ~

17% and an \bar{M}_w of 1.5×10^5 . The amylose triacetate sample was obtained by the acetylation of amylose with acetic anhydride under pyridine catalyst.⁶ The plasticized amylose triacetate films and plates used in the measurements were prepared by casting from appropriate chloroform solutions and by evaporation of the solvent *in vacuo* at 70°C. All samples used were kept in a silicone desiccator.

Diisobutyl phthalate (Wa Ko Pure Chemical Industries Co., Ltd.) was used as plasticizer. 500 cs of TSF451 silicone oil which was supplied by Toshiba Co., Ltd. (Japan) was used.

Methods

Modulus-Temperature Curves

Both torsional and tensile measurements were employed. The torsional modulus $G(10)$ after 10 sec was measured by a home-made apparatus in which a 0.5-kg-m capacity torque meter (supplied by Shin Koh Communication Industry Co., Ltd.) was used as a strain gauge transducer. The tensile modulus $E(10)$ after 10 sec was measured by a modified stress relaxation apparatus.⁷ The values of $G(10)$ were multiplied by 3 to approximate the tensile modulus $E_r(10)$, and $\log 3G(10)/\log E(10)$ -temperature curves were plotted.

Modulus-Time Curves

Stress relaxation measurements were carried out with the use of a modified stress relaxation apparatus.⁷ Values of $\log E_r(t)$ were plotted against time for a wide range of temperatures.

Glass Transition Temperatures (T_g)

The specimens were immersed in silicone oil of selected viscosity. The T_g were obtained from the discontinuous point in the slope of the buoyant weight versus temperature plots.

X-ray Analysis

X-ray photographs were obtained with a flat-film camera with a film-to-sample distance of 5.00 cm; Cu K_α radiation was employed.

RESULTS AND DISCUSSION

The plots of \log torsional modulus $3G(10)$ —that is, $E(10)$ and tensile modulus $E(10)$ —versus temperature T curves for amylose triacetate-amylose triacetate plasticized with varying amounts of diisobutyl phthalate, are shown in Figure 1.

In unplasticized amylose triacetate, the \log modulus curve decreases slowly over a wide temperature range and the acetate may be slight crystalline.⁸ With decreasing concentrations of amylose triacetate in the specimens, the \log modulus curves are depressed rapidly and then flow initially. The modulus curves of plasticized acetate are semicrystalline polymers at the higher concentration of amylose triacetate and pass to those of nearly amorphous

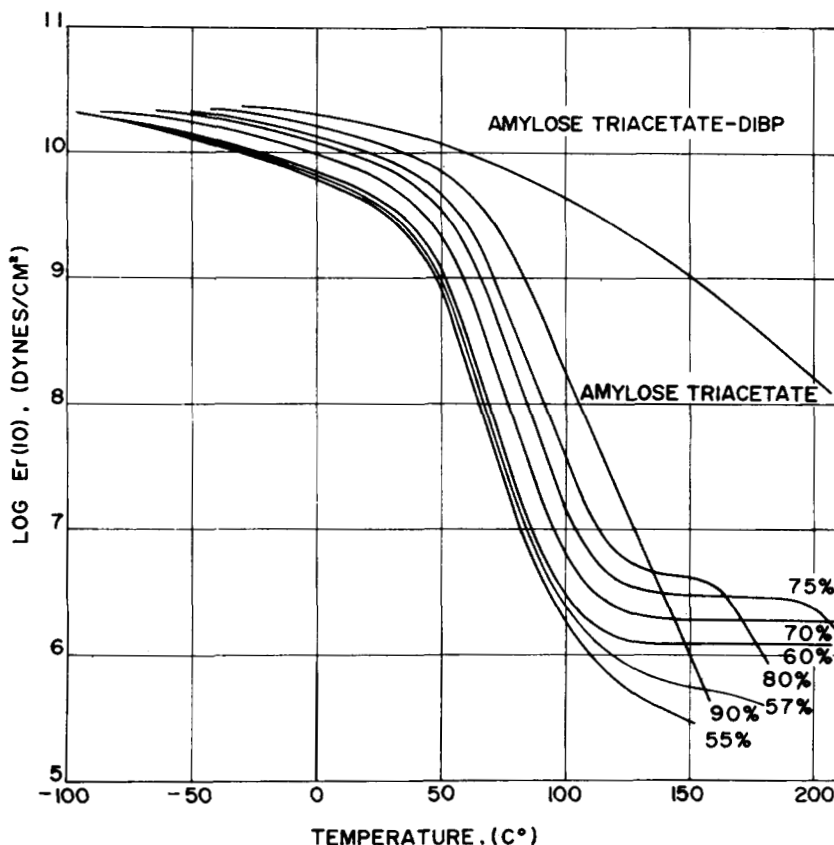


Fig. 1. 10-sec modulus $E_r(10)$ vs. temperature for amylose triacetate-diisobutyl phthalate (DIBP) systems.

polymers, with the decrease of amylose triacetate content. The rubbery plateau appears short at about 80% amylose triacetate and long at 60% amylose triacetate.

Table I gives the values of characteristic parameters obtained from the log modulus versus temperature curves, together with T_g . That is, T_i is defined as the temperature at which $E(10)$ equals 10^9 dyne/cm² and S is the negative

TABLE I
Characteristic Parameters for DIBP^a-Plasticized Amylose Triacetate Films

Amylose triacetate concentration, wt-%	T_i , °C	S	T_g , °C
55	47.7	0.115	
57	49.5	0.113	
60	51.5	0.110	
70	58.7	0.098	
75	65.6	0.092	57.0
80	70.5	0.086	62.0
90	83.5	0.077	

^a Diisobutyl phthalate.

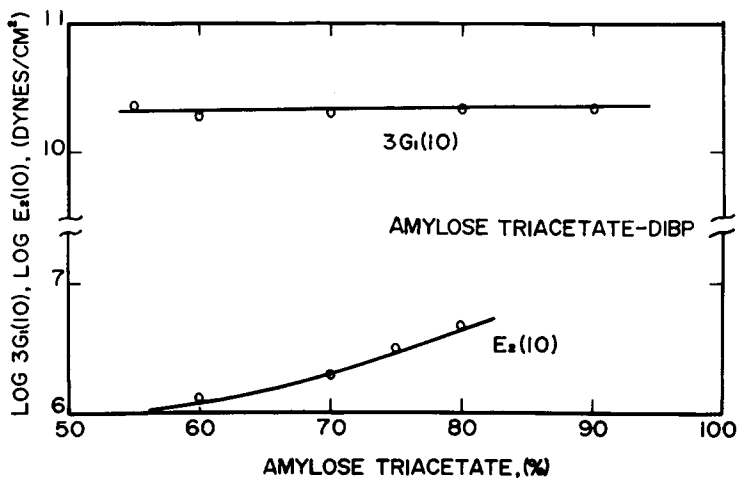


Fig. 2. The glassy modulus $3G_1(10)$ and the rubbery modulus $E_2(10)$ vs. amylose triacetate concentration for amylose triacetate-DIBP systems.

slope of the curve at T_i . Figure 2 shows the plots of $\log 3G_1(10)$ and $\log E_2(10)$ versus amylose triacetate concentration curves.

The glassy modulus $3G_1(10)$ is independent of the incorporation of plasticizer; but T_i , T_g , and the rubbery modulus $E_2(10)$ are depressed with increasing concentrations of plasticizer. On the contrary, the value of S increases with increasing concentration of plasticizer.

The values of S are reported between 0.13 and 0.25 for several linear amorphous polymers.⁹ Therefore, the values S reported in Table I for plasticized amylose triacetate at the lower concentration range are thought to be a little smaller for an amorphous polymer.

Poly(vinyl chloride) and plasticized poly(vinyl chloride) with 30 wt-% of dioctyl phthalate¹⁰ and plasticized amylose with below 40% of dimethyl sulfoxide¹¹ are contrasted with some of these results. In these investigators' results of poly(vinyl chloride), T_i and S were depressed, but $3G_1(10)$ and $3G_2(10)$ do not change with plasticization. Their sample was slightly crystalline in the state of plasticization. The samples of amylose-dimethyl sulfoxide were crystalline above 60% amylose—and the samples containing 40% diisobutyl phthalate used in this experiment were very slightly crystalline, which could be detected from x-ray measurements as shown in Figure 3.

In poly(vinyl chloride) and plasticized poly(vinyl chloride), their constancy of rubbery modulus was explained: the degree of crystallinity and the volume concentration of crystallites are not altered very markedly by the incorporation of diluents beyond the obvious dilution effect.¹⁰

An explanation of the somewhat different behavior of poly(vinyl chloride) and amylose in plasticization was suggested as follows:¹¹ it was supposed that the crystallinity of the sample of poly(vinyl chloride) was not changed by the incorporation of plasticizer—therefore: a same amount of crystallite as that which can support an external strain to constancy. With plasticization, the rubbery modulus $3G_2(10)$ did not decrease but the value of S decreased. In the case of amylose, the crystallinity of the sample increases with the increasing amylose—therefore: the rubbery modulus increase.

An explanation of amylose triacetate in plasticization is as follows: It is supposed that in the case of amylose triacetate, the crystallinity of the sample decreases with the decreasing amylose triacetate and therefore the rubbery modulus decreases, but the interaction fraction of crystallite with plasticizer increases with decreasing amylose triacetate, and therefore the rubbery modulus holds. That is to say, two competitive factors—the decreasing number of crystallite and the increasing interaction fraction of crystallite with plasticizer—exist, and the rubbery modulus holds at the balance of the two competitive factors.

The fact that specimens containing between 80% and 60% amylose triacetate show rubbery moduli that hold for a wide temperature range and do not show any flow until the decomposition of plasticizer (at 327°C for about 60% amylose triacetate), is especially interesting. This is explained by the cross-linking of amylose triacetate under the incorporation of plasticizer during measurement.

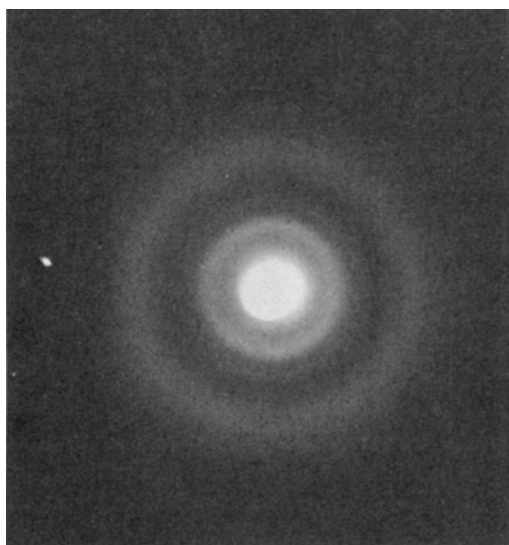


Fig. 3. X-ray diffraction diagram of plasticized amylose triacetate with 40% of DIBP.

Films of amylose triacetate and plasticized amylose triacetate with below 30% of diisobutyl phthalate showed broad diffuse halos and were evidently amorphous. Specimens to amylose triacetate films heated for 15 min at 185°C changed to a more "crystalline" form showing several rather clearly defined rings of x-ray diffraction diagram.¹ Moreover, the x-ray pattern of stretched films of amylose triacetate produces a typical fiber pattern and there occurs a periodicity of 18.3 Å., along the fiber (b) axis.³ The x-ray diffraction diagram of an oriented fiber of amylose triacetate presents evidence for nonintegral helical structure.²

In Figures 4 and 5, the stress relaxation curves for plasticized amylose triacetate samples containing 85%, 80%, and 75% are shown. The $\log E_r(t)$ versus $\log t$ curves for the 85% amylose triacetate sample, as expected, change the transition region with time and the rubbery region is not marked as compared with the typical amorphous polymers.

The sample containing 80% and 75% amylose triacetate shows the behavior of a nearly amorphous polymer. To apply the time-temperature superposition principle to these samples, the master curves obtained by shifting data horizontally along the $\log t$ are shown in Figure 6.

The characteristic parameters for stress relaxation master curves are listed in Table II. In Table II, E_1 and E_2 are the glassy-state modulus and rubbery modulus, respectively. T_i is the temperature at which $K(T) = 10$ sec where $K(T)$ is the time required for $E_r(t)$ to reach a value of 10^9 dyne/cm². n is the negative slope of the $\log E_r(t)$ versus $\log t$ master curve at $E_r = 10^9$ dyne/cm². p is the slope of the $\log [K(T)/K(T_i)]$ versus $T - T_i$, which is nearly linear in the immediate vicinity of T_i .

To compare the characteristic parameters of plasticized polymers with those of linear amorphous polymers: the values of parameters are smaller, with the great difference being the much smaller value of np for plasticized polymers.

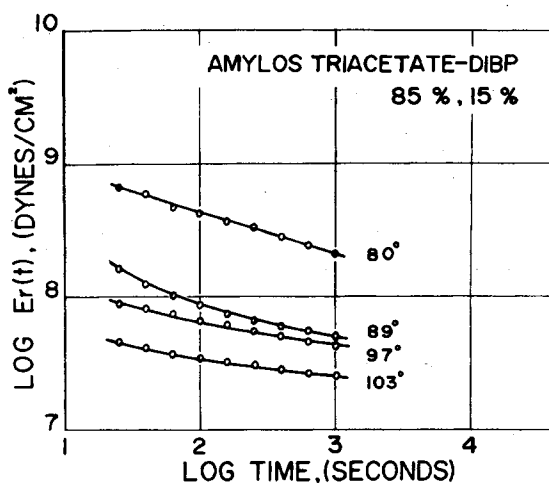


Fig. 4. Modulus-time curves for amylose triacetate-DIBP system (85%, 15%).

In Table II, the n values of plasticized polystyrene and plasticized poly(methyl methacrylate) are nearly equal to 0.5, the theoretical value of Rouse¹³ and Bueche¹⁴ for amorphous polymers. Amylose triacetate, amylose, and poly(vinyl chloride) have values smaller than 0.50 in the plasticized, slightly crystalline form. Unplasticized linear, amorphous polymers often have values larger than 0.50.

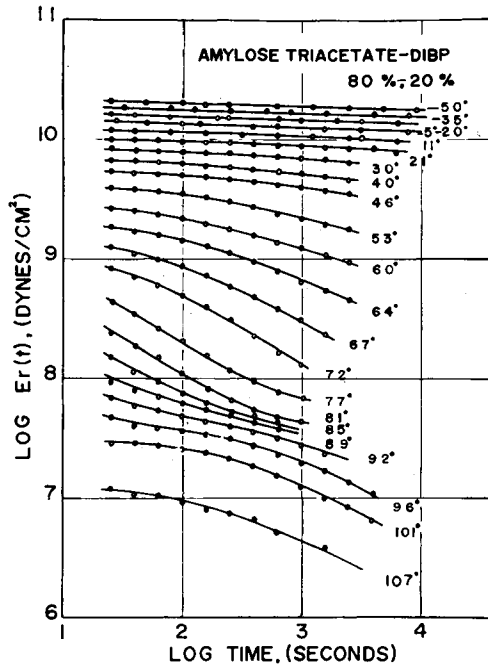
As can be seen in Figure 6, a very broad master curve of amylose triacetate is obtained. This is also reported for plasticized poly(vinyl chloride) having a slightly crystalline and plasticized amylose with 45% of dimethyl sulfoxide.¹¹ These results may be explained by the possibility that some kind of firm aggregation exists. Another possible explanation might be the existence of nonintegral helical conformation of amylose triacetate in diisobutyl phthalate mixtures. Because of this, diisobutyl-phthalate-plasticized amylose triacetate of about 75% amylose triacetate content acts intermediately between semicrystalline and amorphous polymers.

TABLE II
 Characteristic Parameters for Stress Relaxation Master Curves

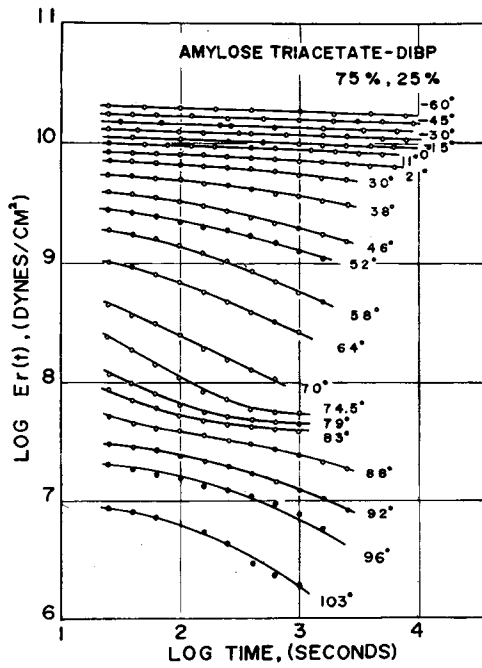
	$E_1 \times 10^{10}$, dyne/cm ²	$E_2 \times 10^{-7}$, dyne/cm ²	T_i , °C	n	p	np
Linear Polymers						
Polyisobutylene ^{ref 9}	3.02	0.759	-64.6	0.75	0.21	0.15
Polystyrene ⁹	2.00	0.339	93.1	0.87	0.26	0.22
PMMA ^{a ref 9}	2.82	2.51	113.3	0.54	0.33	0.18
Plasticized Polymers						
Polystyrene-DOP (100/20) ^{ref 12}			38.2	0.50	0.178	0.089
PMMA-DOP(100/20) ^{ref 12}			69.6	0.49	0.115	0.056
Poly(vinyl chloride)-DOP(100/20) ^{ref 12}			43.6	0.29	0.135	0.056
Amylose-DMSO ^b (55/45) ^{ref 11}	3.62	—	-22.5	0.34	0.18	0.064
Amylose triacetate-DIBP(80/20)	3.00	—	72	0.33	0.135	0.045
Amylose triacetate-DIBP(75/25)	2.85	—	66.5	0.37	0.146	0.054

^a Poly(methyl methacrylate).

^b Dimethyl sulfoxide.



(a)



(b)

Fig. 5. Modulus-time curves for amylose triacetate-DIBP system: (a) 80%, 20%; (b) 75%, 25%.

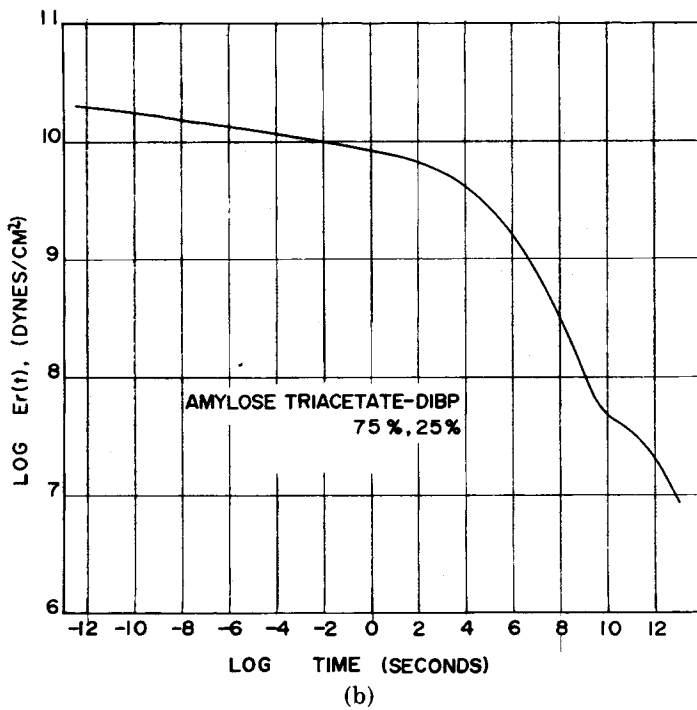
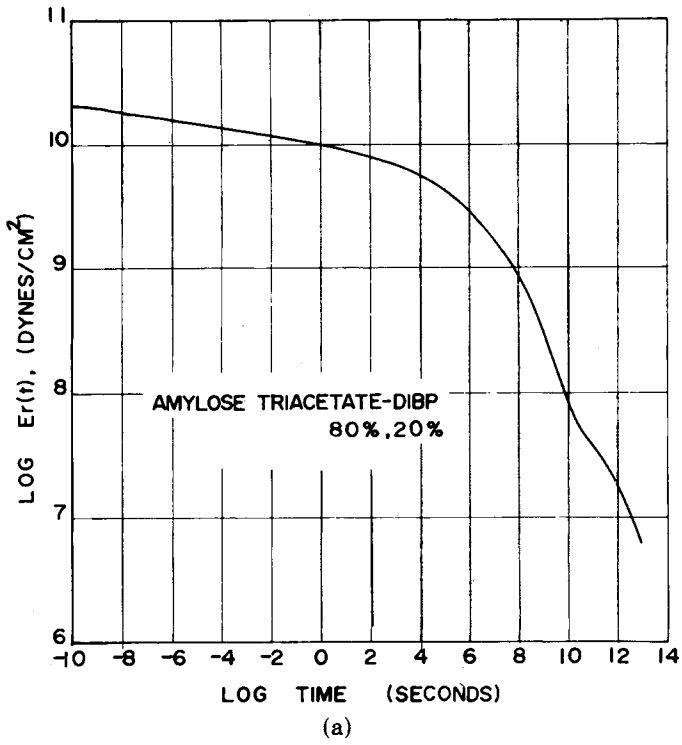


Fig. 6. Master curve plotted as $\log E_r(t/K)$ vs. $\log (t/K)$ for amylose triacetate-DIBP system: (a) 80%, 20%; (b) 75%, 25%.

The following equation¹⁵ deals with the temperature dependence of $K(T)$:

$$\log \frac{K(T)}{K(T_i)} = \frac{-16.14(T - T_i)}{56 + (T - T_i)} \quad (1)$$

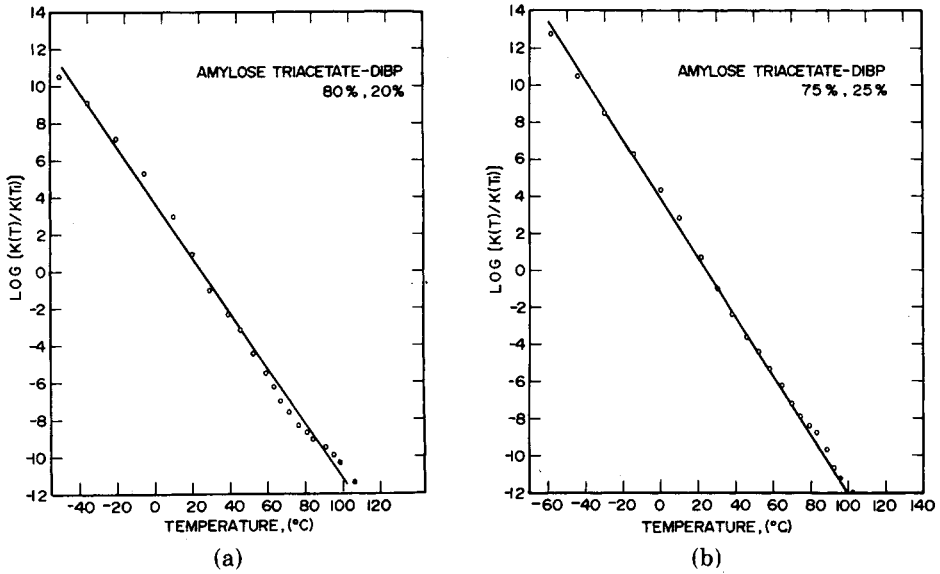


Fig. 7. Log $[K(T)/K(T_i)]$ vs. T for amylose triacetate-DIBP systems: (a) 80%, 20%; (b) 75%, 25%.

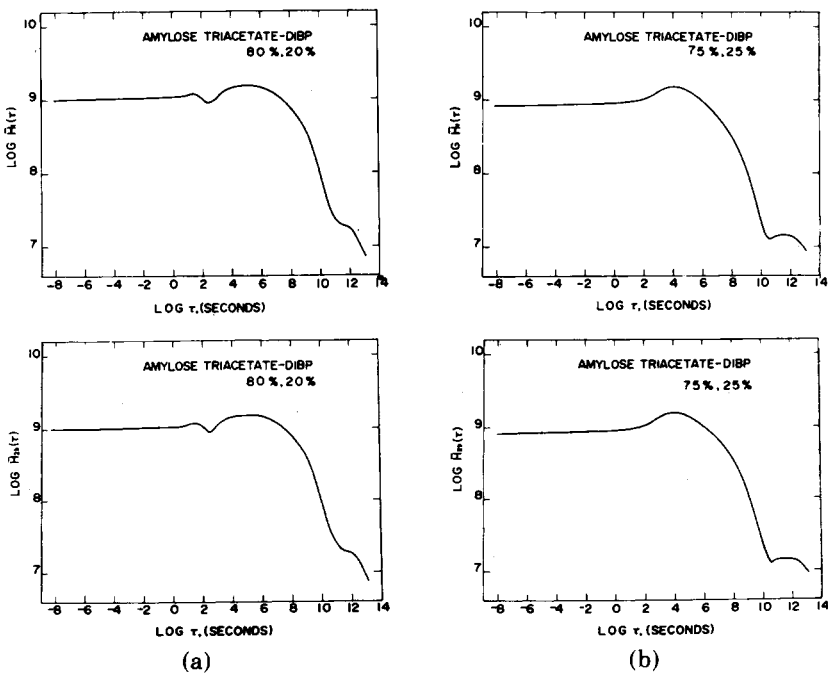


Fig. 8. Relaxation spectrum curve plotted as $\log \bar{H}_1(\tau)$ vs. $\log \tau$ and as $\log \bar{H}_{2b}(\tau)$ vs. $\log \tau$ for amylose triacetate-DIBP system: (a) 80%, 20%; (b) 75%, 25%.

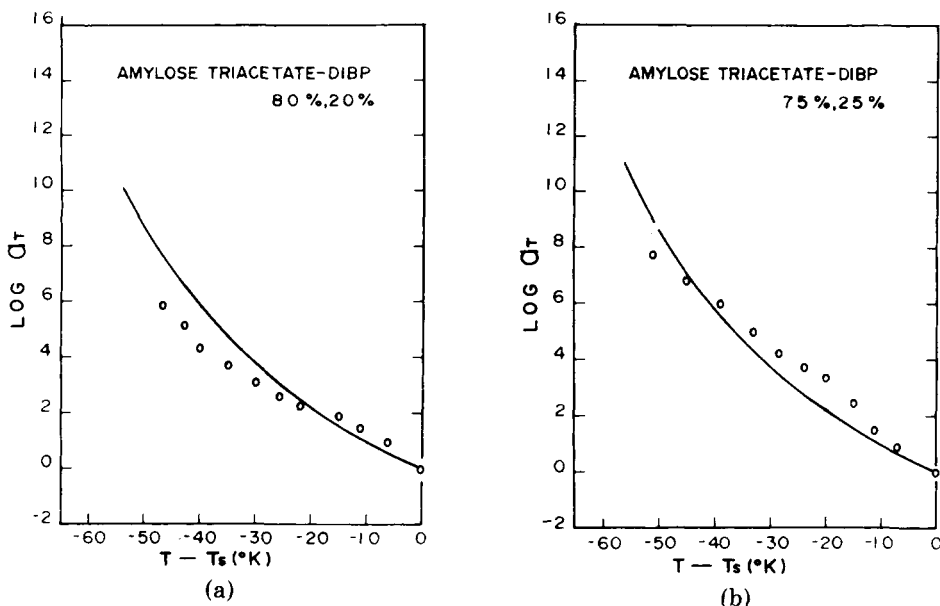


Fig. 9. Log a_T vs. $T - T_s$ for amylose triacetate-DIBP system: (a) 80%, 20%; (b) 75%, 25%.

Numerous amorphous polymers can be applied with the above equation. In the temperature region near T_i , the equation becomes¹⁶

$$\log [K(T)/K(T_i)] = -p(T - T_i). \tag{2}$$

In Figure 7, $\log [K(T)/K(T_i)]$ versus $T - T_i$ for plasticized amylose triacetate is linear for a wide temperature range from -60° to 107°C ; the result indicates that plasticized amylose triacetate can not be applied, and this fact also implies that some kind of firm aggregation exists.

$H(\tau)$, the relaxation-time distribution, is given by the following equation: the first approach:

$$H_1(\tau) = -E_r(t) \left[\frac{d \log E_r(t)}{d \log t} \right]_{t=\tau} \tag{3a}$$

the second approach (Ferry and Williams^{17,18}):

$$H_{2b}(\tau) = \frac{H_1(\tau)}{\Gamma(1 + m)}$$

$$m = - \frac{d \log H_1(\tau)}{d \log \tau}. \tag{3b}$$

The plasticized amylose triacetate samples containing 80% and 75% (by weight) show “wedge”-shaped distribution in the transition region and a typical amorphous “box”-shaped distribution in the rubbery flow region of 75% in Figure 8. In regard to the two approaches of relaxation-time distribution of plasticized amylose triacetate: except for a small part of transition to rubbery region and rubbery flow region of 75%, the other relaxation spectra exhibit nearly same. The results indicate a gradual decrease of relaxation spectra, which seems to indicate the existence of some kind of firm aggregation.

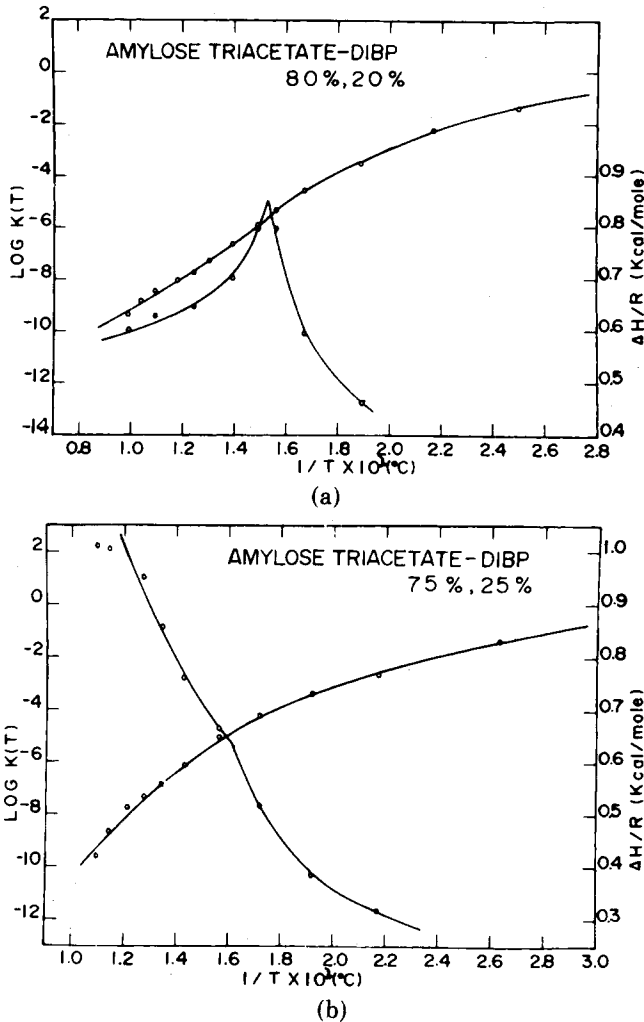


Fig. 10. $\text{Log } K(T)$ and $\Delta H/R$ vs. $1/T$ for amylose triacetate-DIBP system: (a) 80%, 20%; (b) 75%, 25%.

The temperature dependence of a_T is given by the following equation:¹⁹

$$\log a_T = -8.86(T - T_s)/101.6 + T - T_s. \quad (4)$$

The above equation is applicable for many solid states of polymers and for several low-molecular glassy liquids. It is obvious that temperature dependence deviates slightly from the above equation for plasticized amylose triacetate in Figure 9. This might be the effects of some kind of firm aggregation of plasticized amylose triacetate.

The temperature dependence of $K(T)$ and apparent active energy, $\Delta H/R$, of plasticized amylose triacetate are shown in Figure 10. In the case of 75% amylose triacetate, the apparent active energy is larger than that of 80% amylose triacetate at high temperature. The so-called T_d (the Tobolsky temperature) obtained from the maximum point of apparent active energy for 80% amylose triacetate is 65.4°C and, from the intersecting of apparent active en-

ergy for 75% amylose triacetate, is 62°C.

The characteristic parameters of plasticized amylose triacetate and plasticized amylose exhibit smaller values than those of amorphous: the reason may be the fact that they assume helical or nonintegral helical structure in solid, in solution, or in mixed state under the conditions specified. In spite of the difference in molecular structure and given conditions of plasticization, both the plasticized polymers behave nearly the same in viscoelastic properties between semicrystalline and amorphous polymers. If we compare the molecular structure for amylose triacetate with that of amylose: First, except for the substituted $-\text{COCH}_3$ in amylose triacetate, both of them are α -D-(1 \rightarrow 4) linkages and exist in nonintegral helical and helical configurations, respectively.

Amylose, which is crystalline in solid state, is known as an amorphous polymer in dimethyl-sulfoxide-plasticized 55% amylose.¹¹ Its molecular segments mobilize more, and the hydrogen bonding decreases greatly in such solution plasticization.

On the other hand, amylose triacetate which originally is an amorphous, exhibits the same amorphous x-ray diagram in diisobutyl-phthalate-plasticized 75% to 80% amylose triacetate. Its crystallinity is decreased greatly by the substitution effects, to the extent that it does not show rubbery plateau. In addition, the plasticization with not so much diisobutyl phthalate will accelerate the mobility of segments of amylose triacetate.

Assuming helical and nonintegral helical configuration in the given plasticizer and the low degree of crystallinity in each case, both of the plasticized polymers are an approached state. This is why they behave nearly the same in viscoelastic properties.

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