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Viscoelastic Properties of Plasticized Amylose Films

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Synopsis

The viscoelastic properties of amylose films plasticized with dimethyl sulfoxide were studied. The modulus-temperature curves of dimethyl sulfoxide-plasticized amylose are typical for semicrystalline polymers at the higher concentrations of amylose and pass to those of amorphous polymers with the decrease of amylose content. The glassy modulus is not affected by the incorporation of dimethyl sulfoxide, but the rubbery modulus and T_g are depressed with increased dimethyl sulfoxide. The change of T_g with plasticization can be represented by two approximately straight lines, one representing the lower concentration region of amylose and the other the higher one. The critical concentration is about 60% amylose. When the results of modulus-time measurements and x-ray diffraction are considered together, in a system of amylose-dimethyl sulfoxide, amylose exists as a semicrystalline polymer at high concentrations of amylose, and it acts intermediate between semicrystalline and amorphous polymers at lower concentrations below about 60%. From an extrapolation of the data of T_g of plasticized amylose, T_g of pure amylose appears to be approximately 330°C. The viscoelastic properties of amylose films plasticized with dimethyl sulfoxide-sorbitol mixtures were also studied.

INTRODUCTION

Amylose has been studied by many physical methods, especially its structure in the solid state and its conformation in solution.

Amylose is similar to cellulose since both contain *d*-glucopyranose rings; however, in amylose these rings are joined by α-1,4 linkages while in cellulose the linkage is the β-1,4-glucose. Because of this difference, amylose, when compared to cellulose, exhibits very different physical and chemical properties including the ability to exist in a helical configuration.

It is well known that amylose exists in two basically different configurations in the solid state, i.e, an extended form which yields either the A or B type of x-ray diffraction pattern and a helical form which yields the V pattern.[1,2] The A or B x-ray diffraction pattern is obtained from amylose retrograded from aqueous solution or from natural starches. The helical V-type x-ray diffraction pattern results from the amylose-iodine complex,[3] amylose complexes with alcohols, ketones and fatty acids precipitated from aqueous solution, dimethyl sulfoxide,[4] or 2-aminoethanol solution[5] of amylose.

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It is reported that amylose also exists as an interrupted helix in aqueous solution[6] and with increase of pH, the helix–coil transformation occurs. Then at high pH, the molecule may be regarded as a flexible coil.[7]

Some studies have been reported on the viscoelastic properties of amylose or starch on their suspensions and pastes,[8,9] and there has been some reports on the mechanical properties of amylose films.[10] In this paper we report the results of several viscoelastic studies on amylose films plasticized with dimethyl sulfoxide. Also reported are the effects of partial replacement of dimethyl sulfoxide by sorbitol on the viscoelastic properties of amylose films.

EXPERIMENTAL

Materials

The amylose sample used in this experiment was supplied by the Northern Regional Research Laboratory of the U.S. Department of Agriculture. This sample has an iodine number of 198 and $\bar{M}_w$ of 4.74×10^5 calculated using the following viscometric relation.[11]

$$[\eta] = 1.25 \times 10^{-3}(\bar{M}_w)^{0.87}$$

The plasticized amylose films used in the measurements were prepared by evaporation of the solvent *in vacuo* at 40°C. from dimethyl sulfoxide solutions of predried amylose.

Dimethyl sulfoxide (J. T. Baker Chemical Co.) and a mixture of dimethyl sulfoxide and sorbitol (Fischer Scientific Co.) were used as plasticizers.

Methods

Modulus–Temperature Curves. The torsional modulus $G(10)$ after 10 sec. was measured by a modified Gehman apparatus.[12] Silicone oils of appropriate viscosities were used as bath liquids. The values of $G(10)$ were multiplied by 3 to approximate the tensile modulus $E_r(10)$, and log $3G(10)$–temperature curves were plotted.

Modulus–Time Curves. Stress-relaxation measurements were carried out using a standard stress-relaxation balance box.[13] A Tenney environmental test chamber was used with an air bath and the sample was steeped in a specially designed bath with silicone oil to protect the sample from moisture. The values of log $E_r(t)$ were plotted against time for a wide range of temperature.

Glass Transition Temperatures. The specimens were immersed in silicone oil of appropriate viscosity. The glass transition temperatures were obtained from the observed discontinuity in the slope of the buoyant weight vs. temperature plots.

X-Ray Analysis. X-ray photographs were obtained with a flat-film camera with a film-to-sample distance of 5.90 cm., CrK_α radiation being employed.

RESULTS AND DISCUSSION

Amylose–Dimethyl Sulfoxide

The log torsional modulus $3G(10)$ vs. temperature T curves for seven specimens of amylose plasticized with varying amounts of dimethyl sulfoxide (DMSO) are shown in Figure 1. At higher concentrations of amylose, the log modulus curves decrease very slowly with increasing temperature and they seem to be typical for semicrystalline polymers. With decreasing concentration of amylose in the film, the log modulus curves pass to those of nearly amorphous polymers. Specimens containing above 60% amylose do not show any rubbery flow, just like crosslinked polymers.

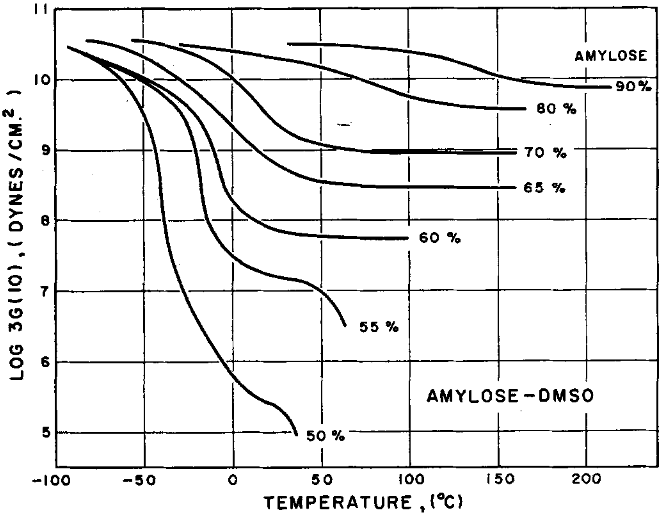

Fig. 1. Ten-second modulus $3G(10)$ vs. temperature for amylose–dimethyl sulfoxide systems.

Table I gives values of characteristic parameters obtained from the log

TABLE I
Characteristic Parameters for DMSO-Plasticized Amylose Films

Amylose concentration, wt.-%	$3G_1$, dyne/cm.^{2}	$3G_2$, dyne/cm.^{2}	T_i, °C.	S	T_g, °C.	d, g./cm.^{3}
50	2.52×10^{10}	2.52×10^{6}	−37	0.099	−50.0	—
55	2.52×10^{10}	1.76×10^{7}	−20	0.088	−48.5	1.328
60	2.82×10^{10}	6.90×10^{7}	−10	0.080	−34.0	1.369
65	3.40×10^{10}	2.83×10^{8}	13	0.023	43.0	1.374
70	3.40×10^{10}	8.55×10^{8}	61	0.005	47.0	1.394
80	2.96×10^{10}	3.56×10^{9}	—	—	141.0	1.438
90	3.02×10^{10}	9.34×10^{9}	—	—	—	1.545

modulus vs. temperature curves, together with T_g and density data at room temperature. That is to say, $3G_1(10)$ is the value of $3G(10)$ in the glassy region; $3G_2(10)$ is the value of $3G(10)$ in the rubbery plateau. T_i is defined as the temperature at which $3G(10)$ equals 10^9 dyne/cm.^{2} and S is the negative slope of the curve at T_i. $3G_1(10)$ and $3G_2(10)$ vs. amylose concentration curves are shown in Figure 2.

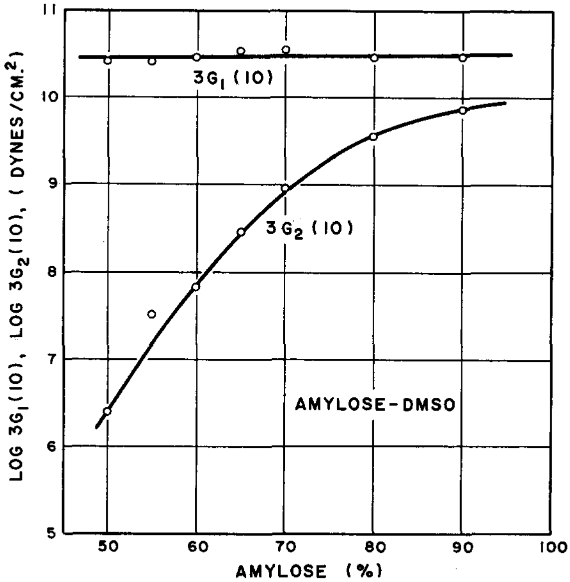

Fig. 2. The glassy modulus $3G_1(10)$ and the rubbery modulus $3G_2(10)$ vs. amylose concentration for amylose–dimethyl sulfoxide systems.

The glassy modulus $3G_1(10)$ is essentially independent of the incorporation of plasticizer, but the rubbery modulus $3G_2(10)$, T_i, and T_g are depressed with increasing concentrations of plasticizer. In the case of specimens containing above 80% amylose, the rubbery modulus is over 10^9 dyne/cm.^{2}. The value of T_i cannot be obtained there. The value of S increases with increasing plasticizer concentration.

Tobolsky and Takahashi[14] have reported tables of characteristic parameters for several linear amorphous polymers. They reported the values of S between 0.13 and 0.25. Therefore, the values of S reported in Table I for plasticized amylose, at the lower concentration range, are thought to be a little smaller for an amorphous polymer.

Some of these results contrast somewhat with those of Shen and Tobolsky[15] on poly(vinyl chloride) and plasticized poly(vinyl chloride) with 30 wt.-% of dioctyl phthalate. In their 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 employed. The samples used in the present study were also definitely crystalline above 60% amylose, as shown below in x-ray measurements.

The constancy of the rubbery modulus in poly(vinyl chloride) and plasticized poly(vinyl chloride) was explained by suggesting that 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.[15]

An explanation of the somewhat different behavior of poly(vinyl chloride) and amylose in plasticization is as follows: it is supposed that in the case of poly(vinyl chloride), the crystallinity of the sample are not changed with the plasticization, and therefore, a same amount of crystallite which can support an external strain still exists. The rubbery modulus $3G_2(10)$ does not decrease but the value of S decreases with plasticization. On the contrary, in the case of amylose, the crystallinity of the sample increases with the increasing amylose, and therefore the rubbery modulus increases.

The fact that specimens containing above 60% amylose do not show any flow is explained by the high melting point of amylose crystallite, not by crosslinking of amylose during measurement, because the specimen was still soluble after modulus–temperature measurement.

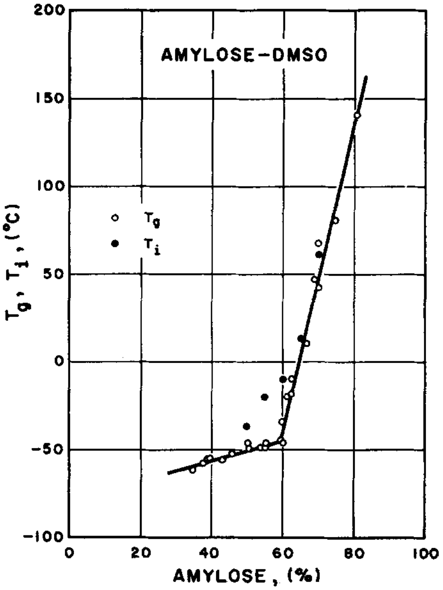

Fig. 3. Glass transition temperature (T_g) vs. amylose concentration for amylose–dimethyl sulfoxide systems.

The T_g data of Table I (together with unlisted data) are plotted against the concentration of amylose in Figure 3. It would appear that the results are represented approximately by two straight lines, one representing the lower concentration region and the other the higher one. The critical concentration is ca. 60% amylose content. In Figure 3, the values of T_i, obtained from the log modulus–temperature curves, are also plotted.

Considering the modulus–temperature curves and T_g data together, it is supposed that at the higher concentrations of amylose, amylose exists as crystallites, the so-called oil plasticization, and at the lower concentrations amylose, it is dissolved homogeneously in the plasticizer, the so-called solution plasticization.

On extrapolation of the higher concentrations of amylose to 100% amylose content, the T_g of pure amylose would be approximately 330°C. There has been no value of T_g of amylose reported from the direct measurement, because T_g of amylose is higher than the thermal decomposition temperature of amylose.[16]

From the results already mentioned (modulus–temperature curves and T_g–concentration curve), we can see that dimethyl sulfoxide-plasticized amylose appears to have a critical point in the vicinity of 60% amylose content, seems to separate the semicrystalline regions from the pure amorphous regions of concentration. To prove this observation x-ray diffraction

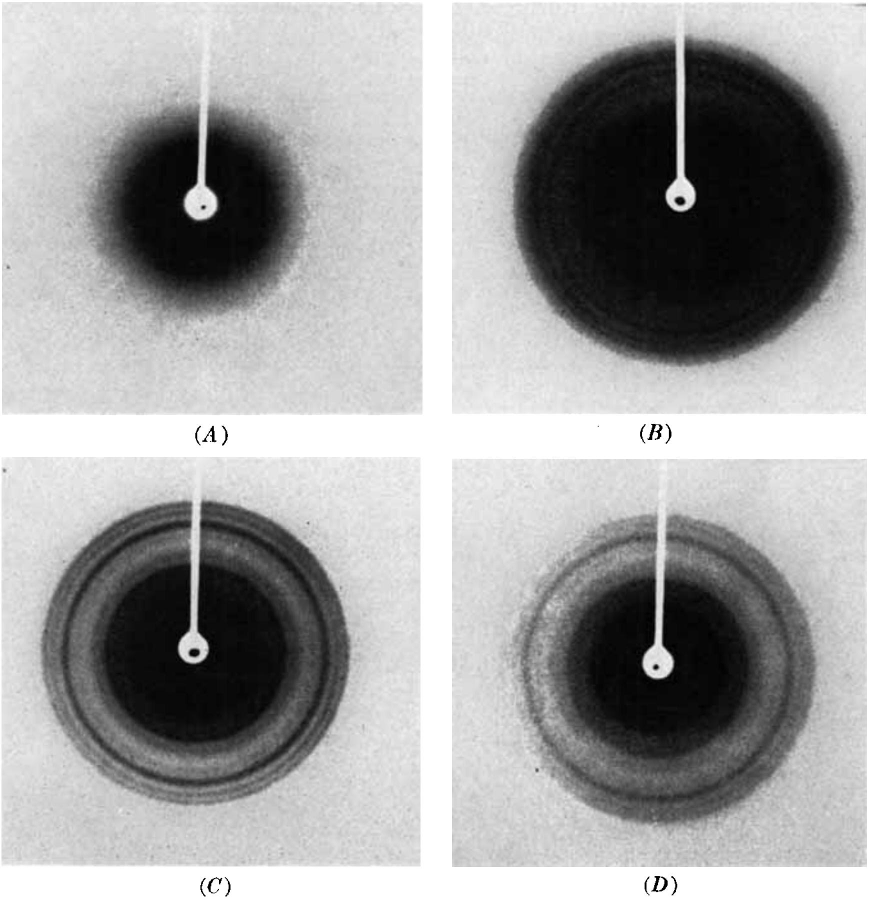
(A) (B) (C) (D)

Fig. 4. X-ray diffraction diagrams of amylose films plasticized with dimethyl sulfoxide. (A) 55% amylose; (B) 57% amylose; (C) 65% amylose; (D) 100% amylose.

measurements have been performed on the samples containing a wide variety of amylose, with dimethyl sulfoxide as a plasticizer. Some of these results are shown in Figure 4.

Films containing above 57% amylose showed clear Debye-Scherer rings and were evidently semicrystalline and those pictures are different from any pattern ever reported on amylose except the picture recently obtained by Zobel and French[17] on the films cast from the same dimethyl sulfoxide solutions. They also indicated that amylose makes complex with the dimethyl sulfoxide and determined that its structure is a pseudotetragonal lattice with the dimensions $a_0 = b_0 = 19.2$ A. and $c_0 = 8.1$ A. and in which amylose assumes a helical conformation.[17] Thus it is thought that amylose exists as amylose-dimethyl sulfoxide complex in the amylose-dimethyl sulfoxide system.

The stress relaxation data for dimethyl sulfoxide-plasticized amylose samples containing 70 and 55% (by weight) are shown in Figures 5 and 6.

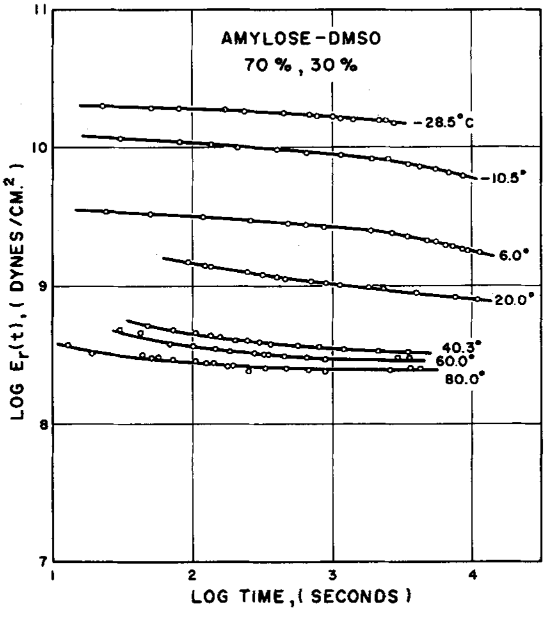

Fig. 5. Modulus-time curves for amylose-dimethyl sulfoxide system (70%, 30%).

As can be expected from the results of modulus-temperature curves and x-ray patterns, log $E_r(t)$ vs. log t curves for the 70% amylose sample are relatively flat and the change in modulus with time in the transition region is much less marked as compared to the typical amorphous polymers. The time-temperature superposition principle is not applicable to this sample. This result indicates the existence of crystalline regions in this sample acting as crosslinks and is consistent with the results of x-ray diffraction studies above.

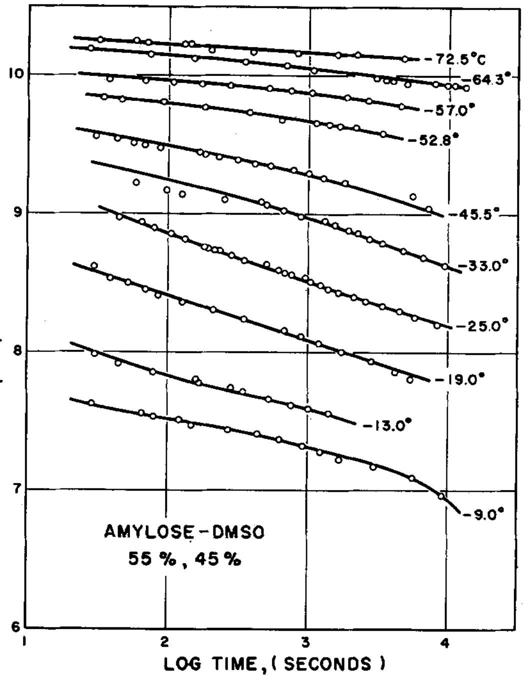

Fig. 6. Modulus-time curves for amylose–dimethyl sulfoxide system (55%, 45%).

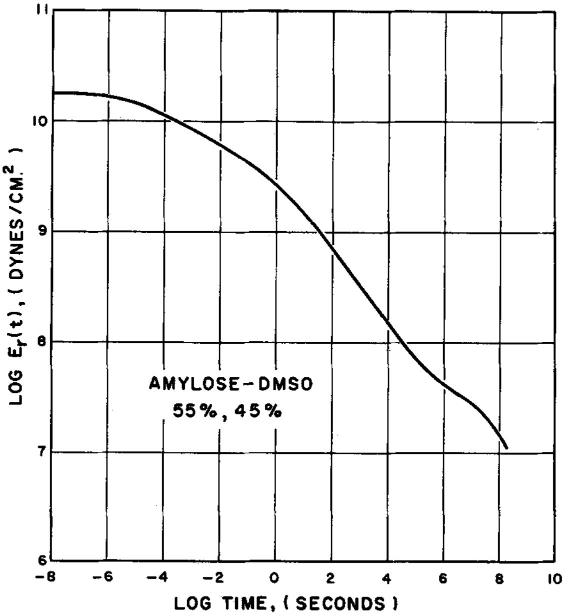

Fig. 7. Master curve plotted as log $E_r(t/K)$ vs. log (t/K) for amylose–dimethyl sulfoxide system (55%, 45%).

On the other hand, the sample containing 55% amylose exhibits the behavior of a nearly amorphous polymer. It is found that the time–temperature superposition principle is applicable to this sample. The master curve obtained by the horizontal shift of data along the log t is shown in Figure 7. The characteristic parameters for a stress-relaxation master curve are listed in Table II, along with data for some linear and plasticized polymers.[14,18] In Table II, E_1 is the glassy state modulus, E_2 is the rubbery modulus, T_i is the temperature at which $K(T) = 10$ sec. where $K(T)$ is the time required for $E_r(t)$ to attain a value of 10^9 dyne/cm.^{2}, and n is the negative slope of the log $E_r(t)$ vs. log t master curve at $E_r = 10^9$ dyne/cm.^{2}, p is the slope of the log $[K(T)/K(T_i)]$ vs. $T - T_i$, which is nearly linear in the immediate vicinity of T_i.

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[14]	3.02	0.759	−64.6	0.75	0.21	0.15
Polystyrene[14]	2.00	0.339	93.1	0.87	0.26	0.22
Poly(methyl methacrylate)[14]	2.82	2.51	113.3	0.54	0.33	0.18
Natural rubber[14]	2.63	1.00	−66.9	1.23	0.31	0.38
Plasticized Polymers						
Polystyrene–DOP(100/20)[18]			38.2	0.50	0.178	0.089
Poly(methyl methacrylate)–DOP(100/20)[18]			69.6	0.49	0.115	0.056
Poly(vinyl chloride)–DOP (100/20)[18]			43.6	0.29	0.135	0.056
Amylose–DMSO(55/45)	3.62	—	−22.5	0.34	0.18	0.064

Comparing the characteristic parameters of plasticized polymers with those of linear amorphous polymers, in addition to the expected decrease in T_i, the most important difference is the much smaller value of np for the plasticized polymers.

Another finding in Table II is that the values of n for plasticized polystyrene and plasticized poly(methyl methacrylate) which are both amorphous polymers, are essentially equal to 0.50, the theoretical value of Rouse[19] and Bueche.[20] Poly(vinyl chloride) and amylose, which are crystalline in the unplasticized form, have smaller values than 0.50. Unplasticized linear amorphous polymers often have values larger than 0.50.

As shown in Figure 7, a very broad master curve is obtained for amylose. This phenomena is also reported for plasticized poly(vinyl chloride),[18] which is found to be slightly crystalline.[21,22] These results may not necessarily exclude the possibility that some kind of firm aggregation exists in spite of the failure to detect crystallinity by x-ray analysis. Another possible explanation might be the fact that amylose assumes a helical configuration both in dimethyl sulfoxide solutions[11,23] and in the crystalline state of the demonstrated amylose–dimethyl sulfoxide complex.[17] Because of this, dimethyl sulfoxide-plasticized amylose below 60% amylose content acts intermediate between crystalline and amorphous polymers.

The temperature dependence of $K(T)$ is given by the following equation:[24]

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

It is found that the above equation is applicable for numerous amorphous polymers. In the temperature region near T_i, the above equation becomes:[25]

$$\log K(T)/K(T_i) = -P(T - T_i) \tag{2}$$

Log $[K(T)/K(T_i)]$ vs. $T - T_i$ for plasticized amylose is linear for a wide range of temperatures (T) from −72.5 to −9°C. (Fig. 8); thus eq. (1) is not applicable to plasticized amylose and this fact also seems to indicate the existence of some kind of firm aggregation.

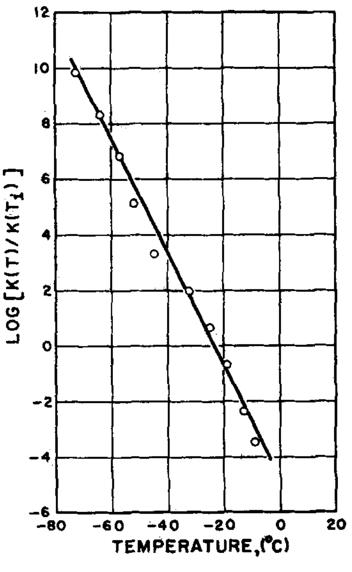

Fig. 8. Log $K(T)/K(T_i)$ vs. T for amylose–dimethyl sulfoxide system (55%, 45%).

Amylose–Dimethyl Sulfoxide–Sorbitol

We have also obtained modulus–temperature curves of several amylose–dimethyl sulfoxide–sorbitol ternary systems. That is to say, a part of dimethyl sulfoxide was replaced by sorbitol. It is found that the compatibility of these three compounds is very good. In the first series, the concentration of amylose in the film was kept constantly at 55% and the compositions of dimethyl sulfoxide and sorbitol were varied (Fig. 9). In the second series, the concentration of dimethyl sulfoxide was kept at 20% and then the ratio of amylose to sorbitol was varied (Fig. 10).

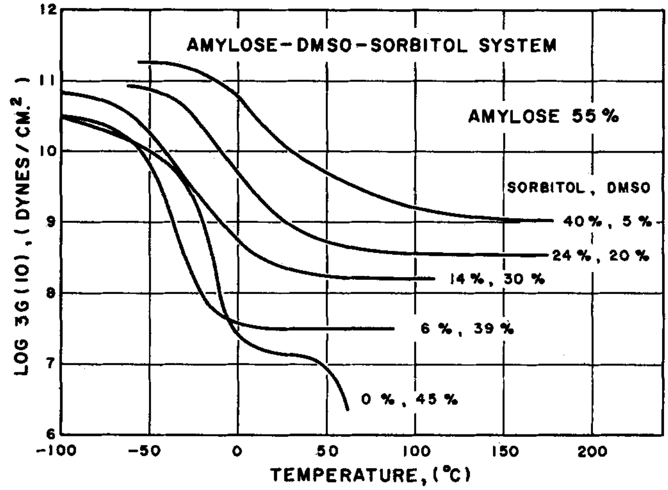

Fig. 9. Ten-second modulus vs. temperature for amylose–dimethyl sulfoxide–sorbitol system (amylose 55%).

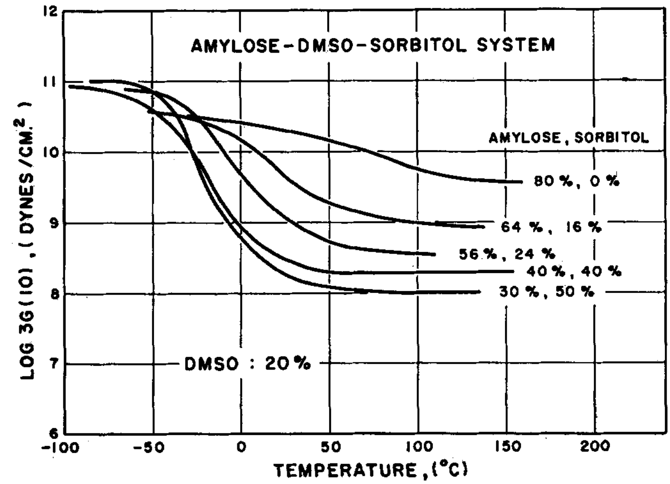

Fig. 10. Ten-second modulus vs. temperature for amlyose–dimethyl sulfoxide–sorbitol system (dimethyl sulfoxide, 20%).

The characteristic parameters obtained from the modulus–temperature curves are shown in Tables III and IV, respectively, together with T_g values. The changes of the glassy modulus, $3G_1(10)$, and the rubbery modulus, $3G_2(10)$, with the composition are plotted in Figures 11 and 12.

TABLE III
Characteristic Parameters for Amylose–DMSO–Sorbitol Systems, Amylose Concentration: 55%

Sorbitol conc., wt.-%	$3G_1$, dyne/cm.^{2}	$3G_2$, dyne/cm.^{2}	T_i, °C.	S	T_g, °C.	d, g./cm.^{3}
0	2.52×10^{10}	1.76×10^{7}	−20	0.088	−48.5	1.328
6	3.09×10^{10}	3.17×10^{7}	−37	0.074	−50.5	1.328
14	6.77×10^{10}	1.59×10^{8}	−10	0.029	−41.0	1.378
24	8.52×10^{10}	3.47×10^{8}	27	0.020	−40.5	1.423
40	1.78×10^{11}	1.05×10^{9}	160	—	−5.0	1.463

TABLE IV
Characteristic Parameters for Amylose–DMSO-Sorbitol Systems, DMSO Concentration: 20%

Amylose conc., wt.-%	$3G_1$, dyne/cm.^{2}	$3G_2$, dyne/cm.^{2}	T_i, °C.	S	T_g, °C.	d, g./cm.^{3}
80	2.96×10^{10}	3.56×10^{9}	—	—	141.0	1.438
64	3.71×10^{10}	8.52×10^{8}	100	0.003	−4.5	1.418
56	7.60×10^{10}	3.55×10^{8}	29	0.017	−40.5	1.421
40	8.60×10^{10}	2.00×10^{8}	−2	0.029	−40.0	1.394
30	1.00×10^{11}	1.00×10^{8}	−8	0.036	−58.0	1.387

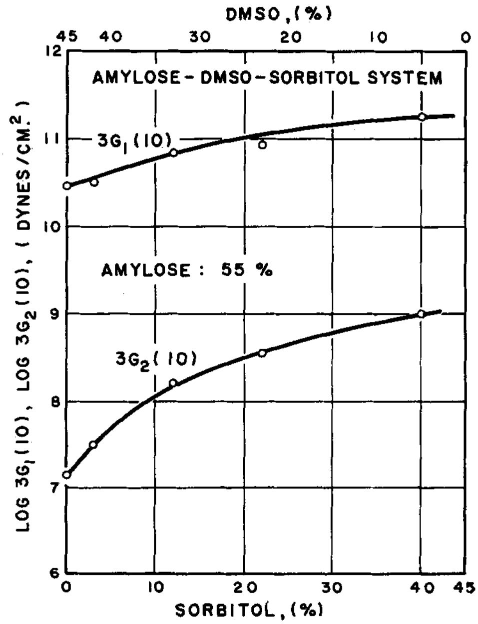

Fig. 11. The glassy modulus $3G_1(10)$ and the rubbery modulus $3G_2(10)$ vs. dimethyl sulfoxide concentration for amylose–dimethyl sulfoxide–sorbitol system (amylose, 55%).

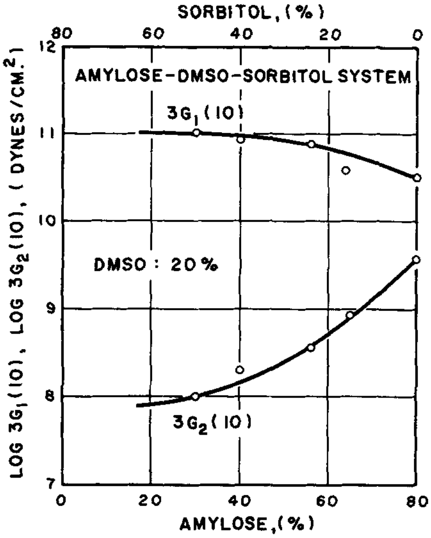

Fig. 12. The glassy modulus $3G_1(10)$ and the rubbery modulus $3G_2(10)$ vs. amylose concentration for amylose–dimethyl sulfoxide–sorbitol system (dimethyl sulfoxide, 20%).

When the amylose concentration in the films was kept at 55%, increases in sorbitol resulted in increases in both $3G_1(10)$ and $3G_2(10)$, a decrease of S and higher T_g and T_i values. These samples were confirmed to be amorphous by x-ray measurements. When the concentration of dimethyl sulfoxide was kept at 20%, T_g, T_i, and $G_1(10)$ decreased, but $G_2(10)$ and S increased with increasing concentrations of sorbitol. The T_g vs. composition plots showed upward curvatures for both systems (Figs. 13 and 14).

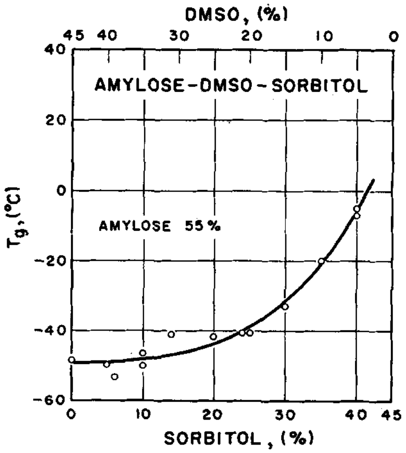

Fig. 13. Glass transition temperature (T_g) vs. dimethyl sulfoxide concentration for amylose–dimethyl sulfoxide–sorbitol system (amylose, 55%).

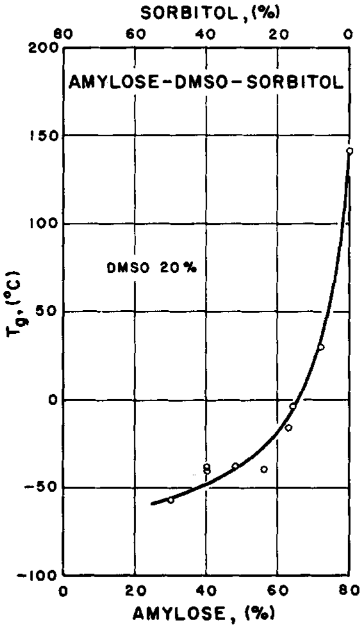

Fig. 14. Glass transition temperature (T_g) vs. amylose concentration for amylose–dimethyl sulfoxide–sorbitol system (dimethyl sulfoxide, 20%).

When a part of the dimethyl sulfoxide was replaced by sorbitol in plasticized amylose films, the polymer network became stiffer both in the glassy and the rubbery regions. On the other hand, when a part of amylose was replaced by sorbitol, the polymer network became stronger in the glassy region, but became weaker in the rubbery region. According to these results, it seems that the addition of sorbitol makes the association of polymer molecules easier and the resulting polymer network stiffer due to its strong interaction with amylose.

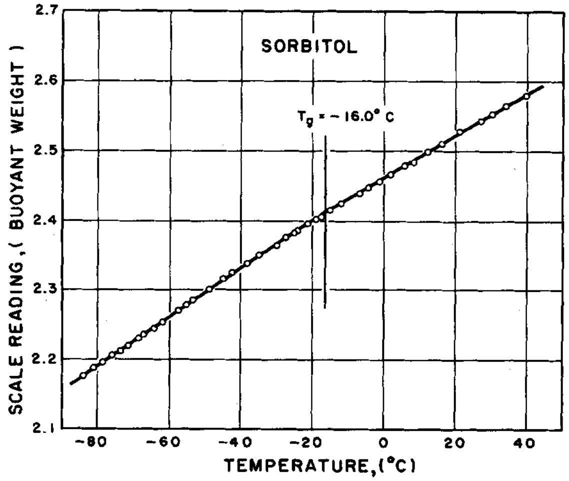

Fig. 15. Buoyant weight vs. temperature for sorbitol.

This result is also due to the high T_g value of sorbitol which is -16.0°C. by the buoyance method (Fig. 15). That of dimethyl sulfoxide is thought to be much lower, but cannot be easily measured.

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Résumé

Les propriétés viscoélastiques des films amylose plastifiés au diméthyl sulfoxyde ont été étudiées. Les courbes module–température de l'amylose plastifiée au diméthyl sulfoxyde sont typiques pour des polymères semicristallins àux concentrations plus élevées en amylose et se rapprochent de celles des polymères amorphes avec une diminution de la teneur en amylose. Le module vitreux n'est pas affecté par l'incorporation de diméthyl sulfoxyde, mais le module caoutchouteux et T_g sont diminués avec une augmentation en diméthyl sulfoxyde. Le changement de T_g avec la plastification peut être représenté par deux lignes approximativement droites, l'une représentant la région des condentrations plus basses en amylose et l'autre, celle des concentrations plus élevée. La concentration critique est d'environ 60% d'amylose. Si l'on considère ensemble les résultats des mesures temps–module et ceux de la diffraction aux rayons-X pour un système amylose–diméthyl sulfoxyde, l'amylose existe comme polymère semi-cristallin aux concentrations élevées en amylose et il agit comme un stade intermédiaire entre les polymères semi-cristallins et amorphes aux concentrations plus basses (en-dessous d'environ 60%). Au départ d'une extrapolation des résultats de T_g de l'amylose plastifiée, le T_g de l'amylose pure s'élève à approximativement 330°C. Les propriétés viscoélastiques des films d'amylose plastifiés avec le diméthyl sulfoxyde et le sorbitol en mélange ont également été étudiées.

Zusammenfassung

Die viskoelastischen Eigenschaften von Amylosefilmen bei Weichmachung mit Dimethylsulfoxyd wurden untersucht. Die Modul–Temperaturkurven der mit Dimethylsulfoxyd weichgemachten Amylose sind bei höheren Amylosekonzentrationen für semikristalline Polymere charakteristisch und gehen mit Abnahme des Amylosegehaltes in diejenigen amorpher Polymerer über. Der Glasmodul wird durch die Aufnahme von Dimethylsulfoxyd nicht beeinflusst, der Kautschukmodul und T_g werden dagegen mit Zunahme an Dimethylsulfoxyd herabgesetzt. Die Abhängigkeit von T_g von der Weichmachung kann durch zwei annähernd gerade Linien dargestellt werden, eine für den Bereich niedrigerer Amylosekonzentration und eine für den höheren. Die kritische Konzentration liegt bei etwa 60% Amylose. Gemeinsam betrachtet lassen die Ergebnisse der Modul–Zeit-Messungen und der Röntgenbeugung erkennen, dass in einem Amylose–Dimethylsulfoxyd-System die Amylose bei hohen Amylosekonzentrationen als ein semikristallines Polymeres vorhanden ist und bei niedrigeren Konzentrationen unterhalb etwa 60% eine Zwischenstellung zwischen einem semikristallinen und einem amorphen Polymeren einnimmt. Aus einer Extrapolation der T_g-Daten von weichgemachter Amylose ergibt sich T_g von reiner Amylose zu etwa 330°C. Schliesslich wurden auch die viskoelastischen Eigenschaften von Amylosefilmen bei Weichmachung mit Dimethylsulfoxyd–Sorbitol-Mischungen untersucht.

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