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Thermodynamics of Amorphous Starch−Water Systems.
1. Volume Fluctuations

D. Benczédi,[†] I. Tomka,* and F. Escher

Institute of Polymers, Institute of Food Science, Swiss Federal Institute of Technology ETH, 8092 Zurich, Switzerland

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ABSTRACT: This paper presents dilatometric and calorimetric experiments on potato starch extruded into a transparent amorphous glass with a density of 1.5 g/cm^3 at room temperature. The specific heat increment at the glass transition is used to estimate the transition temperature of samples containing up to 25 wt % water. The specific volume of the samples is studied between 25 and 165 °C and between 0.1 and 100 MPa. Glass transitions estimated from the compressibility increment at the transition temperature are found in agreement with those detected by calorimetry. In the entire experimental temperature range, a maximal excess volume of mixing is observed at a composition corresponding to three water molecules per anhydroglucose in the mixture. This suggests that the large size difference between the chemical components allows the water molecules to saturate only one hydroxyl group of the anhydroglucose at a time. Specific volumes of starch glasses and melts are superimposed onto a single master curve by a simple empirical relation. The neglect of polar interactions in mean field equations of state results in underestimated internal pressures and cohesive energy densities. Free volumes estimated with the lattice fluid equation of state reflect semiquantitatively the effects of temperature and concentration on the density of starch, which goes through a maximum value at low water concentration. Such a reduction of the free volume of polymer glasses by low plasticizer concentrations is called antiplasticization, as the reduction of the glass transition temperature is then coupled to an increase rather than a decrease of elastic moduli. Antiplasticization reduces gas sorption and permeation rates and the knowledge of its occurrence can be used to optimize the gas barrier properties of polymers.

Introduction

Starch is a cost-effective edible biopolymer with useful functional properties. The moisture of starch determines how its glass transition temperature influences mechanical properties critical for applications. In aqueous solution, starch is used as a texturogen (e.g., thickener, stabilizer), whereas at low moisture, starch glass is used as a gas barrier in films or controlled delivery devices (e.g., drug, flavor).[1,2] Among the factors affecting the gas barrier properties of amorphous starch, the density, the free volume, and the cohesive energy density are the most important. Their concentration and temperature dependence can be estimated from an analysis of the equation of state of starch.[2,3,25−30] The analysis of the sorption of water by starch with concentration fluctuation theory is the subject of another paper.[12]

The linear amylose and the highly branched amylopectin, of which starch is composed, are both polymers of D-α-glucopyranose linked by C(1)−C(4) glucosidic bonds as linear chains in the case of amylose and as chains branched at C(6) in the case of amylopectin. Molecular weights are estimated at 10^5−10^6 and at 10^7−10^8 for the amylose and the amylopectin, respectively. The two polymers are packed during biosynthesis in cold water insoluble ellipsoidal granules of 1−100 μm length, in which 15−40% of the polymer is crystalline and therefore birefringent under crossed polarizers.

In the presence of water, an irreversible process called gelatinization destroys the texture in the crystalline regions of native starch. In the case of potato starch, this structural transformation occurs in aqueous solutions between 56 and 66 °C but temperatures above 170 °C are required to melt the starch crystallites and to leach the amylose and amylopectin molecules out of the granules. The ability of starch to recrystallize partially is only lost at these high temperatures in a transition involving the breakage of intramolecular hydrogen bonds, the precise temperature depending on the nature of the starch and on its water content.[4−7] Extrusion combines thermal with mechanical treatments and the transformation of native starch swollen by water into a fully amorphous thermoplast can be brought about at around 100 °C, as has been the case with the material investigated here.[8−12]

Theory

The compression strain ϵ is defined as the logarithmic ratio of the specific volumes measured at applied and reference pressures $\ln(v_{sp}/v_{sp}^0)$. It can be related to the pressure P by the following empirical equation of state.[13]

$$\epsilon = \int_{P^0}^{P} \ln \frac{\partial v_{sp}}{\partial P}\, dP = \ln\left(\frac{v_{sp}}{v_{sp}^0}\right) - \frac{\ln[1 + B_1(P/B_0)]}{B_1} \qquad (1)$$

The isothermal bulk modulus, B_0, is estimated from the slope of the $v_{sp}(P)$ functions fitted to quadratic equations, and the pressure coefficient B_1 is adjusted by least-squares regression. Materials having the same B_1 satisfy a corresponding state principle, and their reduced pressure−volume−temperature (PVT) data fall onto a single master curve.

In equations of state using a mean-field model, the PVT data are reduced by the scaling parameters P^*, $V^* = v^*r$, and T^* ($\tilde{P} = P/P^*$, $\tilde{V} = V/V^* = \rho^*/\rho$, and $\tilde{T} = T/T^*$),

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* Corresponding author.

[†] Current address: Firmenich Inc. R&D Division, 1211 Geneva 8, Switzerland.

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referring to the state of molecules in which their potential energy is negligible besides their kinetic energy.[16−24] In the so-called hole cell equation of state, the mean potential field is approximated with a Lennard-Jones 6−12 potential, with attractive and repulsive Madelung's constants of 1.011 and 1.2045. The quasi-lattice is characterized by a next-neighbor coordination of 12 and a geometry factor of 0.8909. The liquid character is enhanced by minimizing the free energy with respect to the fraction of occupied sites, y.[19,20] The hole cell equation of state is

$$\tilde{P}\tilde{V}/\tilde{T} = \frac{(y\tilde{V})^{1/3}}{[(y\tilde{V})^{1/3} - 0.8909y]} - \frac{2y}{\tilde{T}}\left[\frac{1.2045}{(y\tilde{V})^2} - \frac{1.011}{(y\tilde{V})^4}\right] \tag{2a}$$

The boundary condition on the occupancy of the quasi-lattice is

$$\frac{r}{3c}[1 + y^{-1}\ln(1 - y)] = -\left[\frac{(y\tilde{V})^{1/3}/3 - 0.8909y}{(y\tilde{V})^{1/3} - 0.8909y}\right] - \frac{y}{6\tilde{T}}\left[\frac{2.409}{(y\tilde{V})^2} - \frac{3.033}{(y\tilde{V})^4}\right] \tag{2b}$$

and the scaling parameters are defined as

$$\frac{P^*V^*}{RT^*} = c/r \tag{3}$$

In a three-dimensional quasi-lattice, a mer can have altogether $3c/r$ external degrees of freedoms and the structural factor c/r is of 1 in the case of an individual spherical mer. As a consequence of the decrease of free volume in the limit of infinite chain length, c/r is 2/3 for a mer composing a completely flexible r-mer and 0 for a mer in a rigid one.[14−17] The cohesive energy density, ced, is defined in the hole cell equation of state as[19,20]

$$\text{ced} = \frac{yP^*}{2\tilde{V}}[2.409(y\tilde{V})^{-2} - 1.011(y\tilde{V})^{-4}] \tag{4}$$

The lattice fluid equation of state applies Guggenheim's grand canonical approximation for infinite coordination numbers to a lattice where the sites are either occupied or vacant. The lattice fluid equation of state is[24]

$$\tilde{\rho} = 1 - \exp[-(\tilde{\rho} + \tilde{P})/\tilde{T} - \tilde{\rho}(1 - 1/r)] \tag{5}$$

where $\tilde{\rho} = \rho/\rho^*$ is the degree of occupancy of the lattice defined as the ratio of measured and close-packed or hard core densities $\rho/\rho^* = V^*/V = rv^*/V$, and r is the number of mers of volume v^* interacting with an energy $\epsilon^* = P^*v^* = RT^*$. The scaling parameters of the lattice fluid equation of state are defined as

$$\frac{P^*V^*}{RT^*} = r \tag{6}$$

and the cohesive energy density is defined as[24]

$$\text{ced} = P^*\tilde{\rho}^2 \tag{7}$$

Experimental Section

Extrusion of Amorphous Starch. Amorphous starch was prepared by extruding native potato starch (lot 51128, Blattmann AG, Switzerland) containing 27 wt % water ($w_1 = 1 - w_2 = 0.27$) at 101−102 °C in a Buss extruder (Buss AG, Pratteln, Switzerland). The specific mechanical energy uptake on extrusion was 0.21−0.24 (kW h)/kg and the transformation was coupled to a decrease of the intrinsic viscosity from originally 314 mL/g for unextruded starch to 116 mL/g following extrusion.

After pelletization, the material was frozen in liquid nitrogen, ground to a fine powder (diameter < 1 mm), and dried at 80 °C in a vacuum oven (P < 100 Pa) over phosphorus pentoxide (Fluka AG, Switzerland) to constant weight. For pressure−volume−temperature experiments involving the confinement of samples in paraffin or mercury, an amorphous starch powder containing 18 wt % water was melted in a press (120 °C, 1 min) to form transparent platelets with dimensions of 3 × 1 × 0.1 cm.[40]

Heat Flow Calorimetry. The glass transition temperature of starch can be estimated from the change of the specific heat at the transition temperature.[31] Measurements were made on samples of 50 mg of amorphous material sealed tightly in stainless steel containers of a Perkin-Elmer calorimeter (DSC 7, Zug, Switzerland). Heating rates applied between −25 and +180 °C were 10 °C/min. To obtain an optimal signal at the transition temperature the samples were annealed before the experiments by heating them to 170 °C and then cooling them to −25 °C at a rate of 200 °C/min. The effect of water vapor pressures of less than 10 bar is neglected since pressures of 1000 bar reduce the glass transitions by much less than 100 °C.

Dilatometry. The concentrations are reported as weight fractions $w_1 = (1 - w_2)$ or mole fractions $x_1 = (1 - x_2)$, where the indices 1 and 2 denote water and anhydroglucose, respectively. The molecular weights of the pure components are $M_1 = 18.0152$ and $M_2 = 162.142$ for water and the anhydroglucose, respectively.

$$x_1 = \frac{w_1/M_1}{w_1/M_1 + w_2/M_2} \tag{8}$$

At 25 °C, the specific volume of amorphous samples containing up to 33 wt % water was measured in a pycnometer on immersing 1−1.5 g of the platelets described above in paraffin (Fluka, Switzerland). A water thermostat was used to keep the temperature within ±0.05 °C of the desired value during the experiment, and the platelets were allowed to thermally equilibrate 24 h.

The molar volumes of the mixture V, the partial molar volumes $\bar{v}_1$ and $\bar{v}_2$ and the volume fractions are calculated with the molecular weight of the pure components and the experimental specific volume v_{sp}.

$$M = x_1M_1 + x_2M_2 \tag{9}$$

$$V = v_{\text{sp}}M \tag{10}$$

$$\bar{v}_1 = V + x_2\frac{\partial V}{\partial x_1} \qquad \bar{v}_2 = V - x_1\frac{\partial V}{\partial x_1} \tag{11}$$

$$\varphi_1 = x_1\bar{v}_1 = 1 - \varphi_2 \tag{12}$$

The excess specific volume of mixing v^{E} is

$$v^{\text{E}} = \frac{(x_1V_1 + x_2V_2) - V}{M} \tag{13}$$

plasticizationwhere V_1 and V_2 are the molar volumes of water and anhydroglucose, respectively.

The pressure and temperature dependence of the specific volume was measured with the *PVT* apparatus (Gnomix Research Inc., Boulder, Colorado). A detailed description of the apparatus and of the method has been given elsewhere.[32] Relative volume changes were recorded on platelets (1−1.5 g) confined in a mercury-filled cell closed at one end with a flexible bellow connected to a linearly variable transducer

Table 1. Calorimetrically Measured Glass Transition Temperatures, T_g, of Amorphous Starch Containing w_1 Weight Fraction or x_1 Mole Fraction Water

w_1	x_1	T_g (°C)	w_1	x_1	T_g (°C)
0.044	0.293	178.7	0.148	0.610	70.0
0.069	0.400	155.5	0.167	0.643	54.7
0.084	0.452	131.0	0.194	0.684	43.3
0.105	0.514	109.5	0.221	0.719	29.0
0.121	0.553	97.0	0.254	0.754	17.0
0.124	0.560	88.7			

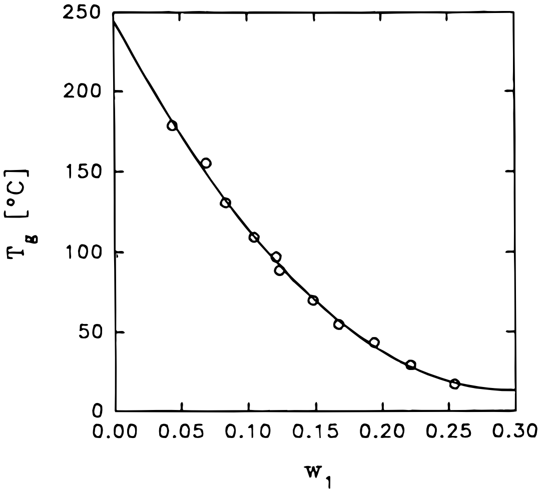

Figure 1. Glass transition temperatures, T_g, as a function of the weight fraction of water w_1 in amorphous starch, as measured by heat flow calorimetry ($T_g(w_1) = 244.9 - 1565w_1 + 2640w_1^2$, regression coefficient $r = 0.999$).

(sensitivity: ±0.0002 cm³/g). A vacuum of 4 mmHg was applied during the cell-filling procedure. The water content of the sample after filling was obtained from measurements on identical samples subjected to the same vacuum. Prior to measurement, samples were brought to 130 °C in the *PVT* cell and cooled to the lowest experimental temperature−pressure condition (25−30 °C and 0.1 MPa) where no volume relaxation was observed in the hours following the annealing. Up to 170 °C, the measured specific volumes were not found to be affected by the duration of the thermal treatment. The experimental pressures were not corrected to take into account the comparatively low-pressure exerted by water in the sample cell. The specific volumes were calculated from the experimental values by fitting $\ln(v_{sp})$ to T and to P with second-order equations used to estimate the thermal expansion coefficient, α, and the isothermal compressibility, κ, of the materials.

$$\alpha = \frac{1}{v_{sp}} \frac{\partial v_{sp}}{\partial T}\bigg|_P = -\frac{\partial \ln v_{sp}}{\partial T}\bigg|_P \tag{14}$$

$$\kappa = -\frac{1}{v_{sp}} \frac{\partial v_{sp}}{\partial P}\bigg|_T = \frac{\partial \ln v_{sp}}{\partial P}\bigg|_T \tag{15}$$

Results

The glass temperature transitions measured on amorphous starch containing between 0.04 and 0.25 weight fraction of water (w_1) are presented in Table 1. Due to enhanced thermal degradation of starch above 180 °C, the glass-melt transition of dry starch remains beyond experimental limits. The melting point of pure ice at the applied heating rate of 10 °C/min was used to calibrate the temperature scale, which was found to be shifted by 5 °C. The composition dependence of the glass transition is shown in Figure 1, where it can be seen that the transitions measured on fully amorphous, extruded samples occur at temperatures higher than reported for native potato starch.[33]

Table 2. Specific Volumes, v_{sp}, Measured by Dilatometry in Paraffin at 25 °C on Amorphous Starch Samples Containing w_1 Weight Fraction Water[a]

w_1	v_{sp} (cm³/g)	M	x_1	V (cm³/mol)	$\bar{v}_1$ (cm³/mol)	$\bar{v}_2$ (cm³/mol)	φ_1
0.0000	0.6677[b]	162.14	0.0000	108.27	6.2190	108.27	0.0000
0.0053	0.6669	155.55	0.0458	103.63	7.2784	108.25	0.0032
0.0135	0.6638	146.34	0.1097	97.222	8.6746	108.13	0.0098
0.0164	0.6638	143.34	0.1305	95.156	9.1087	108.07	0.0125
0.0250	0.6617	135.12	0.1875	89.552	10.245	107.85	0.0215
0.0371	0.6613	125.03	0.2575	87.779	11.534	107.49	0.0359
0.0530	0.6615	113.86	0.3350	75.415	12.826	106.94	0.0570
0.0598	0.6642	109.67	0.3641	72.689	13.274	106.70	0.0665
0.0733	0.6662	102.21	0.4159	67.881	14.023	106.22	0.0859
0.0807	0.6668	98.529	0.4414	65.536	14.368	106.96	0.0968
0.0938	0.6685	92.630	0.4823	61.807	14.890	105.52	0.1162
0.1087	0.6688	86.724	0.5233	58.113	15.373	105.03	0.1384
0.1204	0.6724	82.589	0.5520	55.551	15.687	104.66	0.1559
0.1358	0.6763	77.712	0.5858	52.554	16.033	104.21	0.1787
0.1519	0.6798	73.194	0.6172	49.801	16.329	103.76	0.2024
0.1539	0.6811	72.669	0.6208	49.483	16.362	103.71	0.2053
0.1695	0.6843	68.819	0.6475	47.159	16.593	103.30	0.2278
0.1952	0.6926	63.296	0.6858	43.853	16.896	102.69	0.2642
0.2306	0.7048	56.995	0.7296	40.124	17.199	102.96	0.3127
0.2614	0.7118	52.451	0.7611	37.464	17.389	101.41	0.3533
0.2981	0.7260	47.902	0.7926	34.823	17.556	100.83	0.3996
0.3301	0.7368	44.534	0.8160	32.884	17.664	100.38	0.4383
1.0000	1.0029[b]	18.015	1.0000	18.065	18.065	96.424	1.0000

[a] The table also lists the mean molecular weight, M, and the partial molar volumes, $\bar{v}_1$ and $\bar{v}_2$, used to calculate the volume fractions of water, φ_1, in the mixtures. [b] Extrapolated values for the pure components, as mentioned in the text.

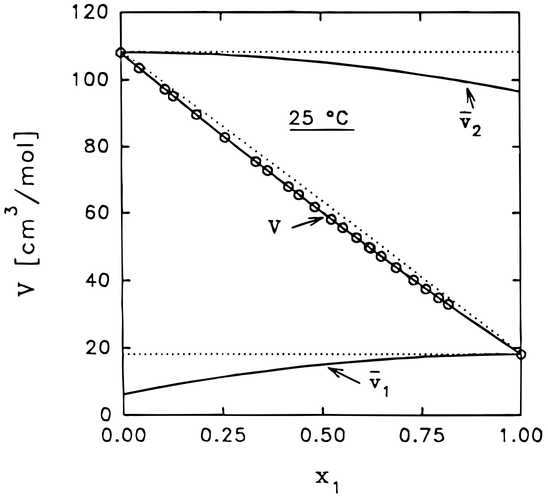

Figure 2. Molar volume, V, measured at 25 °C by dilatometry as a function of the molar water concentration, x_1, in amorphous starch. $V(x_2)$ is fitted to a quadratic equation used to calculate the partial molar volumes, $\bar{v}_1$ and $\bar{v}_2$, of the pure components ($V(x_2) = 18.065 + 78.359x_2 + 11.846x_2^2$, $r = 1$). Dotted lines represent the same quantities calculated by assuming volume additivity.

The experimental results obtained by dilatometry in paraffin at 25 °C are presented in Table 2, which shows the molar volumes obtained as a function of the water content. It can be seen that the volume contraction on mixing starch with water is accurately described over the whole molar concentration range by a single quadratic equation (see legend for Figure 2). The standard deviation in the values measured for v_{sp} was estimated to ±0.001 cm³/g, and the molar volume of pure water could be extrapolated with an accuracy of ±0.0002 cm³/

Table 3. Coefficients *a*, *b*, and *c* of the Quadratic Equations ($V = a + bx_1 + cx_1^2$) Used to Fit the Dependence of the Molar Volume (*V*) on the Mole Fraction x_1 of Water in Amorphous Starch at Temperature T^a

T (°C)	*a*	*b*	*c*
5	108.12	−102.37	12.256
15	108.19	−102.19	12.033
25	108.27	−102.05	11.846
35	108.35	−101.88	11.650
45	108.45	−101.72	11.470
55	108.55	−101.55	11.289
60	108.60	−101.47	11.196
70	108.71	−101.29	11.008
80	108.83	−101.10	10.812
90	108.96	−100.89	10.606
100	109.09	−100.67	10.390
110	109.23	−100.47	10.207
120	109.38	−100.24	10.006
130	109.54	−100.01	9.8050

[a] The whole set of pressure−volume−temperature data of all the investigated mixtures can be found elsewhere.[40]

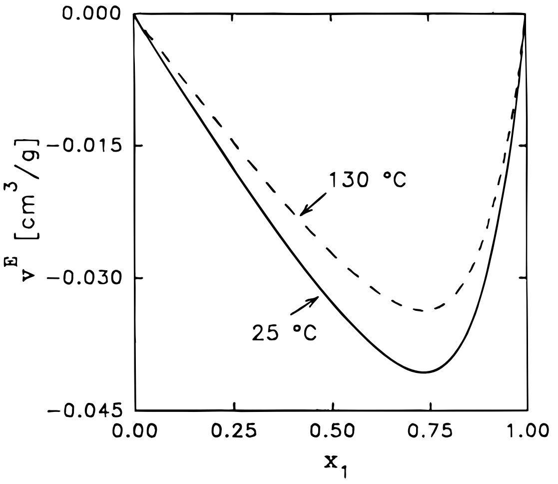

Figure 3. Excess volume of amorphous starch, v^E, containing x_1 mole fraction of water at 25 and 130 °C. The maximum in the volume contraction shows that three water molecules are needed to complete the solvation of an anhydroglucose unit in this temperature range.

g. The density of 1.4975 g/cm^3 extrapolated for dry amorphous starch is close to the value of 1.4988 g/cm^3 reported in the literature[33] for dry native potato starch determined by the same experimental method.

At higher temperatures, the relative volume changes corresponding to variations of the temperature and the pressure were recorded at fixed sample composition and temperature between 25 and 160 °C and between 10 and 100 MPa, with 1 min equilibration time at any temperature−pressure condition. Reproducibility was checked by repeated measurements using the same sample, and the experimental uncertainty was estimated to be ±0.002 cm^3/g. The specific volume of amorphous starch−water mixtures can be calculated with Table 3.

Figure 3 shows that the maximum contraction on mixing water and starch occurs independently from the temperature at a constant composition of $x_1 = 0.75$, where there is one water molecule per hydroxyl group of the anhydroglucose in the mixture. As the temperature is increased from 25 to 130 °C, the maximal intensity of the contraction regresses from −0.041 to −0.033 cm^3/g. This result indicates that the solvation of the anhydroglucose units is completed at the same water concentration over the entire experimental temperature range. On plotting the specific volume on the weight fraction scale shown in Figure 4, another minimum becomes apparent at the low water concentrations where starch is in the glassy state.

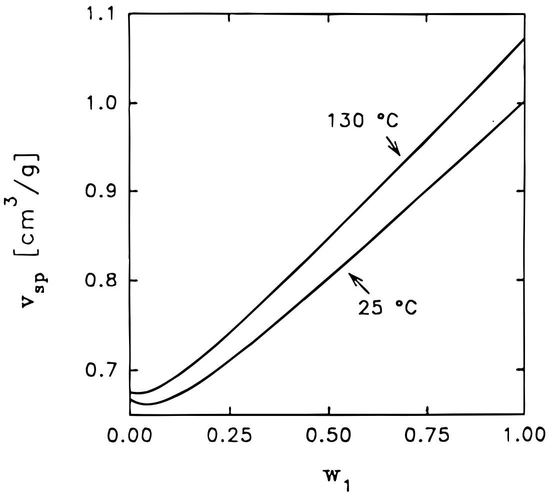

Figure 4. Specific volumes, v_{sp}, of amorphous starch as a function of the weight fraction of water w_1 in the mixture at 25 and 130 °C (values calculated with the analytical functions reported in Table 2). The solvation of anhydroglucose units is not revealed in this representation, as it is in Figure 3.

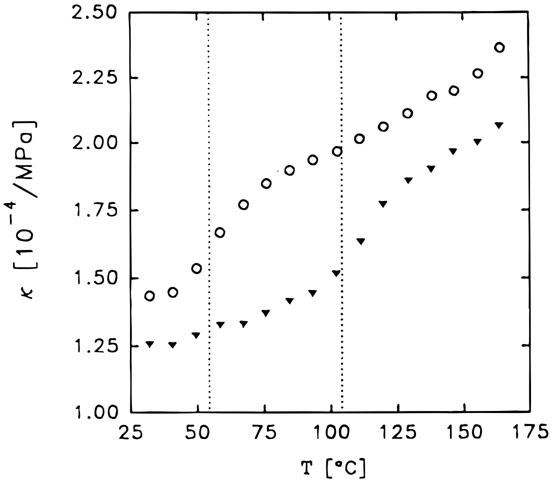

Figure 5. Temperature dependence of the isothermal compressibility of amorphous starch containing $w_1 = 0.164$ (open symbols) and $w_1 = 0.111$ (filled symbols) weight fraction of water. Glass transition temperatures measured calorimetrically are represented by dotted lines corresponding well with the step in the compressibility function at the solidification temperature of the material.

The zero pressure isothermal compressibility increment at the glass transition point is illustrated for two water contents ($w_1 = 0.111$ and 0.164) in Figure 5. It can be seen that the compressibility increments at the transition are in good agreement with the calorimetric results reported in Table 1. Amorphous starch glasses are characterized by compressibilities around 1−1.75 MPa,$^{-1}$ corresponding to bulk moduli between 6 and 9 GPa, while these values are 1.75−3.5 MPa^{-1} and 3−6 GPa for melts. Bulk moduli reported for other polymer melts range generally from 1 to 3 GPa.[34]

Data Analysis and Discussion

The scaling parameters of the various equations of states were obtained from the specific volumes meas-

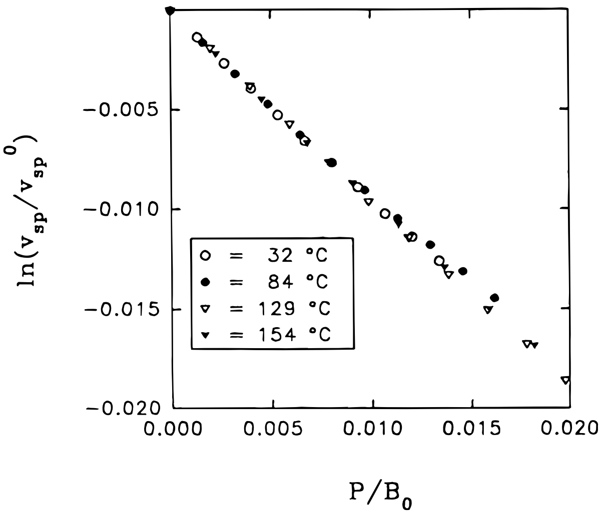

Figure 6. $T-P$ superposition using the compression data of amorphous starch glasses (at 32 and 84 °C) and melts (at 129 and 164 °C) containing $w_1 = 0.111$ weight fraction of water plotted against the reduced pressure variable P/B_0.

Table 4. Hole Cell Scaling Parameters P^*, V^*, and T^* (M Is the Molecular Weight), the Structure Factor, c/r, and Degree of Occupancy, y, of the Lattice (stp = Standard Pressure (0.1 MPa) and Temperature (25 °C)) for Amorphous Starch Containing x_1 Mole Fraction Water

x_1	P^* (GPa)	V^*/M (cm^3/g)	T^* (10^{3}K)	y(stp)	c/r	$\langle\Delta v_{sp}\rangle^a$ (10^{-4} cm^3/g)
0.586	1.834	0.689	12.57	0.978	0.012	>100
0.616	1.783	0.694	12.37	0.983	0.012	>100
0.640	1.732	0.696	12.11	0.981	0.012	>100
0.714	1.538	0.714	11.79	0.978	0.011	26
0.759	1.446	0.724	11.60	0.973	0.011	46
0.803	1.389	0.742	11.37	0.974	0.011	42
1.000	0.830	0.999	10.11	0.959	0.010	29

[a] $\langle\Delta v_{sp}\rangle$ is the average deviation between experimental and calculated specific volumes.

ured between 25 and 165 °C and between 0.1 and 100 MPa using a Marquardt least-squares fit program. The empirical equation of state, eq 1, gave fits characterized by low average deviation between experimental and calculated values, $\langle\Delta v_{sp}\rangle$, of ±0.0002 cm^3/g. Once the experimental pressure has been reduced by B_0, the compression response of starch glasses and melts can be superimposed onto a single nonlinear master curve (pressure−temperature superposition), as shown in Figure 6. The B_1 values reported in the literature[13] at 11 ± 1.5 for polymers and at 6.1 for water could be confirmed with the exception of the two lowest water contents where $B_1 = 13$. The $(P-T-w_1)$ superposition satisfied by the specific volumes of mixtures over a wide concentration range is therefore not valid for the pure components.

The results obtained with the equation of state, eq 2, of the hole cell equation of state, are presented in Table 4. The average deviations reflect a rapid decrease of the fit quality as the concentration of starch is increased, and the fits could not be improved on setting a constant y below the glass transition. The structure factors c/r calculated from eq 3 with the scaling parameters are also reported in Table 4 to show that a fairly constant value of 0.01, corresponding to a stiff r-mer, is derived independently of the concentration. Figure 7 shows that the agreement between the experimental cohesive energy densities[12] and those predicted by eq 5 using P^* in the calculation is not satisfying and the agreement is only slightly better if T^* is substituted for P^* in the same equation. The values obtained with water show how the cohesive energy density is affected by the neglect of polar forces.

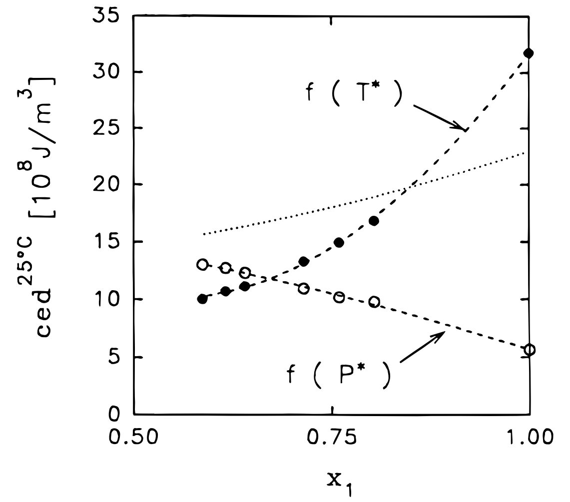

Figure 7. Cohesive energy densities at 25 °C, ced$^{25°}$C, as a function of the molar water concentration, x_1, in amorphous starch, as estimated from vapor pressure experiments[12] (dotted line) and as calculated with the hole cell eq 4 using P^* (open symbols) or T^* (filled symbols).

Table 5. Lattice Fluid Scaling Parameters r, v^*, P^*, ρ^*, and T^* at Molar Concentration x_1 of Water in Amorphous Starch

x_1	r	v^* (cm^3/mol)	P^* (MPa)	ρ^* (g/cm^3)	T^* (K)	$\langle\Delta v_{sp}\rangle^a$ (10^{-4} cm^3/g)
0.043	6.63	15.4	558	1.526	1035	9
0.142	3.88	24.0	388	1.524	1117	11
0.181	3.63	24.6	385	1.524	1138	6
0.288	4.49	17.5	502	1.531	1060	9
0.357	4.64	15.6	536	1.534	1002	10
0.442	4.66	13.8	590	1.530	977	9
0.529	5.31	10.6	695	1.529	884	14
0.586	5.81	8.78	790	1.523	833	9
0.616	5.85	8.26	811	1.520	806	9
0.640	5.72	8.06	809	1.516	784	9
0.714	5.32	7.46	824	1.492	739	15
0.759	4.99	7.19	838	1.469	725	13
0.803	4.25	7.60	789	1.434	721	11
1.000	1.47	11.5	451	1.070	623	20

[a] $\langle\Delta v_{sp}\rangle$ stands for the average deviation between experimental and calculated specific volumes.

The results obtained with the lattice fluid are presented in Table 5, where it can be seen that the average deviations, $\langle\Delta v_{sp}\rangle$, reported are typical for polymers.[18] The incorporation of data on the glassy state did not influence the value of the scaling parameters, which remained within their confidence intervals of 1−3% for ρ^* and 3−8% for T^* and P^*. A typical fit obtained with this model is illustrated in Figure 8, which shows three isotherms measured on glasses and three isotherms measured on melts of a mixture containing 0.52 mole fraction water. It can be seen that the thermal expansion coefficient is somewhat overestimated by the values predicted with the model at low pressures and is underestimated at high pressures. The scaling temperature T^* of 350 °C for water is in close agreement with its critical temperature, but the neglect of polar forces in the lattice fluid treatment is apparent in the underestimation of the internal pressure. This is reflected in the cohesive energy densities calculated with eq 7 and shown in Figure 9. An equation of state

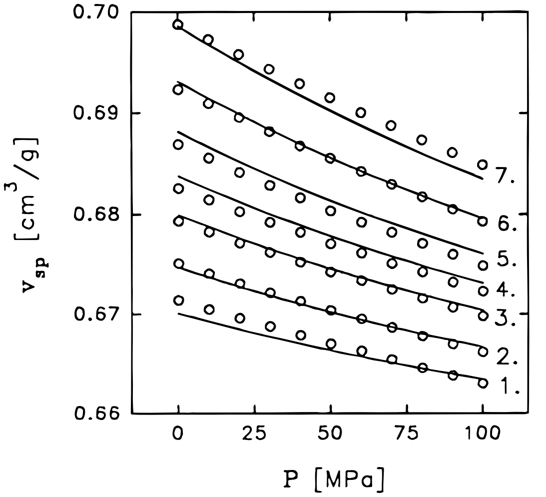

Figure 8. Isothermal *PVT* data of an amorphous starch−water mixture containing $x_1 = 0.52$ mole fraction (0.111 weight fraction water) at (1) 32.2, (2) 58.4, (3) 84.4, (4) 101.8, (5) 119.2, and (6) 154.4 °C. Symbols refer to experimental values and solid lines were calculated using the lattice fluid.

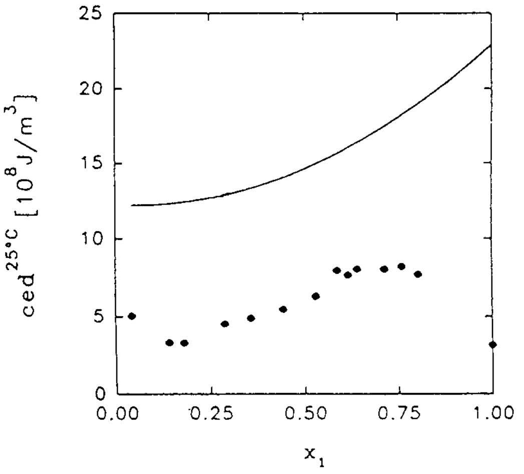

Figure 9. Cohesive energy densities at 25 °C, ced$^{25°C}$, as a function of the mole fraction, x_1, of water in the starch. The solid line shows values calculated from vapor pressure measurements, and the symbols show values calculated with the lattice fluid equation using eq 7 and the values reported in Table 5.

accounting for the effect of hydrogen bonding has been proposed to overcome this problem and is discussed elsewhere using notably hydrogen-bonding parameters estimated from an atomistic modeling of the same material.[11,35−37,40,41]

The degree of occupancy of the lattice, ρ/ρ^*, shown in Figure 10, can be used to approximate the free volume $(1 - \rho/\rho^*)$.[3,25−30] Close-packed densities ρ^* calculated with group contribution methods are generally used to correlate the gas permeation data of polymers to the size of the diffusant as well as to the free volume available for the diffusion in the polymer.[25−30,38,39] The close-packed densities estimated with the lattice fluid (ρ^*, Table 5) reveal the same maximum as the density of starch at low water concentration ($\rho = 1/v_{sp}$ in Table 2). This minimization of the free volume of a glass at low plasticizer concentrations is called antiplasticization and has been observed on polycarbonate, poly(vinyl chloride), and polysulfone glasses. Antiplasticization increases the elastic modulus of glasses at low plasticizer concentration and reduces the glass transition temperature, whereas during plasticization the elastic moduli are generally reduced with the glass transition temperature.[26] The minimization of the free volume of a glass by antiplasticization results generally in a substantial reduction of gas sorption and permeation rates.[30] At higher water concentrations, the free volume of starch−water glasses becomes larger than that of neat starch and the material loses its gas barrier properties as it is brought toward its glass transition point.[2,37]

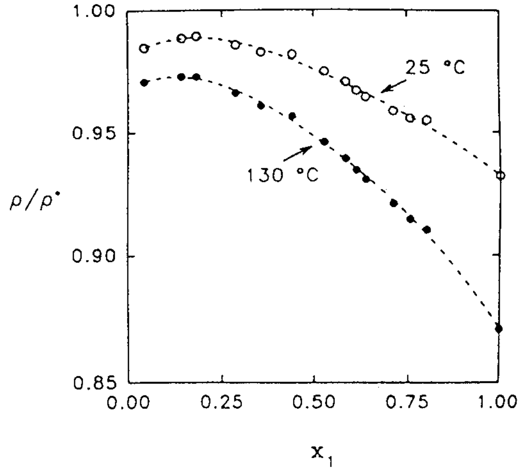

Figure 10. Degree of occupancy of the lattice, ρ/ρ^*, as a function of the molar fraction of water in starch, x_1. The free volume, $(1 - \rho/\rho^*)$, is a minimum at the low water concentrations where the density of the system goes through a maximum, as shown in Figure 4 (see also $\rho = 1/v_{sp}$ in Table 2).

Conclusion

The dilatometric and calorimetric results show that glass transitions estimated from the compressibility increment at the transition temperature are in agreement with those detected by calorimetry. The dependence of the excess volume of starch on the molar concentration of water reveals that three water molecules are needed to complete the solvation of an anhydroglucose unit by water. The pressure−volume−temperature relationships of starch−water systems have been correlated with an empirical analytical function, which was used to reduce the specific volume of mixtures to a single master curve by temperature−pressure−composition superposition. A satisfying specific volume correlation could also be obtained for melts and glasses with the lattice fluid equation of state but not with the hole cell model. The neglect of polar interactions in mean-field approaches results further in an underestimation of the internal pressure and therefore of the cohesive energy density. Free volumes estimated with the lattice fluid equation of state reflect semiquantitatively the temperature and concentration dependence of the density of starch, which goes through a maximum value at low water concentrations. The reduction of the free volume of polymer glasses by low plasticizer concentrations is called antiplasticization, as the reduction of the glass transition temperature is coupled to an increase rather than a decrease of the Young modulus. Antiplasticization is generally correlated to reductions in gas sorption and permeation rates, and its occurrence can be used to optimize the gas barrier properties of polymer glasses. The second part of this paper is dedicated to the investigation of the effects of antiplasticization on the water sorption isotherms of starch.

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