

Aqueous-Solution and Solid-Film Properties of Poly(vinyl alcohol), Poly(vinyl pyrrolidone), Gelatin, Starch, and Carboxymethylcellulose Polymers

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ABSTRACT: With the density and viscosity results for five polymers—poly(vinyl alcohol) (PVA), poly(vinyl pyrrolidone) (PVP), gelatin (Ge), starch (St), and carboxymethylcellulose (CMC)—measured in aqueous solutions at different temperatures, we have computed the excess molar volumes and activities. Smaller excess molar volumes for PVA solutions are attributed to specific types of interactions, whereas for other polymers, these data are quite large, indicating dispersion-type interactions. The activity data of the polymer solutions vary widely, depending on the nature of the polymers and

their intermolecular interactions. The freestanding film properties of the polymers indicate that Ge and PVA produce stable films, whereas brittle films can be obtained for PVP and St. The mechanical strength properties of PVA and CMC have been found to be suitable for membrane fabrication. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 106: 765–774, 2007

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INTRODUCTION

The thermodynamics of polymer solutions have been extensively studied^{1–4} over many decades since the pioneering work of Flory⁵ and Huggins.⁶ Such studies have been useful for predicting the solution properties of polymers before their usage in various disciplines.^{7–10} There have been many approaches used to predict thermodynamic interactions in polymer solutions, including hard-sphere, noncompressible, compressible-lattice, and off-lattice models and the van der Waals partition function.^{11,12} The equation-of-state models of Prigogine¹³ and others^{14,15} have led to a clear understanding of the solution properties and phase behavior of polymers.^{16–18} Experimental techni-

ques such as light scattering, ultracentrifugation, viscometry, and densimetry have been used to test these theories.^{19,20} Of these, densimetry and viscometry have been used to obtain useful thermodynamic information on polymer solutions.^{21,22} In the literature, synthetic and natural polymers have been widely used as membranes²³ or as drug-delivery devices.²⁴ It is thus important to understand their solution and film properties. For this study, we selected five water-soluble polymers—poly(vinyl alcohol) (PVA), poly(vinyl pyrrolidone) (PVP), gelatin (Ge), starch (St), and carboxymethylcellulose (CMC)—to study their aqueous-solution and film properties. Their thermodynamic properties in aqueous media have been studied in terms of the excess molar volumes and activities with density data along with viscosity data to calculate the viscosity-average molecular weight (M_η).

Of the polymers employed in this work, CMC is a derivative of cellulose formed by a reaction with alkali and chloroacetic acid. Its structure is based on the (1,4)-D-glucopyranose ring of cellulose. Different preparations may give different degrees of substitution, but generally, 0.6–0.95 derivatives per monomer unit are possible. CMC dissolves rapidly in cold water and is used to control the viscosity without gelling. It is used as a thickener and emulsion stabilizer (e.g., with milk casein). Ge is a protein derived from the partial hydrolysis of collagen extracted from skin, bones, cartilage,

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ligaments, and so forth. The natural molecular bonds between individual collagen strands are broken down into a form that rearranges more easily. Ge melts when heated and solidifies when cooled. When dissolved in water, it forms a semisolid, colloidal gel. St is the major carbohydrate reserve in plants and seed endosperm, in which it is found as granules, each typically containing several million amylopectin molecules accompanied by a much larger number of smaller amylose molecules. By far the largest source of St is corn (maize), whereas other commonly used sources are wheat, potatoes, tapioca, and rice. The genetic modification of St crops has recently led to the development of St with improved and targeted functionality. PVA and PVP are well-known synthetic polymers that are biocompatible and find applications in controlled-release studies^{25,26} as well as membranes in separation science.^{27,28}

In this investigation, we have made an effort to understand the solution properties of the aforementioned polymers by measuring their densities at temperatures from 298.15 to 338.15 K to evaluate the excess molar volumes and activities in 1% aqueous solutions. The density results have been analyzed with the thermodynamic activity models of Flory and Huggins, whereas excess molar volumes have been computed from density data. The computed results are discussed in terms of the thermodynamic interactions between the polymers and water. Mathematical equations are presented for data analysis to show the agreement of the activity data with the experiments. A similar study was proposed before,^{29–31} but this study deals with five important biopolymers. The viscosities of the polymer solutions have been measured to compute the molecular weights of the polymers. The polymer film properties have been measured by dynamic mechanical thermal analysis (DMTA) and thermogravimetric analysis (TGA) to understand their morphological characteristics and glass-transition behavior. The results of such a study would be useful before the applications of these polymers as controlled-release devices or barrier membranes in separation science.

EXPERIMENTAL

Materials

PVA, St, Ge, and CMC were all purchased from S.D. Fine Chemicals (Mumbai, India). PVP was purchased from Aldrich Chemicals (Milwaukee, WI).

Methods

Stock aqueous solutions of different polymers (1%) were prepared by the dissolution of 1 g of each polymer in 100 mL of water. Solutions for the density and viscosity measurements were prepared from these stock solutions in different concentrations of the weight fractions of the polymers. The molecular

weights of the monomers of the polymers were taken as the basis for calculating the weight fractions. Double-distilled water, produced in the laboratory itself with a Permionics (Vadodara, India) pilot plant, was used throughout the research.

Density measurements

The densities of the pure polymer solutions and solutions of different weight fractions were measured with a DMA model 4500/5000 high-precision, vibrating-tube digital densitometer from Anton Paar (Graz, Austria). The temperature of the measuring cell was automatically controlled within an uncertainty of $\pm 0.01^\circ\text{C}$ by an inbuilt, integrated Pt-100 measuring sensor. The instrument was calibrated with air and double-distilled and freshly degassed water at the temperature of the measurement during each session. The densities of the mixtures belonging to a given system (including the pure components) were measured during a continuous session. The experimental uncertainty (i.e., the reproducibility of the measured densities) was up to five units in the second decimal place.

Before each sample was injected, adjustments were made if the deviations between the displayed values and reference values of the density standards exceeded the specifications of the instrument. Air and double-distilled, freshly degassed water were used for calibration. The density values of water and dry air at the specific atmospheric pressure were stored in the memory of the instrument for the complete temperature range investigated. If the compared values agreed within $\pm 0.05 \text{ kg/m}^3$, then measurements were continued after the measuring cell was dried.

Viscosity measurements

Solutions of known concentrations of the polymers were prepared in water. The kinematic viscosities of the solutions were measured at 30°C with a Schott-Gerate (Hofheim, Germany) model AVS 350 viscometer according to the detailed procedure reported earlier.³² In brief, approximately 5 cm^3 of the liquid was injected into the viscometer and equilibrated to a constant temperature maintained within an accuracy of $\pm 0.1^\circ\text{C}$ for about 20 min. Then, the flow times of the pure solvent (t_0) and polymer solutions (t) were measured. With these data, the reduced viscosity [$\eta_{\text{red}} = \eta_{\text{sp}}/c$, where η_{sp} is the specific viscosity and c is the concentration] and inherent viscosity were calculated. Plots of η_{red} versus the concentration and the inherent viscosity versus the concentration were constructed to calculate the intrinsic viscosity ($[\eta]$) of the polymers.³³

DMTA

DMTA of the polymers was performed with a Rheometric Scientific DMTA instrument operating at a fre-

quency of 1 Hz. DMTA scans were performed between 25 and 300°C at a heating rate of 5°C/min.

TGA

TGA thermograms of the polymers were recorded on a Mettler TGA/SDTA 851° system (Zurich, Switzerland). TGA scans were conducted from 25°C to 800°C at a heating rate of 20°C/min under an inert nitrogen atmosphere.

Activity

The solution nonidealities of mixtures have been studied in terms of the activity and activity coefficient, which represent the intermolecular interactions between the components of mixtures.^{13,14} The activity coefficient of a pure component (γ_i) is given by

$$RT \ln \gamma_i = \left(\frac{\partial g^E}{\partial n_i} \right)_{T,P,n_{i=1}} \quad (1)$$

where R is the gas constant, T is the temperature, P is the pressure, g^E is the molar Gibbs excess function, and n is the total number of moles of the components, which is given by $n = \sum_{i=1}^c n_i$. g^E is given as follows:

$$g^E = u^E + Pv^E - Ts^E \quad (2)$$

where u^E is the molar Gibbs excess internal energy, v^E is the excess molar volume, and s^E is the excess molar entropy. To obtain γ_i at temperature T and pressure P , the exact composition-dependent functions for u^E , v^E , and s^E are required. With the original lattice theory of Guggenheim, Flory¹⁷ derived an expression for s^E for polymer solutions:

$$\frac{s^E}{R} = -x_1 \ln \left[1 - (1 - \phi_1) \left(1 - \frac{1}{r} \right) \right] - x_2 \ln [-\phi_2(-1)] \quad (3)$$

where x_i and ϕ_i are the molar fraction and volume fraction of the solvent (1) and polymer (2), respectively, and r is the number of segments of the polymer chain. ϕ_i is calculated as follows:

$$\phi_1 = \frac{x_1 v_1}{x_1 v_1 + x_2 v_2} \quad \text{and} \quad \phi_1 = (1 - \phi_2) \quad (4)$$

Here r is defined as the ratio of the molar volume of the polymer (2) to that of the solvent (1):

$$r = \frac{v_2}{v_1} \quad (5)$$

where v_1 and v_2 are molar volumes of polymer 1 and polymer 2, respectively. According to Flory,¹⁷ v^E is 0; therefore, g^E can be expressed as follows:

$$g^E = u^E - s^E \quad (6)$$

u^E is obtained with the Scatchard–Hildebrand equation.¹⁵ In this work, a simple model is used to predict the solvent activities in polymer solutions by the rewriting of eq. (1) in terms of x_1 :

$$RT \ln \gamma_1 = g^E + (1 - x_1) \frac{\partial g^E}{\partial x_1} \quad (7)$$

Inserting eq. (2) into eq. (7) and further simplification yield

$$RT \ln \gamma_1 = \left[u^E + (1 - x_1) \frac{\partial}{\partial x_1} (u^E) \right] + \left[Pv^E + (1 - x_1) \frac{\partial}{\partial x_1} (Pv^E) \right] + \left[-Ts^E + (1 - x_1) \frac{\partial}{\partial x_1} (-Ts^E) \right] \quad (8)$$

The activity coefficient of the solvent (γ_1) is divided into internal energy (γ_1^U), volume (γ_1^V), and entropy (γ_1^S) contributions:

$$\gamma_1 = \gamma_1^U \gamma_1^V \gamma_1^S \quad (9)$$

The quantities are computed as follows:

$$RT \ln \gamma_1^U = u^E + (1 - x_1) \frac{\partial u^E}{\partial x_1} \quad (10)$$

$$RT \ln \gamma_1^V = Pv^E + (1 - x_1) \frac{\partial (Pv^E)}{\partial x_1} \quad (11)$$

$$RT \ln \gamma_1^S = -Ts^E + (1 - x_1) \frac{\partial (-Ts^E)}{\partial x_1} \quad (12)$$

The activity of the solvent (a_1) can be expressed as $a_1 = x_1 \gamma_1$. Hence, we have

$$x_1^3 \gamma_1 = x_1 \gamma_1^U x_1 \gamma_1^V x_1 \gamma_1^S \quad (13)$$

so that a_1 is given by

$$a_1 = \frac{1}{x_1^2} (a_1^U a_1^V a_1^S) \quad (14)$$

where a_1^U , a_1^V , and a_1^S are the contributions of the internal energy, volume, and entropy, respectively, to the activity. With eq. (11), the excess molar volume part of the activity of the solvent can be calculated as follows:

$$\ln a_1^V = \frac{P}{RT} \left(v^E + (1 - x_1) \frac{\partial v^E}{\partial x_1} \right) + \ln x_1 \quad (15)$$

The excess enthalpy part of the activity of solvent can be derived from eq. 3:

$$\ln a_1^S = \ln \phi_1 + \left(1 - \frac{1}{r}\right) (1 - \phi_1) \quad (16)$$

The internal energy part of the activity is affected by molecular interactions that depend on molecular rearrangements defined by entropy and molecular separations in terms of volume. Thus, a_1^U is a function of the excess entropy as well as the excess volume, as shown in eq. (14), which upon arrangement gives

$$\frac{a_1^U}{x_1^2} = \frac{a_1}{a_1^V a_1^S} \quad (17)$$

The right-hand side of eq. (17) can be expressed as

$$\frac{a_1}{a_1^V a_1^S} = (a_1^S)^{f_1^S} (a_1^V)^{f_1^V} \quad (18)$$

where f_1^V and f_1^S are weighing factors. In a logarithmic form, eq. (17) can be written as follows:

$$\ln \left(\frac{a_1^U}{x_1^2} \right) = f_1^S \ln a_1^S + f_1^V \ln a_1^V \quad (19)$$

Similarly, eq. (14) can be expressed in the logarithmic form as follows:

$$\ln a_1 = (1 + f_1^S) \ln a_1^S + (1 + f_1^V) \ln a_1^V \quad (20)$$

By substituting for a_1^V and a_1^S from eqs. (15) and (16), respectively, into eq. (20), we get

$$\ln a_1 = f^C \left[\ln \phi_1 + \left(1 - \frac{1}{r}\right) (1 - \phi_1) \right] + f^R \left[\frac{P}{RT} \left(v^E + (1 - x_1) \frac{\partial v^E}{\partial x_1} \right) + \ln x_1 \right] \quad (21)$$

where $f^C = 1 + f_1^S$ and $f^R = 1 + f_1^V$. Equation (21) can be expressed in terms of the volume fraction with eq. (4) to give the final equation for activity:

$$\ln a_1 = f^C \left[\ln \phi_1 + \left(1 - \frac{1}{r}\right) (1 - \phi_1) \right] + f^R \left\{ \left[\frac{P}{RT} \left(V^E + \phi_2 \left(\phi_1 + \frac{1}{r} \phi_2 \right) \frac{\partial V^E}{\partial \phi_1} \right) \right] + \ln \left(\frac{r \phi_1}{r \phi_1 + \phi_2} \right) \right\} \quad (22)$$

To use this equation, we require the density values of the polymer and solvent, their compositions in

solution, and the values of the weighing factors, f^C and f^R , which in this case are assumed to be $f^C = f^R = 0.5$.

TABLE I
Densities of the Polymer Solutions in Water at Different Temperatures

Weight fraction	Density (g/cm ³)			
	298.15 K	308.15 K	318.15 K	328.15 K
PVA				
0.1	0.99768	0.99468	0.99085	0.98628
0.2	0.99783	0.99482	0.99098	0.98645
0.3	0.99806	0.99505	0.99118	0.98631
0.4	0.99832	0.99530	0.99145	0.98693
0.5	0.99843	0.99540	0.99153	0.98697
0.6	0.99885	0.99582	0.99199	0.98744
0.7	0.99903	0.99600	0.99217	0.98763
0.8	0.99933	0.99631	0.99247	0.98793
0.9	0.99956	0.99653	0.99269	0.98815
1.0	0.99978	0.99673	0.99287	0.98827
PVP				
0.1	0.99757	0.99453	0.99012	0.98623
0.2	0.99781	0.99477	0.99097	0.98492
0.3	0.99801	0.99499	0.99111	0.98540
0.4	0.99819	0.99517	0.99131	0.98661
0.5	0.99838	0.99534	0.99146	0.98677
0.6	0.99857	0.99554	0.99168	0.98708
0.7	0.99876	0.99573	0.99188	0.98730
0.8	0.99892	0.99586	0.99197	0.98734
0.9	0.99912	0.99608	0.99220	0.98746
1.0	0.99929	0.99623	0.99228	0.98754
Ge				
0.1	0.99802	0.99520	0.99076	0.98570
0.2	0.99828	0.99528	0.99114	0.98643
0.3	0.99841	0.99536	0.99146	0.98678
0.4	0.99859	0.99556	0.99171	0.98686
0.5	0.99887	0.99583	0.99195	0.98770
0.6	0.99913	0.99608	0.99224	0.98793
0.7	0.99936	0.99632	0.99245	0.98815
0.8	0.99967	0.99664	0.99279	0.98837
0.9	0.99985	0.99682	0.99295	0.98880
1.0	1.00021	0.99719	0.99335	0.98897
St				
0.1	0.99799	0.99497	0.99115	0.98663
0.2	0.99832	0.99529	0.99146	0.98683
0.3	0.99871	0.99566	0.99170	0.98737
0.4	0.99913	0.99609	0.99227	0.98775
0.5	0.99955	0.99652	0.99261	0.98802
0.6	0.99993	0.99689	0.99307	0.98853
0.7	1.00035	0.99731	0.99346	0.98887
0.8	1.00068	0.99764	0.99380	0.98926
0.9	1.00112	0.99808	0.99423	0.98961
1.0	1.00142	0.99833	0.99310	0.99240
CMC				
0.1	0.99786	0.99484	0.99047	0.98176
0.2	0.99820	0.99518	0.99072	0.98499
0.3	0.99859	0.99556	0.99164	0.98693
0.4	0.99890	0.99587	0.99201	0.98674
0.5	0.99927	0.99625	0.99232	0.98677
0.6	0.99957	0.99650	0.99258	0.98725
0.7	0.99980	0.99665	0.99311	0.98760
0.8	1.00036	0.99732	0.99334	0.98794
0.9	1.00072	0.99762	0.99375	0.98824
1.0	1.00107	0.99802	0.99415	0.99874

TABLE II
Estimated Parameters of Eq. (24) for the Polymers at Different Temperatures

Temperature (K)	A	B	C	D	σ
PVA					
298.15	0.0782	0.0258	-0.0644	0.0033	0.0056
308.15	0.0737	0.0145	-0.0264	0.0017	0.0021
318.15	0.0528	-0.0192	-0.0888	0.0025	0.0036
328.15	-0.0267	-0.1421	-0.2988	0.0086	0.0141
PVP					
298.15	0.1583	0.0114	0.0130	0.0009	0.0010
308.15	0.1537	0.0169	0.0179	0.0017	0.0022
318.15	0.1108	0.0240	0.0041	0.0055	0.0062
328.15	0.0458	0.0796	-0.0904	0.0232	0.0426
Ge					
298.15	0.0073	-0.0658	-0.0144	0.0046	0.0051
308.15	0.3504	-0.0835	-0.0506	0.0054	0.0052
318.15	0.3295	-0.0759	0.0529	0.0051	0.0078
328.15	0.2692	-0.0483	-0.1587	0.0135	0.0162
St					
298.15	0.5383	0.0472	-0.0514	0.0033	0.0050
308.15	0.5276	0.0762	-0.0869	0.0041	0.0069
318.15	0.1032	0.8051	-1.1908	0.0300	0.0573
328.15	1.1758	-1.4941	1.5470	0.0551	0.0507
CMC					
298.15	1.9790	-0.146	-0.090	0.0254	0.0243
308.15	1.9940	-0.270	0.040	0.0385	0.0486
318.15	1.9340	0.023	0.493	0.0280	0.0329
328.15	11.8520	-18.520	27.314	0.6736	0.6471

RESULTS AND DISCUSSION

Density, excess molar volume, and activity

The excess molar volume (v^E) was calculated from the experimental densities as follows:

$$v^E = \frac{1}{\rho} - \left(\frac{w_1}{\rho_1} + \frac{w_2}{\rho_2} \right) \quad (23)$$

where ρ is the density of the polymer solution; w_1 and w_2 are the weight fractions of components 1 and 2, respectively; and ρ_1 and ρ_2 are the respective pure component densities. The density results for different polymers at different temperatures and concentrations (weight fractions) are presented in Table I. Before the ρ values were used in eq. (23), the density results were fitted to the polynomial equation:

$$\rho / (\text{g/cm}^3) = A + B\omega_2 + C\omega_2^2 + D\omega_2^3 \quad (24)$$

where A , B , C , and D are the coefficients (g/cm^3) and ω_2 is the weight fraction of the polymer in solution. The values of the coefficients obtained by regression analysis with the Marquardt equation³⁴ are given in Table II. With eqs. (23) and (24), the excess molar volumes were calculated, and the results are displayed in Figures 1 and 2. These data have been fitted to eq. (25) by the method of least squares to estimate the coefficients (A , B , C , and D) along with the correlation coefficient (σ):

$$\sigma = \frac{100}{n} \sum_{i=1}^n \left[\frac{(\rho_i^{\text{exp}t} - \rho_i^{\text{cal}})}{\rho_i^{\text{exp}t}} \right] \quad (25)$$

where n is number of experimental data and $\rho_i^{\text{exp}t}$ and ρ_i^{cal} are the experimental and calculated densities with eq. (24), respectively. The estimated σ values are

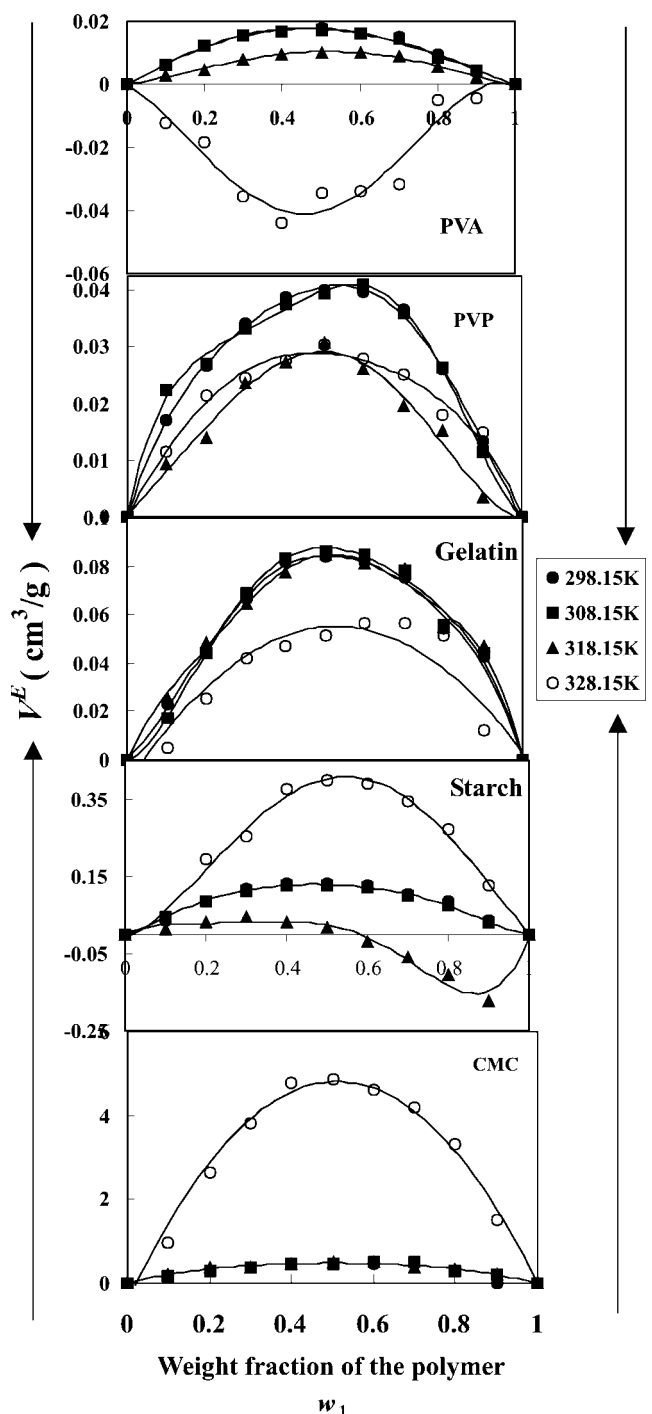


Figure 1 Excess molar volume (v^E) of the polymer solutions at different temperatures.

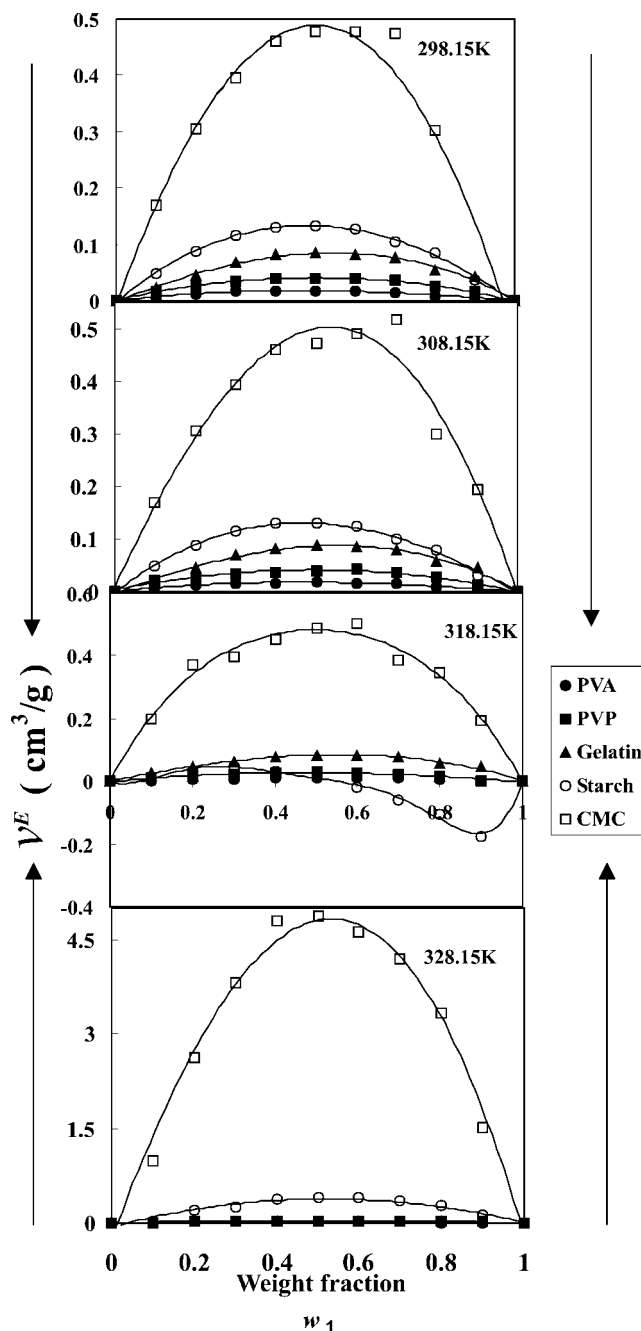


Figure 2 Excess molar volume (v^E) of the polymers at different temperatures.

also included in Table II. The calculated values of the excess molar volumes with eq. (23) are presented in Table III. The activity data are compiled in Table IV and displayed in Figure 3.

The results of the excess molar volumes versus the weight fractions of the polymer solutions are displayed in Figures 1 and 2, respectively. For PVA, with a rise in the temperature, the excess molar volumes become more negative, suggesting specific interactions between the hydroxyl groups of PVA with water molecules (see Fig. 1). At 298.15 and 308.15 K,

almost identical excess molar volumes can be observed, and hence their dependence for PVA is described by a single curve. On the other hand, with CMC and St, the excess molar volumes increase with increasing temperature, and this suggests increased polymer chain expansion. Particularly with St, a sigmoidal trend can be observed at 318.15 K; that is, at

TABLE III
Excess Molar Volumes of the Polymer Solutions at Different Temperatures

Weight fraction	Excess molar volume			
	298.15 K	308.15 K	318.15 K	328.15 K
PVA				
0.1	0.0063	0.0062	0.0028	-0.0122
0.2	0.0124	0.0123	0.0047	-0.0183
0.3	0.0157	0.0154	0.0078	-0.0355
0.4	0.0169	0.0166	0.0097	-0.0440
0.5	0.0178	0.0174	0.0098	-0.0345
0.6	0.0162	0.0159	0.0101	-0.0338
0.7	0.0148	0.0145	0.0091	-0.0314
0.8	0.0092	0.0083	0.0053	-0.0049
0.9	0.0041	0.0043	0.0023	-0.0045
PVP				
0.1	0.0170	0.0224	0.0214	0.0115
0.2	0.0267	0.0270	0.0141	0.0214
0.3	0.0340	0.0332	0.0235	0.0245
0.4	0.0388	0.0376	0.0272	0.0275
0.5	0.0399	0.0395	0.0306	0.0305
0.6	0.0396	0.0410	0.0262	0.0278
0.7	0.0365	0.0360	0.0196	0.0250
0.8	0.0260	0.0264	0.0193	0.0180
0.9	0.0132	0.0114	0.0037	0.0150
Ge				
0.1	0.0231	0.0174	0.0257	0.0050
0.2	0.0444	0.0441	0.0482	0.0257
0.3	0.0664	0.0687	0.0644	0.0420
0.4	0.0816	0.0830	0.0773	0.0472
0.5	0.0842	0.0865	0.0846	0.0511
0.6	0.0816	0.0851	0.0810	0.0566
0.7	0.0756	0.0783	0.0787	0.0562
0.8	0.0544	0.0560	0.0553	0.0512
0.9	0.0424	0.0440	0.0470	0.0120
St				
0.1	0.0476	0.0471	0.0134	0.0367
0.2	0.0886	0.0876	0.0328	0.1942
0.3	0.1164	0.1158	0.0475	0.2558
0.4	0.1307	0.1286	0.0298	0.3759
0.5	0.1328	0.1290	0.0165	0.4022
0.6	0.1271	0.1233	-0.0194	0.3917
0.7	0.1057	0.1009	-0.0603	0.3433
0.8	0.0842	0.0784	-0.1058	0.2713
0.9	0.0371	0.0301	-0.1746	0.1291
CMC				
0.1	0.1706	0.1703	0.1977	0.9734
0.2	0.3052	0.3041	0.3721	2.6336
0.3	0.3948	0.3943	0.3986	3.8078
0.4	0.4614	0.4601	0.4546	4.7894
0.5	0.4779	0.4728	0.4881	4.8756
0.6	0.4788	0.4889	0.5053	4.6332
0.7	0.4752	0.5176	0.3879	4.2013
0.8	0.3011	0.2986	0.3481	3.3345
0.9	0.0167	0.1928	0.1933	1.5067

TABLE IV
Activity of the Polymer Solutions at Different Temperatures

Weight fraction	Activity			
	298.15 K	308.15 K	318.15 K	328.15 K
PVA				
0.1	0.9992	0.9992	0.9986	0.9903
0.2	0.9920	0.9922	0.9909	0.9845
0.3	0.9726	0.9729	0.9720	0.9688
0.4	0.9313	0.9320	0.9316	0.9287
0.5	0.8512	0.8523	0.8526	0.8529
0.6	0.7081	0.7096	0.7112	0.7141
0.7	0.4890	0.4909	0.4942	0.5004
0.8	0.2351	0.2373	0.2417	0.2544
0.9	0.0401	0.0402	0.0491	0.0891
PVP				
0.1	1.0030	1.0030	1.0023	1.0028
0.2	1.0035	1.0034	1.0018	1.0031
0.3	1.0011	1.0008	0.9986	1.0008
0.4	0.9935	0.9931	0.9906	0.9933
0.5	0.9741	0.9741	0.9723	0.9745
0.6	0.9277	0.9278	0.9277	0.9291
0.7	0.8156	0.8164	0.8175	0.8190
0.8	0.5690	0.5701	0.5741	0.5743
0.9	0.1839	0.1882	0.2026	0.1887
Ge				
0.1	1.0045	1.0032	1.0047	1.0007
0.2	1.0079	1.0076	1.0081	1.0038
0.3	1.0102	1.0103	1.0090	1.0061
0.4	1.0082	1.0080	1.0065	1.0072
0.5	0.9969	0.9969	0.9963	0.9908
0.6	0.9672	0.9676	0.9671	0.9642
0.7	0.8879	0.8885	0.8892	0.8892
0.8	0.6805	0.6815	0.6833	0.6863
0.9	0.2462	0.2468	0.2462	0.2862
St				
0.1	1.0095	1.0091	1.0024	1.0066
0.2	1.0171	1.0164	1.0054	1.0231
0.3	1.0209	1.0201	1.0066	1.0332
0.4	1.0194	1.0182	0.9996	1.0398
0.5	1.0095	1.0082	0.9888	1.0385
0.6	0.9829	0.9820	0.9622	1.0119
0.7	0.9105	0.9105	0.9010	0.9290
0.8	0.7152	0.7175	0.7328	0.6778
0.9	0.2939	0.3030	0.3548	0.0991
CMC				
0.1	1.0350	1.0338	1.0381	1.0600
0.2	1.0634	1.0610	1.0727	1.0972
0.3	1.0822	1.0794	1.0776	1.0993
0.4	1.0956	1.0921	1.0879	1.1011
0.5	1.0964	1.0924	1.0921	1.1134
0.6	1.0898	1.0887	1.0888	1.1258
0.7	1.0693	1.0740	1.0501	1.1101
0.8	0.9759	0.9752	0.9792	0.9985
0.9	0.6695	0.6655	0.6682	0.8180

weight fractions of 0.6–1.0, the excess molar volumes are negative, suggesting higher specific interactions. For PVP and Ge, the excess molar volumes are positive, suggesting mild types of dispersion interactions. Also, the excess molar volumes decrease with increasing temperature, suggesting increased chain contraction with increasing temperature. Figure 2 displays the dependence of the excess molar volumes of all the

polymers at different temperatures. Figure 3 displays a plot of the activity versus the weight fraction at different temperatures. We find agreement between the theory and experiment in all cases, suggesting the validity of the theory for calculating the activity. Temperature differences are clearly visible for St and CMC, whereas for PVA, PVP, and Ge, not much difference can be observed, so a single curve has been drawn, representing the variation of all the temperatures.

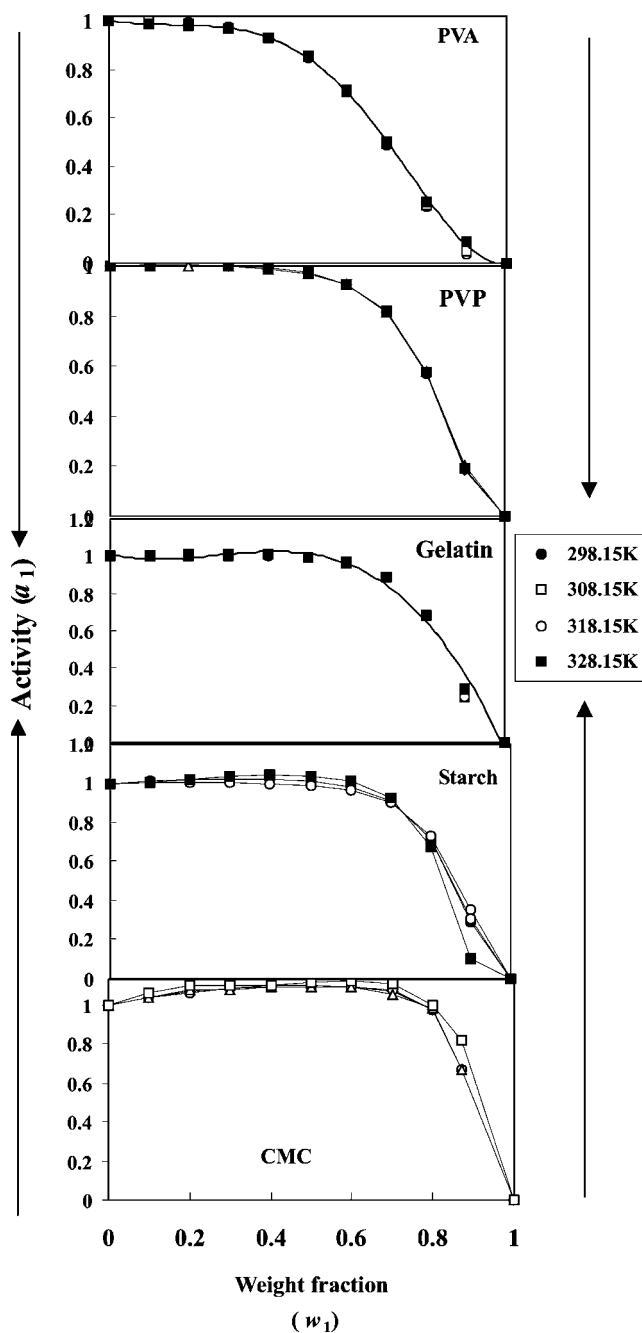


Figure 3 Activity of the polymers (a_1) in water at different temperatures.

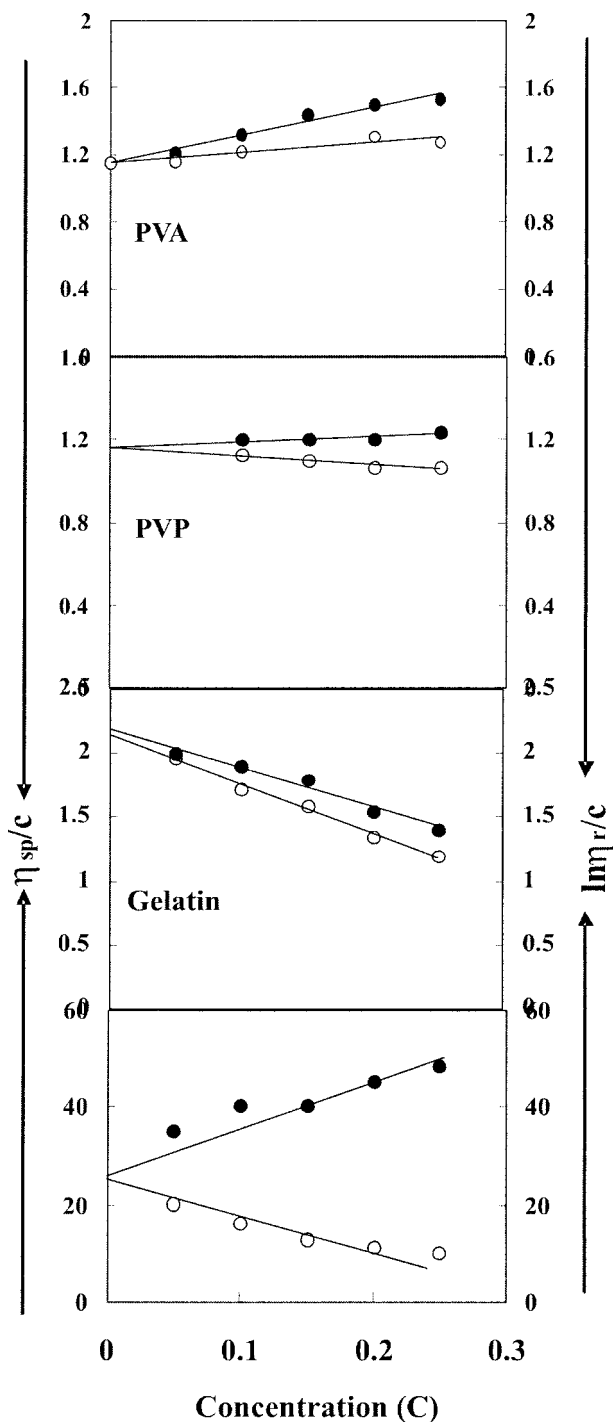


Figure 4 Plots of (●) η_{sp}/c and (○) $\ln \eta_r/c$ versus the concentration of the polymers (C) in water at 30°C.

Viscosity

The rheological properties of polymer solutions are important in designing and processing polymer-solvent mixtures.³⁵ Solutions of high-molecular-weight polymers, even at low concentrations, can flow slowly. The solution viscosity is thus a measure of the size or extension of polymer chains in space and is related to the molecular weight of the polymers. The

TABLE V
Viscosity of the Polymer Solutions at 303 K

c (g/dL)	t (s)	$t/t_0 = \eta_r$	$N = \eta_{sp}/c$	$L = \ln \eta_r/c$
PVA (t_0 for the solvent water = 6.76 s)				
0.05	7.17	1.06	1.21	1.17
0.10	7.65	1.13	1.32	1.22
0.15	8.22	1.22	1.44	1.32
0.20	8.79	1.30	1.50	1.31
0.25	9.34	1.38	1.53	1.28
PVP (t_0 for the solvent water = 6.76 s)				
0.05	7.35	1.09	1.80	1.72
0.10	7.56	1.12	1.20	1.13
0.15	7.98	1.18	1.20	1.10
0.20	8.35	1.24	1.20	1.07
0.25	8.84	1.31	1.24	1.08
Ge (t_0 for the solvent water = 6.76 s)				
0.05	7.44	1.10	2.00	1.91
0.10	8.01	1.19	1.90	1.73
0.15	8.58	1.27	1.80	1.59
0.20	8.91	1.31	1.55	1.35
0.25	9.18	1.35	1.41	1.20
CMC (t_0 for the solvent water = 6.76 s)				
0.05	18.69	2.76	35.28	20.33
0.10	34.17	5.06	40.55	16.20
0.15	47.94	7.09	40.67	13.10
0.20	68.06	10.07	45.34	11.55
0.25	88.85	13.14	48.57	10.30

$L = \ln \eta_r/c$ is inherent viscosity and $N = \eta_{sp}/c$ is reduced viscosity.

simplicity of measurement and usefulness of viscosity/molecular-weight correlations are important for determining the molecular weights of polymers.³⁶ M_{η} of a polymer in a dilute solution can be computed from a linear plot of η_{red} . Thus, by extrapolation to $c = 0$, $[\eta]$ can be obtained, which can be used to calculate M_{η} with the Mark-Houwink-Sakurada (MHS) equation.³⁶

$$[\eta] = K\overline{M}_{\eta}^a \quad (26)$$

where K and a are constants for a given polymer-solvent system at different temperatures. Generally, we find $0.5 \leq a \leq 0.8$ for flexible polymers and $0.8 \leq a \leq 1.0$ for stiff polymers. The values of K for flexible

TABLE VI
Values of E' , $\tan \delta$, the Moisture Content, and the Total Weight Loss for the Polymers

Polymer	E'	$\tan \delta$	Moisture content (%)	Total weight loss (%)
PVA	7.045×10^7	32.3	1.8	70.2
Ge	4.043×10^9	87.7	4.8	99.6
CMC	1.661×10^8	37.5	1.8	76.0
PVP	— ^a	— ^a	5.4	88.1
St	— ^a	— ^a	6.6	96.7

^a The data were not obtainable.

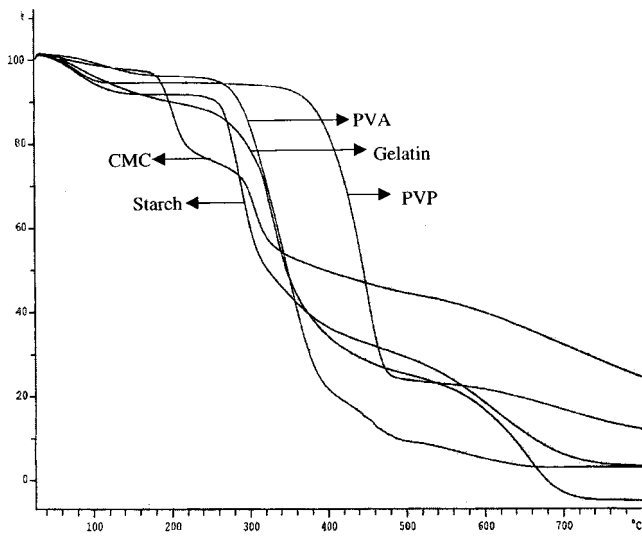


Figure 5 TGA thermograms of the polymers.

polymers are typically in the range of more than 10^{-3} to 10^{-1} cm^3/g . Equation (26) allows the evaluation of M_η from $[\eta]$ values of polymer solutions as long as the constants, K and a , are known from the literature. The most widely used method to calculate K and a involves the measurement of $[\eta]$ for a series of polymer standards of known molecular weights. Then, a plot of $\log [\eta]$ versus $\log [M]$ is fitted to a straight line, from which K and a are determined. The η_{sp} values of polymer solutions [$\eta_{sp} = (t - t_0)/t_0$] are determined from t_0 and t at low polymer concentrations. Then, we can use the Huggins equation, which reveals a correlation between η_{sp}/c and c in dilute solutions: $\eta_{red} = \eta_{sp}/c = k^1[\eta]^2c + [\eta]$, where $k^1[\eta]^2$ is the slope of the line and $[\eta]$ is the intercept. Figure 4 shows plots of η_{red} (i.e., η_{sp}/c) versus c for CMC and Ge in water at 303 K. The $a = 0.64$ and $K = 45.3 \times 10^{-3}$ values for PVA were used to calculate the molecular weights of the CMC and Ge polymers.

The viscosities of polymer solutions determined at five different concentrations are compiled in Table V, whereas the graphs of η_{sp}/c and $\ln \eta_r/c$ versus the concentration at 303 K are displayed in Figure 4. Numerical data for $[\eta]$ and M_η are given in Table VI. With the viscosity data and the well-known MHS relation,³⁶ the molecular weights of the polymers were calculated with the K and a values of PVA as standards. The molecular weight of Ge (571,404) thus obtained was higher than that of CMC (117,862).

TGA

The thermal degradation profiles of PVA, Ge, St, PVP, and CMC films are shown in Figure 5. Except for PVP, all the other polymers show two-step degradation, with an initial weight loss of about 1.8–6.66% below 100°C due to the release of moisture. On the

other hand, PVP has the highest thermal stability, showing an onset of degradation at 417°C. However, CMC has the least thermal stability, with an onset of degradation at 185°C. In general, the trends for the thermal stability of the studied polymers follow this sequence: PVP > PVA = Ge > St > CMC. The total

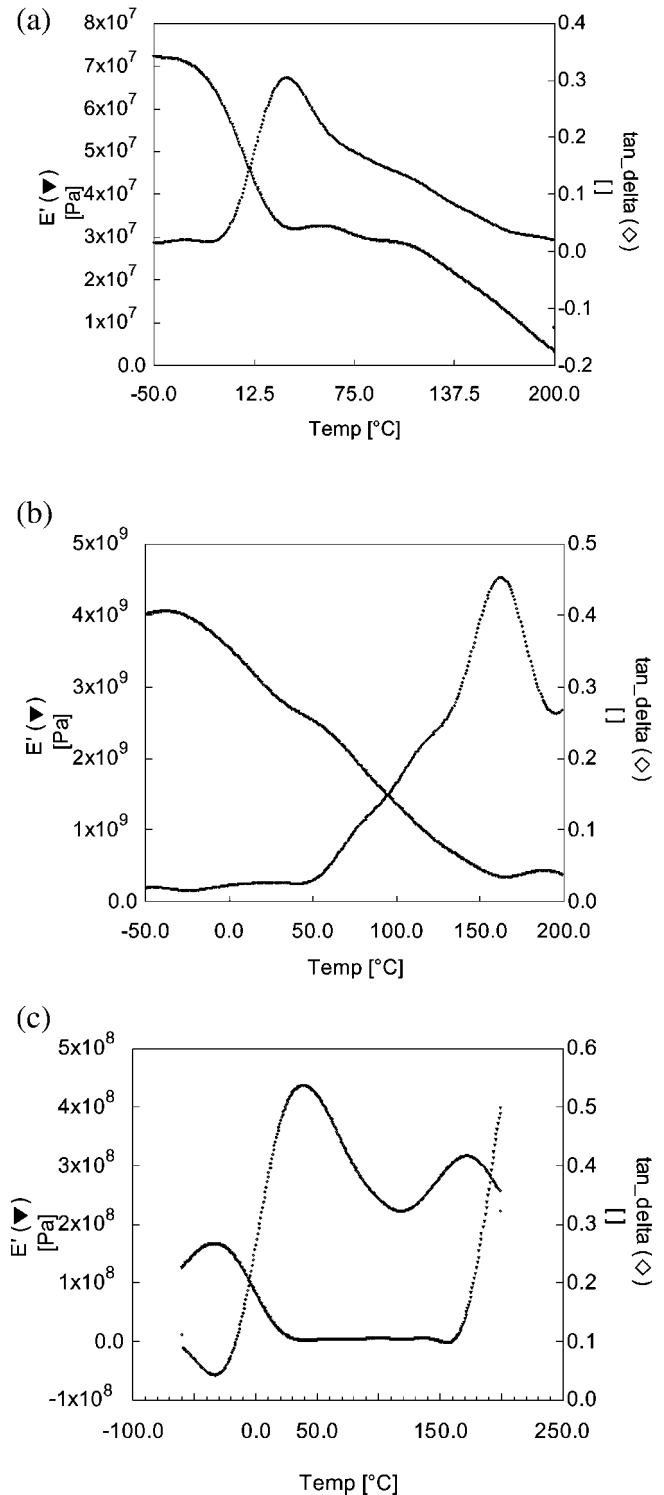


Figure 6 E' and $\tan \delta$ curves of the polymers. (a) PVA, (b) Ge and (c) CMC.

weight losses and moisture contents for various polymers are given in Table VI.

DMTA

DMTA results for PVA, Ge, and CMC have been studied in terms of the loss tangent ($\tan \delta$) and storage modulus (E') as functions of temperature (see Fig. 6). DMTA for PVP and St was not done because PVP is highly hygroscopic and produced only brittle films. Similarly, St films were quite brittle. The $\tan \delta$ and E' values for various polymers are included in Table VI. Of the three polymers, Ge shows the highest E' value (4.043×10^9) and $\tan \delta$ value (87.7). However, the lowest values of E' have been observed for PVA.

CONCLUSIONS

This study is a novel approach to the use of thermodynamic and hydrodynamic concepts to estimate excess molar volumes and activities of five different biopolymers in aqueous media. The studied polymer properties have relevance to the development of applications for these polymers in controlled-release devices for encapsulated drug matrices and in membranes for liquid or gas separation. This study demonstrates the usefulness of thermodynamic/hydrodynamic analysis with the density and viscosity properties of polymer solutions. The films of polymers, when subjected to DMTA and TGA, could yield important information on their mechanical strengths and morphological aspects that are important to field applications.

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