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Thermodynamics/hydrodynamics of aqueous polymer solutions and dynamic mechanical characterization of solid films of chitosan, sodium alginate, guar gum, hydroxy ethyl cellulose and hydroxypropyl methylcellulose at different temperatures

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Abstract

Experimental densities and viscosities of five important carbohydrate polymers viz. chitosan, sodium alginate, guar gum, hydroxy ethyl cellulose and hydroxypropyl methylcellulose have been measured in aqueous media at five different temperatures and at nine weight fractions. Using the density data, excess molar volumes have been computed. Mathematical equations are proposed to calculate the activity, which agreed well with the experimental data. Viscosity data at different concentrations of carbohydrate polymer solutions have been used to calculate the viscosity average molecular weight of the polymers. Thin free standing films of these polymers have been prepared by solution casting method and were tested for dynamic mechanical behavior as well as glass transition of the polymers were evaluated by dynamic mechanical testing analyzer and thermogravimetry, respectively.

Keywords: Density; Excess molar volume; Activity; Flory–Huggins theory

1. Introduction

Thermodynamic properties of polymer solutions have been studied extensively ever since the pioneering research by Flory and Huggins in the early forties (Flory, 1941; Huggins, 1941). In later years, innumerable studies (***Aminabhavi, & Munk, 1979a,b; Costas, Epstein, Sanctuary, Richon, & Renon, 1981; Song, Lambert, & Prausnitz, 1994) have been made to extend both theoretical and experimental aspects of these concepts to many polymer systems in order to understand the intermolecular interactions between the polymer and the solvent molecules. Such studies are useful to predict solution properties of polymers before their intended applications in various disciplines (Chiew, 1990; High, & Danner, 1990; Panayioutou, & Vera, 1982; Sanchez, & Lacomb, 1976). Other approaches to predict thermodynamic properties of polymer solutions include hard-sphere, non-compressible, compressible lattice, off-lattice models as well as models based on the generalized van der Waals partition function (Beret, & Prausnitz, 1975; Honnell, & Hall, 1989). In the compressible model, free volume concept was used in understanding thermodynamics of phase behavior in polymers. In this aspect, several new theories have emerged in addition to equation of state theory of Prigogine and coworkers (Prigogine, 1957) as well as others (Prausnitz, Lichtenthaler, & Azevedo, 1999; Sako, Wu, & Prausnitz, 1989) that led to a newer understanding of solution properties and phase behavior of long-chain polymers. Even though many more celebrated theories have been advanced in this direction over the past many decades, yet such studies have remained active, since these are quite fundamental in nature and are useful in understanding the theory of polymer solutions (Aminabhavi, Balundgi, & Joshi, 1988; Sako, Wu, & Prausnitz, 1989; Wohlfarth, 1994; Flory, 1953).

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In order to understand polymer-solvent interactions, many sophisticated experimental techniques such as light scattering, ultracentrifuge, etc. have been employed (Kratohvil, & Aminabhavi, 1982; Patel, & Aminabhavi, 1982). However, conventional techniques like densitometry and viscometry have been quite useful to obtain thermodynamic information (Gonzalez-Tello, Camacho, & Blazquez, 1994; Herskowitz, & Gottlieb, 1985). In the earlier literature, synthetic polymers have been the main target for such investigations due to their ease of preparation, applications in industries, etc. However, due to the recent environmental pollution concerns, naturally available carbohydrate polymers are considered in place of synthetic polymers for various applications. In particular, carbohydrate polymers like sodium alginate (NaAlg), chitosan (CS), hydroxy ethyl cellulose (HEC), hydroxypropyl methylcellulose (HPMC) and guar gum (GG) have been used in drug delivery applications due to their biocompatibility (Li, Lin, Daggy, Mirchandani, & Chien, 2003). Also, they find applications as membranes in liquid or gaseous mixture separations (Aminabhavi, & Aithal, 1991; Moon, Pal, & Haung, 1999; Naidu, Sairam, Raju, & Aminabhavi, 2005; Yang, Sua, Leu, & Yang, 2004). In these applications, it is helpful to predict their thermodynamic properties in aqueous media since such a data-base would be useful in formulating drug delivery systems as well as to prepare separation membranes.

The carbohydrate polymers of this study are abundant in nature. Of these, NaAlg occurs as a white to yellowish brown filamentous, grainy, and granular or in powdered form, which is used as a stabilizer, thickener, gelling agent, and emulsifier in chemical/pharmaceutical industries. GG is a polysaccharide, a long chain biopolymer, made of sugar galactose and mannose. It is available as a white to yellowish odorless, available in different viscosity grades as well as in granule form. Depending upon its viscosity, it is used as a thickener and emulsifier in commercial food processing. It is also used in dressings, milk products and baking mixes. It finds usage in paper manufacturing, textiles, printing, cosmetics, and pharmaceuticals. Chitosan, a derivative of chitin, is manufactured commercially on a large scale from the outer shells of crustaceans. It is used in a wide variety of forms including powder, solution or gel. HEC is water-soluble ether and is a non-ionic polymer that is compatible with a wide variety of other water-soluble polymers, which is used as a thickener in latex paints and paper finishes. HPMC is cellulose ether, derived from the alkali-treated cellulose by reacting with methyl chloride and propylene oxide. It is used as an emulsifier, thickening agent, stabilizer, gellant and suspending agent.

The present investigation is an effort to understand the solution properties of these carbohydrate polymers by measuring their densities at different temperatures from 298.15 to 338.15 K in order to evaluate excess molar volumes (V^E) and activity of 1% aqueous polymer solutions. Density results have been analyzed using the thermodynamic activity models derived from the Flory–Huggins theory (Flory, 1953), while excess molar volumes have been computed from density results. These results are discussed to understand thermodynamic interactions between the polymer-water systems. Mathematical equations are presented for data analysis to find an agreement between the activity of solvent computed by theory and experiments. The theory has the advantages that only density measurements are required to calculate excess molar volume and activity. Note that a similar study was made earlier by Eliassi et al. (Eliassi, & Modarress, 2005; Taghizadeh, Eliassi, & Sisakht, 2005). However, in the present study, carbohydrate polymers have been selected in view of their importance in biology and medicine. Viscosity data on all polymers have been obtained to understand hydrodynamic interactions and to compute molecular weights of the polymers. In addition, polymers were characterized in their thin film forms by dynamic mechanical thermal analyser (DMTA) and thermogravimetric analyzer (TGA) to understand morphological characteristics and the transition behavior. Results of this study would be useful in seeking commercial applications of these polymers in medicine/separation science.

2. Experimental

2.1. Materials and methods

Chitosan and hydroxypropyl methylcellulose were purchased from Aldrich Chemicals, USA. Hydroxy ethyl cellulose was purchased from Loba chemicals, Mumbai, India. Guar gum and sodium alginate were procured from s.d. fine chemicals, Mumbai, India.

2.2. Preparation of polymer solutions

Stock solutions of different polymers (1%) were prepared by dissolving 1 g of the polymer in 100 mL of water. Solutions for density and viscosity measurements were prepared from the above stock solutions in different concentrations of weight fractions of the polymers. Molecular weight of the monomers of each polymers were taken as the basis for calculating weight fractions. Double distilled water produced in the laboratory itself was used throughout the research.

2.3. Density measurements

Densities of pure polymer solutions and different weight fraction solutions were measured using a high precision vibrating tube digital densitymeter, Anton Paar, DMA model 4500/5000 (Graz, Austria). Temperature of the measuring cell was automatically controlled within an uncertainty of ±0.01 °C by an inbuilt integrated Pt-100 measuring sensor. The instrument was calibrated with air, double distilled, and freshly degassed water at the temperature of the measurement during each session. Densities of the mixtures belonging to a given system (including pure components) were measured during one session. Experimental uncertainty (i.e. reproducibility of the measured densities) was up to five units in the second decimal place. Before injecting the sample, adjustments were made if deviations between displayed values and reference values of the density standards exceeded specifications of the instrument. Air and double distilled freshly degassed water were used for calibration. Density values of water and dry air at the specific atmospheric pressure are stored in the memory of the instrument for the complete temperature range investigated. If the compared values agreed within ±0.05 kgm^{-3}, measurements were continued after drying the measuring cell.

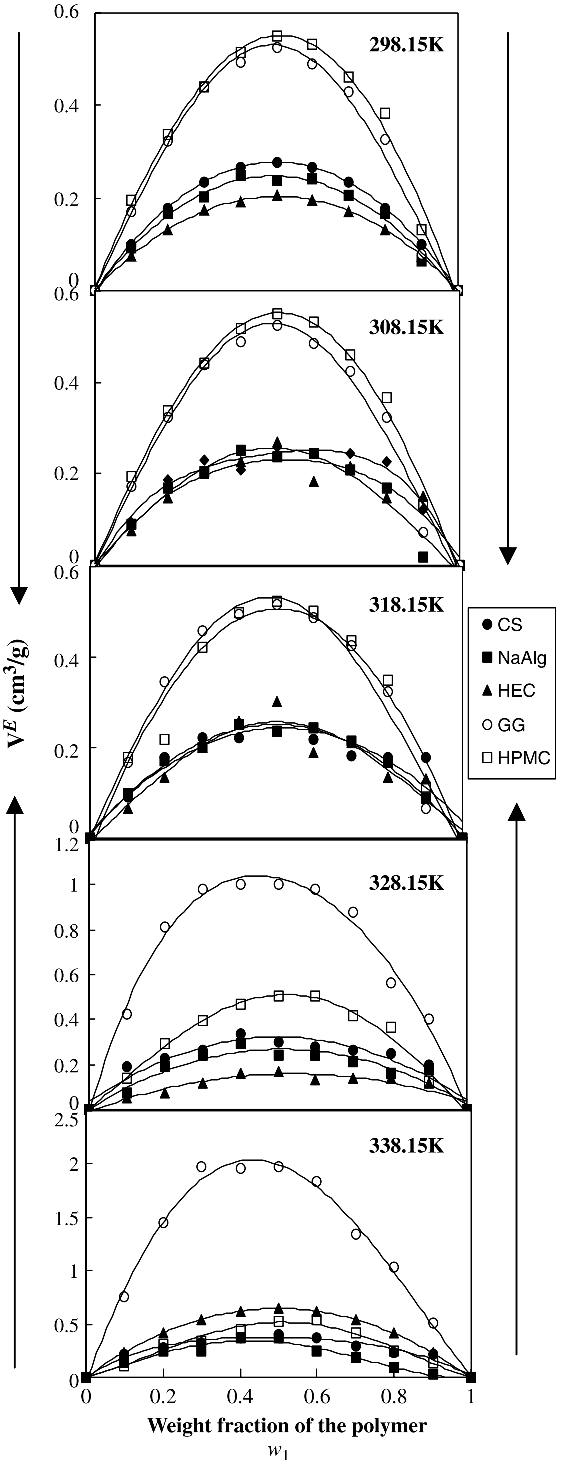

Fig. 1. Excess molar volumes of different polymer solutions at different temperatures.

2.4. Viscosity measurement

Solutions of known concentrations of the polymers were prepared in water. Kinematic viscosities of the solutions were measured at 30 °C using Schott-Gerate Viscometer (Model AVS 350, Germany) as per the detailed procedure reported earlier (Aminabhavi, Patil, Banerjee, & Balundgi, 1999). In brief, approximately 5 cm^3 volume of the liquid was injected into the viscometer and equilibrated to a constant temperature maintained within an accuracy ±0.1 °C for about 20 min. Then, flow times of pure solvent (t_0) as well as of polymer solutions (t) were measured. Using these data, reduced

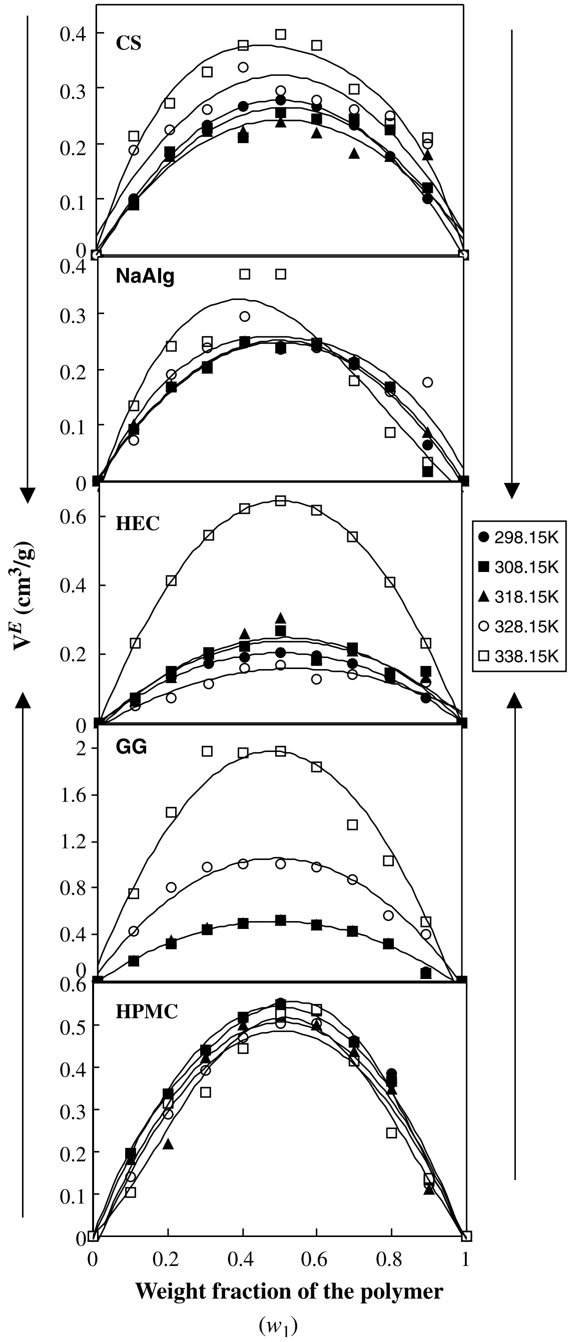

Fig. 2. Excess volumes of different polymers at different temperatures.

Table 1
Density (g/cm^3) of different polymer solutions in water at different temperatures

Wt fraction of polymer	298.15 K	308.15 K	318.15 K	328.15 K	338.15 K
Chitosan					
0.1	0.99816	0.99514	0.99072	0.98399	0.97401
0.2	0.99881	0.99579	0.99142	0.98488	0.97512
0.3	0.99947	0.99643	0.99212	0.98576	0.97622
0.4	1.00012	0.99708	0.99281	0.98664	0.97732
0.5	1.00078	0.99772	0.99352	0.98752	0.97843
0.6	1.00143	0.99836	0.99421	0.98841	0.97953
0.7	1.00209	0.99901	0.99491	0.98929	0.98064
0.8	1.00274	0.99965	0.99561	0.99017	0.98174
0.9	1.00339	1.00030	0.99631	0.99106	0.98284
1.0	1.00405	1.00094	0.99701	0.99194	0.98395
Sodium alginate					
0.1	0.99785	0.99485	0.99079	0.98563	0.97630
0.2	0.99827	0.99525	0.99121	0.98568	0.97800
0.3	0.99906	0.99602	0.99212	0.98665	0.98017
0.4	0.99941	0.99637	0.99247	0.98716	0.98025
0.5	1.00018	0.99714	0.99327	0.98848	0.98139
0.6	1.00061	0.99757	0.99370	0.98904	0.98318
0.7	1.00120	0.99816	0.99426	0.98962	0.98414
0.8	1.00169	0.99866	0.99481	0.99025	0.98504
0.9	1.00245	0.99938	0.99544	0.99035	0.98555
1.0	1.00287	0.99984	0.99599	0.99142	0.98587
Hydroxy ethyl cellulose					
0.1	0.99789	0.99489	0.99046	0.98373	0.97412
0.2	0.99829	0.99529	0.99091	0.98435	0.97533
0.3	0.99869	0.99568	0.99135	0.98497	0.97654
0.4	0.99909	0.99607	0.99180	0.98559	0.97775
0.5	0.99949	0.99646	0.99223	0.98621	0.97897
0.6	0.99989	0.99686	0.99268	0.98683	0.98018
0.7	1.00029	0.99725	0.99312	0.98745	0.98139
0.8	1.00068	0.99764	0.99356	0.98807	0.98261
0.9	1.00108	0.99804	0.99401	0.98869	0.98381
1.0	1.00148	0.99843	0.99445	0.98931	0.98502
Guar gum					
0.1	0.99788	0.99484	0.99093	0.98203	0.97160
0.2	0.99811	0.99508	0.99098	0.98224	0.97191
0.3	0.99842	0.99541	0.99140	0.98359	0.97303
0.4	0.99887	0.99587	0.99199	0.98691	0.97603
0.5	0.99925	0.99623	0.99240	0.98784	0.97785
0.6	0.99973	0.99671	0.99285	0.98812	0.97830
0.7	1.00014	0.99713	0.99327	0.98854	0.98176
0.8	1.00057	0.99754	0.99369	0.98914	0.98302
0.9	1.00122	0.99820	0.99436	0.98980	0.98447
1.0	1.00141	0.99837	0.99452	0.98996	0.98560
Hydroxypropyl methylcellulose					
0.1	0.99770	0.99470	0.99088	0.98633	0.98060
0.2	0.99803	0.99502	0.99177	0.98662	0.98082
0.3	0.99831	0.99529	0.99146	0.98691	0.98160
0.4	0.99854	0.99551	0.99167	0.98713	0.98179
0.5	0.99878	0.99576	0.99193	0.98738	0.98196
0.6	0.99905	0.99603	0.99220	0.98761	0.98211
0.7	0.99934	0.99632	0.99247	0.98793	0.98262
0.8	0.99957	0.99657	0.99271	0.98812	0.98299
0.9	0.99999	0.99696	0.99310	0.98852	0.98322
1.0	1.00018	0.99715	0.99326	0.98870	0.98343

viscosity (η_{sp}/C) and inherent viscosity were calculated. Reduced viscosity vs concentration and inherent viscosity vs concentration plots were made. From these plots, intrinsic viscosity [η] was calculated (Toti, Amur, Kariduraganavar, Manjeshwar, Aralaguppi and Aminabhavi, 2002).

2.5. Dynamic mechanical thermal analysis (DMTA)

Dynamic mechanical thermal analysis (DMTA) of the polymers have been performed by using a Rheometric Scientific DMTA instrument operating at 1 Hz frequency.

DMTA scans have been performed between 25 and 300 °C at the heating rate of 10 °C/min.

2.6. Thermogravimetric analysis (TGA)

TGA thermograms of the polymers were recorded on a Mettler TGA/SDTA 851^e system. TGA scans were done from 25 to 800 °C at the heating rate of 20 °C/min under an inert nitrogen atmosphere.

3. Theory

Solution nonidealities of the mixtures can be represented by the activity coefficients that arise due to intermolecular interactions between components of the mixture. Thus, activity coefficient, γ_i of a component can be derived from the thermodynamic equation,

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

where g^{E} is molar Gibbs excess function and n is total number of moles of the components given by: $n=\sum_{i=1}^{c} n_i$.

3.1. Excess quantities

The molar Gibbs excess function is given by the relation,

$$g^{\mathrm{E}} = u^{\mathrm{E}} + Pv^{\mathrm{E}} - Ts^{\mathrm{E}} \tag{2}$$

where u^{E} is molar Gibbs excess internal energy, v^{E} is molar excess volume, and s^E is molar excess entropy. In order to obtain γ_{i} at temperature, T and pressure, P, the exact composition dependent functions for u^E, v^{E}, and s^E are needed. Since attempts to obtain exact functionality for g^{E} have not been successful and hence, the proposed activity models suffer from limitations imposed by the assumptions. In this regard, Margules and van Laar equations (Prausnitz, Lichtenthaler, & Azevedo, 1999), wherein it was tacitly assumed that $s^{\mathrm{E}}=0$, and no volume change was observed upon mixing, i.e. $V^{\mathrm{E}}=0$. Thus, solution non-idealities were attributed to molecular interactions between pair molecules and functionality for u^{E} was derived. In some cases, nonrandomness was considered to be the main cause of such deviations. Based on the original lattice model of Guggenheim, Flory (Flory, 1953) derived the expression for s^E for polymer solutions. Flory considered the arrangement of polymer chains and solvent molecules in the lattice to derive an equation for s^{E} in the following form:

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

where x_i and ϕ_i are mole fraction and volume fraction of solvent (1) and polymer (2), respectively; r is number of segments of the polymer chain. The volume fraction, ϕ_i is expressed as,

$$\phi_1 = \frac{x_1v_1}{x_1v_1+x_2v_2} \quad \text{and} \quad \phi_1=(1-\phi_2) \tag{4}$$

The quantity, r is defined as the ratio of molar volume of the polymer (2) to that of solvent (1) given by,

$$r=\frac{v_2}{v_1} \tag{5}$$

However, Flory (1953) assumed that, $v^{\mathrm{E}}=0$ and hence, g^{E} is expressed as:

$$g^{\mathrm{E}} = u^{\mathrm{E}} - s^{\mathrm{E}} \tag{6}$$

where, u^{E} was obtained from the Scatchard–Hildebrand equation (Sako, Wu, & Prausnitz, 1989). In the present work, a simple model is used to predict solvent activities in polymer solutions.

The excess molar volume was calculated from the experimental density values using,

$$v^{\mathrm{E}} = \frac{1}{\rho} - \left(\frac{w_1}{\rho_1}+\frac{w_2}{\rho_2}\right) \tag{7}$$

where ρ is density of the polymer solution, w_1 and w_2 are weight fractions of components 1 and 2, respectively; ρ_1 and ρ_2 are respective pure component densities. While using ρ values in Eq. (7), density results were fitted to polynomial equation of the type

$$\rho/(g/cm^3) = A + B\omega_2 + C\omega_2^2 + D\omega_2^3 \tag{8}$$

where A, B, C, and D are coefficients (g/cm^3) and ω_2 is weight fraction of the polymer in solution. The values of coefficients were obtained by regression analysis using Marquardt equation (Marquardt, 1963) and these are given in Table 2. By using Eqs. (7) and (8), v^{E} values were calculated and results are displayed in Figs. 1 and 2.

3.2. Activity model

Eq. (1) can also be written in terms of mole fraction of the solvent (x_1) as:

$$\mathrm{RT}\ln\gamma_1 = g^{\mathrm{E}} + (1-x_1)\frac{\partial g^{\mathrm{E}}}{\partial x_1} \tag{9}$$

Inserting Eq (2) into Eq (9), we get,

$$\mathrm{RT}\ln\gamma_1 = u^{\mathrm{E}} + Pv^{\mathrm{E}} - Ts^{\mathrm{E}} + (1-x_1)\frac{\partial}{\partial x_1}(u^{\mathrm{E}} + Pv^{\mathrm{E}} - Ts^{\mathrm{E}}) \tag{10}$$

or

$$\begin{aligned}\mathrm{RT}\ln\gamma_1 = {} & \left[u^{\mathrm{E}} + (1-x_1)\frac{\partial}{\partial x_1}(u^{\mathrm{E}})\right] \\ & + \left[Pv^{\mathrm{E}} + (1-x_1)\frac{\partial}{\partial x_1}(Pv^{\mathrm{E}})\right] \\ & + \left[-Ts^{\mathrm{E}} + (1-x_1)\frac{\partial}{\partial x_1}(-Ts^{\mathrm{E}})\right]\end{aligned} \tag{11}$$

From Eq. (11), it can be seen that activity coefficient of the solvent (γ_1) can be divided as internal energy (γ_1^U), volume

Table 2
Estimated parameters of polynomial (Eq. (8)) for different polymers at different temperatures

Temperature (K)	*A*	*B*	*C*	*D*	*σ*
Chitosan					
298.15	1.1123	0.0027	0.0050	0.0004	0.0006
308.15	0.6950	0.2940	0.8393	0.0276	0.0392
318.15	0.8245	−0.0605	0.9293	0.0306	0.0339
328.15	1.2329	−1.0892	2.8260	0.0474	0.0393
338.15	0.6007	0.6291	2.0754	0.0589	0.0996
Sodium alginate					
298.15	0.9923	0.0417	-0.0344	0.0127	0.0203
308.15	1.0017	0.0287	-0.0134	0.0109	0.0157
318.15	0.9938	-0.0058	0.0688	0.0090	0.0114
328.15	1.0308	0.0038	0.3655	0.0386	0.0412
338.15	1.3150	0.7070	-0.8713	0.0350	0.0587
Hydroxy ethyl cellulose					
298.15	0.7686	0.2967	0.0257	0.0290	0.0431
308.15	0.9240	−0.0968	0.2671	0.0338	0.0468
318.15	1.0250	−0.0486	−0.2565	0.0383	0.0573
328.15	0.5970	−0.2479	0.3108	0.0232	0.0287
338.15	0.6975	−0.3721	−0.1785	0.0128	0.0157
Guar gum					
298.15	2.1268	0.1528	−0.6772	0.0324	0.0625
308.15	2.1132	0.1838	0.6889	0.0347	0.0669
318.15	2.1276	0.2627	−0.6289	0.0385	0.0712
328.15	2.4320	2.4952	2.3581	0.1309	0.1415
338.15	8.4260	2.0575	−2.1044	0.1804	0.1814
Hydoxypropyl methylcellulose					
298.15	2.2083	−0.0528	−0.2577	0.0293	0.0550
308.15	2.2101	−0.0129	−0.3343	0.0248	0.0471
318.15	2.1236	−0.1900	−0.8380	0.0404	0.0563
328.15	2.0435	−0.1935	−0.4984	0.0279	0.0463
338.15	2.0684	−0.1525	−1.0632	0.0403	0.0443

(γ_1^V), and entropy (γ_1^S) contributions:

$$\gamma_1 = \gamma_1^U \gamma_1^V \gamma_1^S \tag{12}$$

where each of the quantities are computed as,

$$\mathrm{RT}\ln\gamma_1^U = u^{\mathrm{E}} + (1-x_1)\frac{\partial u^{\mathrm{E}}}{\partial x_1} \tag{13}$$

$$\mathrm{RT}\ln\gamma_1^V = Pv^{\mathrm{E}} + (1-x_1)\frac{\partial (Pv^{\mathrm{E}})}{\partial x_1} \tag{14}$$

$$\mathrm{RT}\ln\gamma_1^S = -Ts^{\mathrm{E}} + (1-x_1)\frac{\partial (-Ts^{\mathrm{E}})}{\partial x_1} \tag{15}$$

Activity of the solvent (a_1) can be expressed as: $a_1 = x_1\gamma_1$ and hence, we have

$$x_1^3\gamma_1 = x_1\gamma_1^U x_1\gamma_1^V x_1\gamma_1^S \tag{16}$$

so that a_1 is given by,

$$a_1 = \frac{1}{x_1^2}(a_1^U a_1^V a_1^S) \tag{17}$$

where a_1^u, a_1^v, and a_1^s are, respectively internal energy, volume, and entropy contributions to activity. By using Eq. (14), excess volume part of activity of solvent can be calculated as

$$\ln a_1^V = \frac{P}{RT}\left(v^E + (1-x_1)\frac{\partial v^E}{\partial x_1}\right) + \ln x_1 \tag{18}$$

Excess enthalpy part of activity of solvent can then be derived from Eq. (3) to give,

$$\ln a_1^S = \ln\phi_1 + \left(1-\frac{1}{r}\right)(1-\phi_1) \tag{19}$$

However, internal energy part of activity is affected by molecular interactions that depend upon molecular rearrangements defined by entropy and molecular separations in terms of volume. Therefore, internal energy part of activity (a_1^U) is a function of excess entropy as well as excess volume as seen in Eq. (17), which upon rearrangement gives,

$$\frac{a_1^U}{x_1^2} = \frac{a_1}{a_1^V a_1^S} \tag{20}$$

Right hand side of Eq. (20) can be expressed as:

$$\frac{a_1}{a_1^V a_1^S} = (a_1^S)^{f_1^S}(a_1^V)^{f_1^V} \tag{21}$$

where f_1^v and f_1^S are weighing factors. In the logarithmic form,

Table 3
Excess molar *v*olumes of different polymer solutions at different temperatures

Wt fraction of polymer	298.15 K	308.15 K	318.15 K	328.15 K	338.15 K
Chitosan					
0.1	0.1003	0.0928	0.0895	0.1875	0.2128
0.2	0.1786	0.1855	0.1778	0.2243	0.2715
0.3	0.2339	0.2291	0.2224	0.2619	0.3296
0.4	0.2675	0.2096	0.2227	0.3364	0.3765
0.5	0.2780	0.2571	0.1878	0.2965	0.3978
0.6	0.2672	0.2439	0.2190	0.2775	0.3758
0.7	0.2329	0.2440	0.1824	0.2623	0.2968
0.8	0.1779	0.2252	0.1772	0.2496	0.2369
0.9	0.1008	0.1223	0.1794	0.2003	0.2123
Sodium alginate					
0.1	0.0917	0.0916	0.0996	0.0729	0.1352
0.2	0.1672	0.1682	0.1705	0.1898	0.2398
0.3	0.2017	0.2040	0.2011	0.2380	0.2476
0.4	0.2473	0.2501	0.2495	0.2929	0.3694
0.5	0.2361	0.2389	0.2371	0.2414	0.3684
0.6	0.2399	0.2428	0.2425	0.2388	0.2459
0.7	0.2060	0.2088	0.2141	0.2131	0.1789
0.8	0.1673	0.1684	0.1674	0.1586	0.0872
0.9	0.0641	0.0176	0.0870	0.1770	0.0338
Hydroxy ethyl cellulose					
0.1	0.0742	0.0746	0.0654	0.0520	0.2339
0.2	0.1316	0.1487	0.1335	0.0714	0.4153
0.3	0.1725	0.2024	0.1984	0.1159	0.5445
0.4	0.1916	0.2250	0.2591	0.1595	0.6217
0.5	0.2048	0.2687	0.3032	0.1669	0.6457
0.6	0.1962	0.1821	0.1885	0.1294	0.6191
0.7	0.1712	0.2166	0.2107	0.1415	0.5411
0.8	0.1316	0.1473	0.1337	0.1360	0.4099
0.9	0.0740	0.1522	0.1298	0.1196	0.2313
Guar gum					
0.1	0.1711	0.1728	0.1678	0.4276	0.7564
0.2	0.3227	0.3241	0.3465	0.8101	1.4501
0.3	0.4387	0.4370	0.4589	0.9790	1.9723
0.4	0.4950	0.4900	0.4933	1.0003	1.9621
0.5	0.5260	0.5243	0.5174	1.0023	1.9716
0.6	0.4893	0.4864	0.4887	0.9826	1.8396
0.7	0.4313	0.4234	0.4268	0.8786	1.3445
0.8	0.3256	0.3236	0.3239	0.5651	1.0314
0.9	0.0789	0.0703	0.0652	0.3996	0.5044
Hydroxypropyl methylcellulose					
0.1	0.1961	0.1948	0.1797	0.1411	0.1048
0.2	0.3378	0.3368	0.2169	0.2899	0.3147
0.3	0.4403	0.4409	0.4213	0.3920	0.3415
0.4	0.5155	0.5190	0.4997	0.4713	0.4445
0.5	0.5504	0.5499	0.5238	0.5026	0.5252
0.6	0.5331	0.5315	0.5016	0.5038	0.5377
0.7	0.4618	0.4591	0.4364	0.4158	0.4157
0.8	0.3840	0.3669	0.3480	0.3623	0.2451
0.9	0.1327	0.1335	0.1115	0.1229	0.1374

Eq (20) can be written as,

$$\ln\left(\frac{a_1^U}{x_1^2}\right) = f_1^S \ln a_1^S + f_1^V \ln a_1^V \tag{22}$$

Similarly, Eq. (17) is expressed in logarithmic form,

$$\ln a_1 = (1+f_1^S)\ln a_1^S + (1+f_1^V)\ln a_1^V \tag{23}$$

By substituting for a_1^V and a_1^S from Eqs. (18) and (19), respectively into Eq. (23), we get

$$\ln a_1 = f^c\left[\ln\phi_1 + \left(1-\frac{1}{r}\right)(1-\phi_1)\right] + f^R\left[\frac{P}{RT}\left(v^E + (1-x_1)\frac{\partial v^E}{\partial x_1}\right) + \ln x_1\right] \tag{24}$$

where $f^C = (1+f_1^S)$ and $f^R = 1 + f_1^V$. Eq. (24) can be expressed in terms of volume fraction (ϕ) using Eq. (4) to give the final

Table 4
Activity of different polymer solutions at different temperatures

Wt fraction of polymer	298.15 K	308.15 K	318.15 K	328.15 K	338.15 K
Chitosan					
0.1	0.9999	0.9999	0.9999	0.9999	0.9999
0.2	0.9995	0.9994	0.9995	0.9995	0.9995
0.3	0.9983	0.9983	0.9983	0.9984	0.9984
0.4	0.9957	0.9957	0.9957	0.9958	0.9959
0.5	0.9894	0.9895	0.9896	0.9897	0.9900
0.6	0.9730	0.9732	0.9734	0.9738	0.9742
0.7	0.9244	0.9248	0.9253	0.9261	0.9272
0.8	0.7731	0.7739	0.7750	0.7763	0.7791
0.9	0.3855	0.3863	0.3874	0.3891	0.3915
Sodium alginate					
0.1	1.0186	0.9999	0.9999	0.9996	0.9995
0.2	1.0336	0.9995	0.9995	0.9993	0.9991
0.3	1.0391	0.9984	0.9983	0.9982	0.9979
0.4	1.0447	0.9959	0.9959	0.9958	0.9957
0.5	1.0335	0.9899	0.9899	0.9899	0.9900
0.6	1.0119	0.9743	0.9744	0.9746	0.9748
0.7	0.9454	0.9275	0.9278	0.9285	0.9294
0.8	0.7608	0.7795	0.7806	0.7822	0.7845
0.9	0.3353	0.3918	0.3945	0.3958	0.3991
Hydroxy ethyl cellulose					
0.1	0.9999	1.0024	0.9999	0.9999	0.9999
0.2	0.9996	1.0041	0.9996	0.9996	0.9996
0.3	0.9988	1.0052	0.9988	0.9988	0.9988
0.4	0.9969	1.0051	0.9971	0.9970	0.9971
0.5	0.9924	1.0018	0.9925	0.9926	0.9927
0.6	0.9803	0.9895	0.9806	0.9809	0.9811
0.7	0.9429	0.9477	0.9436	0.9442	0.9451
0.8	0.8159	0.8034	0.8175	0.8189	0.8209
0.9	0.4424	0.3599	0.4444	0.4462	0.4485
Guar gum					
0.1	0.9999	0.9999	0.9999	1.0003	1.0005
0.2	0.9999	0.9999	0.9999	1.0003	1.0006
0.3	0.9998	0.9998	0.9998	1.0000	1.0005
0.4	0.9994	0.9994	0.9994	0.9992	0.9998
0.5	0.9985	0.9985	0.9984	0.9983	0.9988
0.6	0.9958	0.9958	0.9958	0.9957	0.9963
0.7	0.9862	0.9863	0.9864	0.9865	0.9868
0.8	0.9409	0.9411	0.9415	0.9421	0.9430
0.9	0.6914	0.6923	0.6933	0.6951	0.6972
Hydroxypropyl methylcellulose					
0.1	1.0000	1.0000	0.9999	0.9995	0.9988
0.2	0.9999	0.9999	0.9998	0.9995	0.9989
0.3	0.9999	0.9999	0.9998	0.9995	0.9989
0.4	0.9998	0.9998	0.9997	0.9994	0.9989
0.5	0.9994	0.9994	0.9993	0.9991	0.9987
0.6	0.9983	0.9983	0.9983	0.9981	0.9979
0.7	0.9942	0.9942	0.9943	0.9942	0.9941
0.8	0.9722	0.9724	0.9726	0.9729	0.9732
0.9	0.8021	0.8027	0.8036	0.8050	0.8071

equation for activity.

$$\ln a_1 = f^C\left[\ln\phi_1 + \left(1-\frac{1}{r}\right)(1-\phi_1)\right] + f^R\left\{\left[\frac{P}{RT}\left(V^{\mathrm{E}} + \phi_2\left(\phi_1 + \frac{1}{r}\phi_2\right)\frac{\partial V^{\mathrm{E}}}{\partial \phi_1}\right)\right] + \ln\left(\frac{r\phi_1}{r\phi_1+\phi_2}\right)\right\} \tag{25}$$

In order to apply the above equation, we need density values of the polymer and solvent, their compositions in solution, and values of weighing factors, f^C and f^R. In the present research, we have used:

$$f^C = f^R = 0.5 \tag{26}$$

This gave the same weight to effects of entropy and volume contribution of activity to compute the activity of component 1 in a given mixture.

4. Results and discussion

4.1. Density, activity and excess molar volume

Density results of different polymers at different temperatures and concentrations (weight fractions) are presented in Table 1. These data are fitted to Eq. (8) by the method of least squares to estimate the coefficients (*A, B, C,* and *D*) along with the correlation coefficient, σ calculated as:

$$\sigma = \frac{100}{n}\sum_{i=1}^{n}\left[\frac{(\rho_i^{\text{expt}}-\rho_i^{\text{cal}})}{\rho_i^{\text{expt}}}\right] \tag{27}$$

where n is number of experimental data; ρ_i^{expt} and ρ_i^{cal} are experimental and calculated densities using Eq. (8). These results are given in Table 2. The calculated values of V^E using Eq. (7) are presented in Table 3. Activity data are compiled in Table 4.

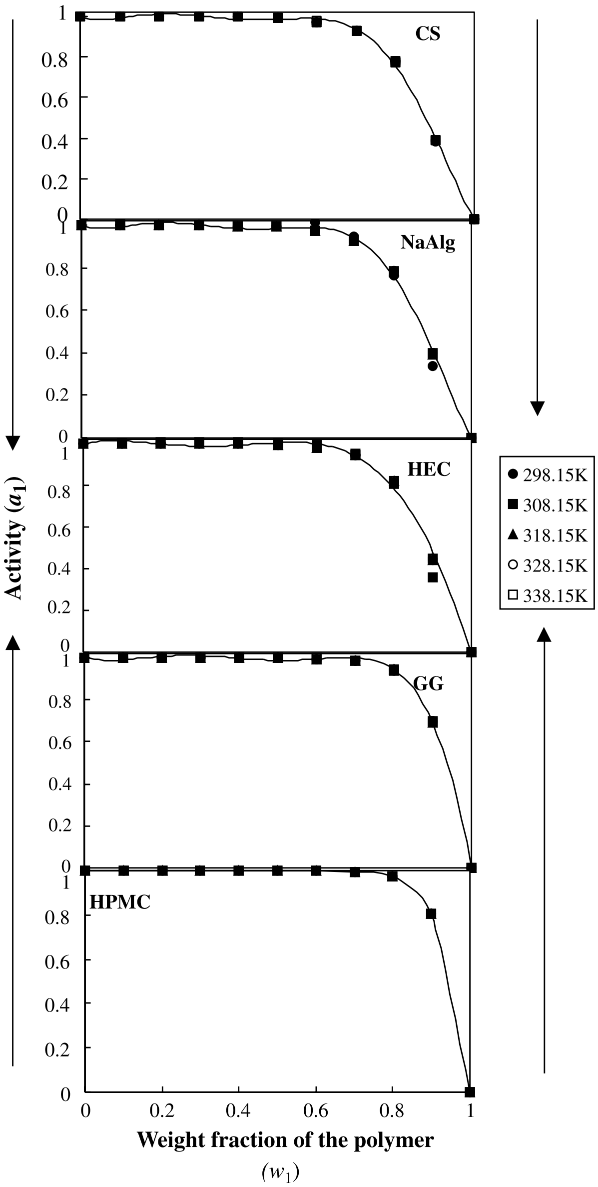

Fig. 3. Activity coefficient of water in water and different polymers at different temperatures.

The results of V^E represent the deviations from ideal behavior. These are related to intermolecular interactions between water (solvent) and carbohydrate polymers. The V^E values result from chemical, physical, and structural effects of polymers when they are dissolved in aqueous media. Physical effects (dispersion forces) contribute to positive V^E; chemical and structural effects (specific interactions) contribute to negative V^E. In the present study, in all cases, the V^E values exhibit positive deviations, indicating mild dispersion-type interactions.

Fig. 1 displays the plots of V^E vs weight fraction (w_1) of the polymer for the five different polymers employed at five different temperatures. The V^E values are found vary in the same range for CS, NaAlg and HEC at all the temperatures, whereas HPMC and GG have shown large positive V^E values at 298.15 and 308.15 K, which decreased considerably with a further rise in temperature.

In these polymers (HPMC and GG), temperature has a considerable effect on V^E. For instance, when the temperature is raised from 318.15 to 338.15 K, the V^E values for GG become large as compared to HPMC. Nearly a four-fold increase in V^E is observed at 328.15 and 338.15 K as compared

Table 5
Viscosity data of polymer solutions

Concentration, C (g/dL)	Flow time, t (s)	$t/t_0=\eta_r$	$N=\eta_{sp}/c$	$L=\ln \eta_r/c$
Chitosan [time flow (t_0) for solvent 2% acetic acid=8.01]				
0.05	14.47	1.81	16.12	11.8
0.10	29.05	3.63	26.26	12.9
0.15	43.62	5.45	29.64	11.3
0.20	58.18	7.26	31.32	9.9
0.25	72.42	9.04	32.16	8.8
Sodium alginate [time flow (t_0) for solvent water=6.76 s]				
0.05	20.83	3.08	41.6	22.5
0.10	41.73	6.17	51.7	18.2
0.15	62.56	9.25	55.0	14.8
0.20	83.39	12.34	56.7	12.6
0.25	104.22	15.41	57.6	10.9
Hydroxy ethyl cellulose [time flow (t_0) for solvent water=6.76 s]				
0.05	8.06	1.19	3.84	3.51
0.10	9.72	1.44	4.38	3.63
0.15	11.37	1.68	4.55	3.48
0.20	13.02	1.92	4.63	3.27
0.25	15.71	2.32	5.29	3.37
Guar gum [time flow (t_0) for solvent water=6.76 s]				
0.05	7.67	1.14	2.8	2.6
0.10	15.52	2.31	13.0	8.3
0.15	23.23	3.44	16.3	8.2
0.20	30.91	4.57	17.9	7.6
0.25	38.57	5.71	18.8	7.0
Hydroxypropyl methylcellulose [time flow (t_0) for the solvent water=6.76 s]				
0.05	8.95	1.32	6.4	5.6
0.10	18.21	2.69	16.9	9.9
0.15	27.16	4.02	20.1	9.3
0.20	36.15	5.35	21.8	8.4
0.25	46.21	6.84	23.4	7.7

to V^E from 298.15 and 318.15 K. Such large positive V^E values observed for GG is due to the breaking of hydrogen bonds of the associated polymer molecules in the presence of H-bonded water molecules.

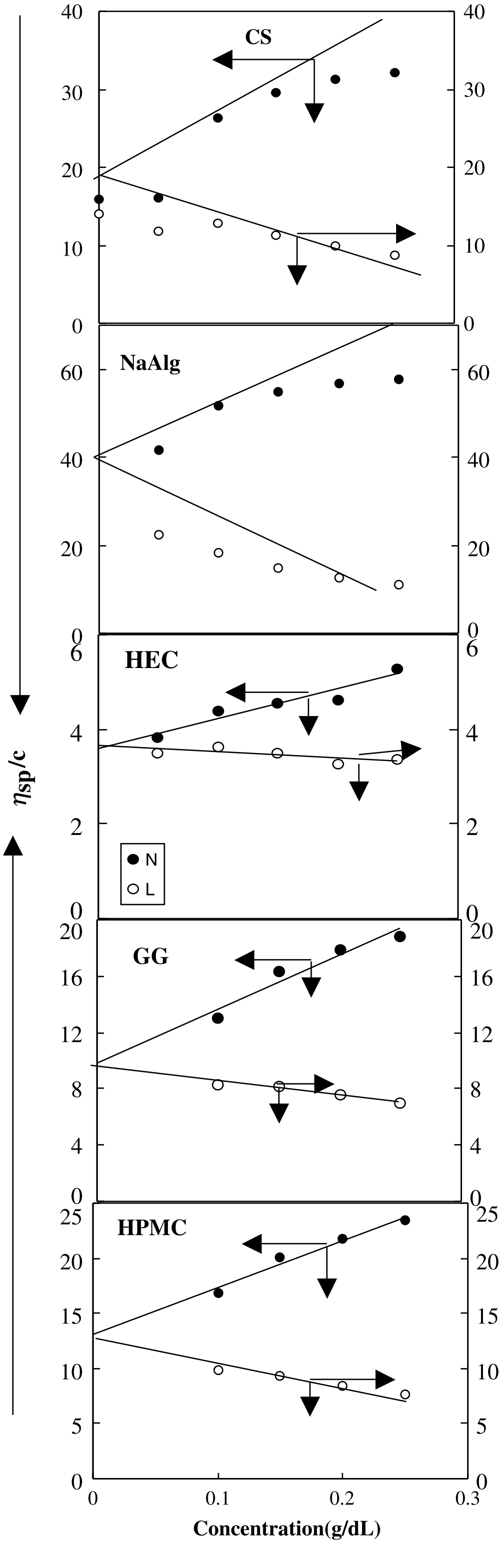

Fig. 4. Plots of η_{SP}/c (●) and $\ln\eta_r/c$ (○) versus concentration of different polymers in water (Chitosan in 2% acetic acid) at 30 °C.

Table 6
Results of viscosity and molecular weight of different polymers

Polymer	Intrinsic viscosity $[\eta]$	Molecular weight ($[\eta]=K\,M^a$)
CS	15.96	2,63,883
NaAlg	39.5	1,22,594
HEC	3.65	2,16,400
GG	9.92	1,17,862
HPMC	13.13	1,89,555

K and a values of PVP are taken as standards for the calculation of molecular weight. $K=39.3\times10^{-3}$ and $a=0.59$.

Fig. 2 displays the dependence of V^E vs w_1 for all polymers at different temperatures. It is noticed that considerable differences are observed for the dependence of V^E on temperature depending upon the nature of the polymer. Notice that HPMC exhibits almost identical trends in V^E between 298.15 and 338.15 K.

Fig. 3 displays the plots of activity (a_1) vs w_1 for all polymers at the studied temperatures. It is observed that temperature variations are distinct for activity calculations. Almost single curve is obtained within the studied temperature interval. In any case, the proposed model is reliable in predicting solvent activities of the binary polymer solutions as seen by the observed agreement.

4.2. Viscosity

Viscosities of polymer solutions determined at five different concentrations are compiled in Table 5, while the graphs of η_{sp}/c and $\ln\eta_r$/c vs concentration are displayed in Fig. 4. The numerical data of intrinsic viscosity, $[\eta]$ and molecular weight, M_n are given in Table 6. Using the viscosity data and the well-known M.H.S relation (Flory, 1953): $[\eta]=K\cdot M^a$, molecular weight of the polymers was calculated. The K and a values of the poly(vinyl pyrrolidone), (PVP) were taken as the standard to calculate molecular weights of all other carbohydrate polymers. Molecular weights of the polymers vary in the order: CS > HEC > HPMC > NaAlg > GG.

4.3. Thermogravimetric analysis (TGA)

Thermal degradation profiles of CS, GG, HEC, HPMC, and NaAlg films are shown in Fig. 5. All polymers have shown a single step degradation with an initial weight loss of about

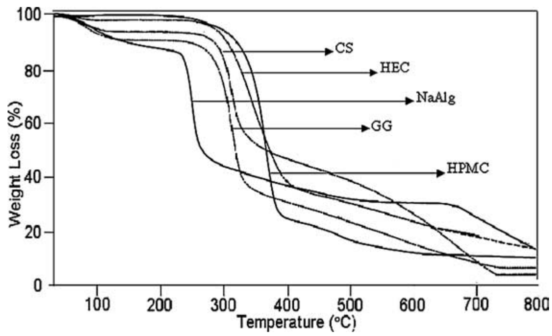

Fig. 5. TGA thermograms of different carbohydrate polymers.

Table 7
E', tan δ, onset, end-set and %wt. loss of different carbohydrate polymers

Polymer	E'	tan δ	Onset	End set	%wt loss
HEC	4.09×10^8	45.1	289.72	392.98	60.2
NaAlg	4.27×10^9	102.7	235.49	259.37	46.6
CS	2.17×10^9	42.35	287.75	325.36	39.8
GG	2.7×10^9	38.36	271.42	326.22	59.5
HPMC	1.44×10^9	90.7	311.69	502.23	69.5

1–7% below 100 °C due to release of moisture from the polymers. Of all the polymers studied, HPMC has shown higher thermal stability with the onset of degradation at 311 °C, whereas NaAlg has shown the lowest thermal stability with an onset of degradation around 235 °C. In general, thermal stability of the polymers followed the trend: HPMC > HEC > CS > GG > NaAlg. This trend is quite different than that observed for molecular weight dependence as discussed

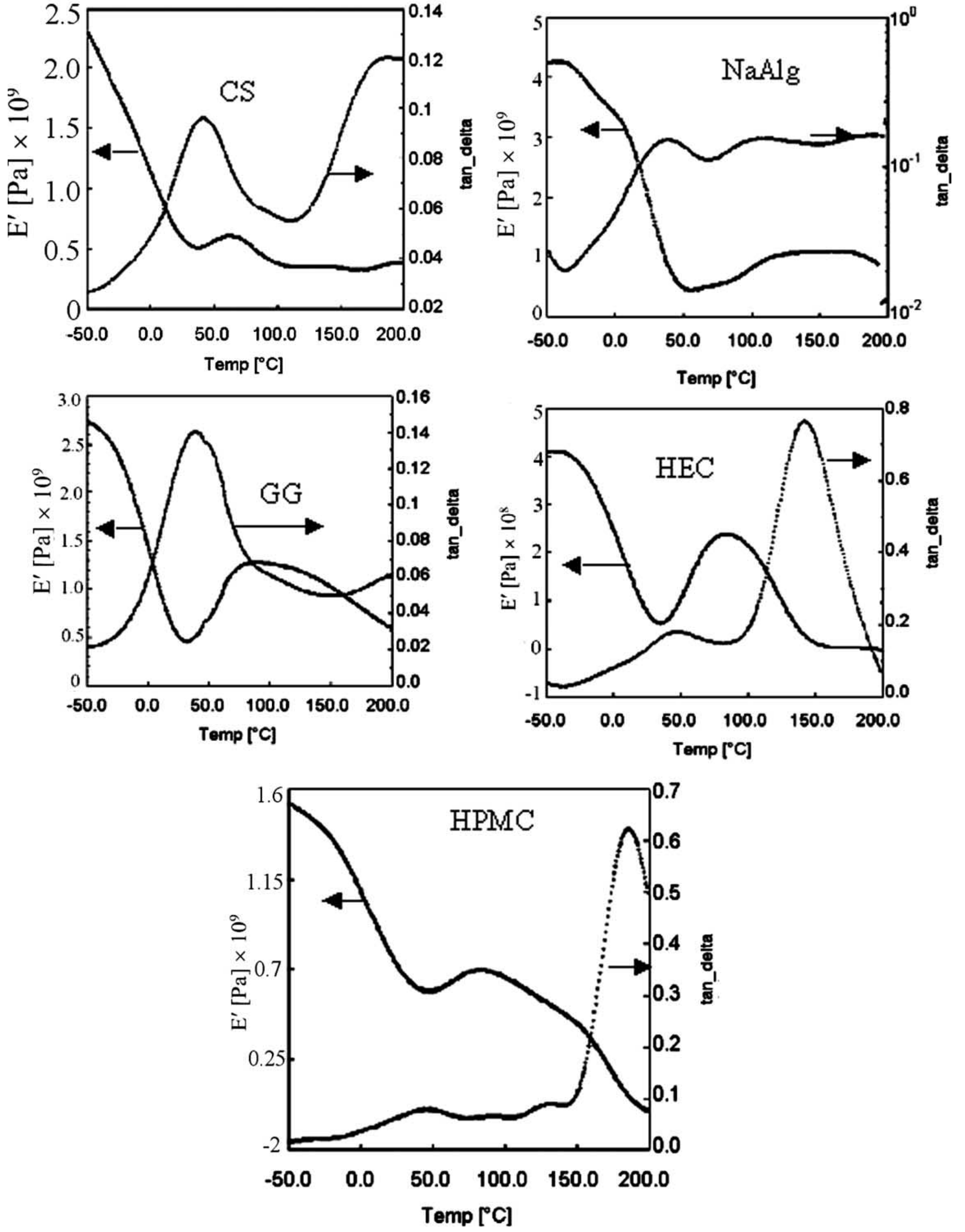

Fig. 6. E' and tan δ curves of different carbohydrate polymers.

before. The % weight loss, onset and end-set degradation temperatures for various polymers are given in Table 7.

4.4. Dynamic mechanical thermal analysis (DMTA)

DMTA results of CS, NaAlg, GG, HEC, and HPMC have been studied in terms of loss tangent (tan δ) and storage modulus (E') as a function of temperature (see Fig. 6). The tan δ and E' values for various polymers are included in Table 7. The polymer viz. NaAlg having the least thermal stability exhibited the highest value of tan δ (102.7 °C) and E' (4.27×10^9) compared to all other polymers. However, the weight loss of NaAlg was only 46.6%, whereas HPMC exhibited highest thermal stability as well as highest % weight loss (69.5) compared to other polymers.

5. Conclusions

The present study is an unified approach to understand solution thermodynamics and hydrodynamics of five carbohydrate polymers in aqueous media. These polymers have a great relevance as controlled release matrices in drug delivery as well as membranes in separation science. Solution properties (density and viscosity) of the polymers studied are important in understanding their solution as well as film forming properties. The films of these polymers were subjected to DMTA and TGA analyses to understand their dynamic mechanical properties. The present study would have great relevance in application areas of the polymers, particularly in drug delivery and membrane science.

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