R. K. WANCHOO et al., Viscometric and Rheological Behaviour of …, *Chem. Biochem. Eng. Q.* **22** (1) 15–24 (2008)

15

Viscometric and Rheological Behaviour of Chitosan-Hydrophilic Polymer Blends

R. K. Wanchoo, A. Thakur,[*] **and Sweta**
Department of Chemical Engineering and Technology
Panjab University, Chandigarh – 160 014, India

Blends of chitosan with hydrophilic polymers were investigated for miscibility. Chitosan/poly (vinyl alcohol) (CS/PVA), chitosan/poly vinylpyrollidone (CS/PVP) and chitosan/poly (ethylene oxide) (CS/PEO) blends were prepared in dilute aqueous acetic acid (φ = 1 %) and found to be miscible over the entire composition range by dilute solution viscosity and rheological measurements. The miscibility of blends by viscosity measurements at 25 ± 0.1 °C was estimated on the basis of experimental and ideal values of miscibility parameters Δb_m, $\Delta[\eta]_m$ and μ. The rheological studies were performed on blends of mass fraction w = 2 % in dilute aqueous acetic acid (φ = 1 %) at 25 ± 0.1 °C in controlled rate mode. The flow curves of blends and viscosities were found to lie between those of principal components of the blend over the entire compositional range. The flow behaviour index of blends was determined by the Power law model, indicating pseudoplastic behaviour with pseudoplasticity increasing with CS mass concentration. The rheological data of blends was best described by the Cross model. Results from Fourier transform infrared spectroscopy also indicate the blends to be miscible.

Key words:

Chitosan, poly (vinyl alcohol), poly vinylpyrollidone, poly (ethylene oxide), blends, miscibility, rheology, dilute solution viscosity

Introduction

Natural polymers have an important role in drug delivery, for example chitosan, is of special interest because of its intrinsic properties such as its ability to interact with mucosal surfaces and to provide a bioadhesive effect that will retain drugs at target sites. In addition, it has been demonstrated to be bacteriostatic, haemostatic, biocompatible etc.[1] Chitosan (CS) is a natural polysaccharide produced from *N*-deacetylation of chitin under alkaline conditions. Chitin occurs mainly in the cuticles of anthropods, the endoskeletons of cephalopods and fungi.[2] Chitosan is thus a collective name representing a family of *N*-deacetylated chitins with different degrees of deacetylation (DDA). Degree of acetylation (DA) corresponds to the mole fraction of acetyl units within the polymer chains. Chitosan is generally referred to polymers soluble in dilute acidic aqueous solutions with DAs below 60 %.

Chitosan and its derivatives have been increasingly applied to biomedical, pharmaceutical, food, industrial and agricultural sectors to tap its potential properties.[3-10] In the recent past, polymer blending has emerged as a novel tool to obtain materials with different properties from the original polymers, with the added advantage that the time and costs involved are smaller than those necessary to obtain new materials. A blend can be defined as a mixture prepared from at least two structurally different polymers that interact without covalent bond formation. CS is generally blended with other hydrophilic polymers[11-15] to overcome the disadvantage of the loss in mechanical strength in the wet state. Numerous papers can be found in the literature on its use in drug delivery in biochemical, pharmaceutical and other applications; however, studies on its rheological behaviour have been few.[16-18] Not many reports have been published concerning rheological behaviour of blends in dilute solution and its use in establishing miscibility between the polymers. Polymer-polymer miscibility is a very significant factor especially for the mechanical property of the blend.

The present work aims to investigate the rheological studies as a tool for establishing the miscibility between CS and hydrophilic polymers of commercial importance, vis. PVA, PVP and PEO. The rheological data will be tested for its consistency using models of Sisko and Cross.[19] In addition, miscibility between two polymers will be investigated by studying the molecular interactions using dilute solution viscosity measurements and FTIR spectroscopy.

[*] Author for correspondence: E-mail: anupamat@pu.ac.in
Fax: +91-0172-2779173; Tel.: +91-0172-2534930

Experimental

Materials used

Materials used in this study are listed below:

1. Chitosan (CS), (low viscosity) was obtained from Fluka

2. Poly (vinyl alcohol) (PVA) was purchased from S.D. Fine Chem. Ltd., Mumbai with degree of hydrolysis 98 %

3. Poly vinylpyrrolidone (PVP) was obtained from Hi Media Lab. Pvt. Ltd., Mumbai

4. Poly (ethylene oxide) (PEO) was obtained from National Chemicals, Baroda.

All the reagents were used as received. Acetic acid, NaCl were of reagent grade.
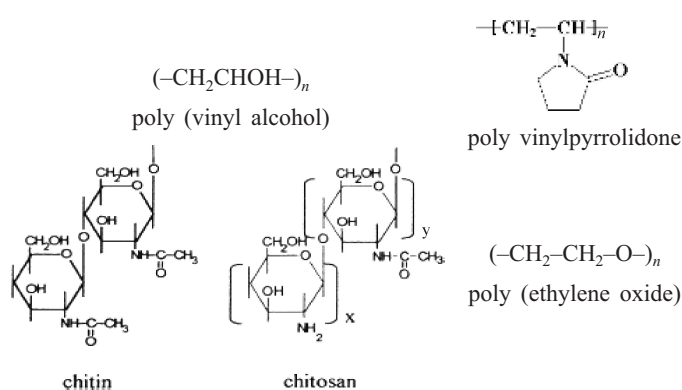
Characterization of chitosan for degree of deacetylation (DDA)

The DDA can significantly affect the behaviour of chitosan. The elemental composition of chitosan was determined using a Perkin Elmer Elemental Analyzer. The carbon/nitrogen mole ratio ($r_{C/N}$) varies from 5.145 in completely *N*-deacetylated chitosan to 6.861 in the fully *N*-acetylated chitin. The degree of deacetylation, DDA, was therefore calculated according to:[20]

$$\mathrm{DDA} = \frac{6.861 - (r_{C/N})}{6.861 - 5.145} \cdot 100. \qquad (1)$$

Dilute solution viscosity measurements

The intrinsic viscosity measurements were carried out on dilute solutions of polymer. The intrinsic viscosity of one polymer and blend solutions was measured using the Ubbelohde viscometer at 25 ± 0.1 °C immersed in a constant temperature bath (model CT 1450, Schott Gerate, Germany). For each solution, a 50 mL sample was loaded into the viscometer and allowed to come to equilibrium with the bath temperature by providing an equilibration time of 30 min prior to measurements. The elution time of each solution was taken as the aver-

age of five concordant readings with agreement within ± 0.5 % and care was taken while preparing polymer solutions so that relative viscosity of the solution was ≤ 2.0. Efflux time of solvent was always above 100 s. Intrinsic viscosity [η] was determined as follows:[21]

$$[\eta] = (\eta_{sp}/\gamma)_{c=0} = [(\ln \eta_r)/\gamma]_{c=0} \qquad (2)$$

where $\eta_{sp} = (\eta - \eta_s)/\eta_s$, $\eta_r = \eta/\eta_s$, η is the solution viscosity, η_s is the solvent viscosity and γ is the solution mass concentration.

The Huggins eq. (3) and Kraemer equation eq. (4) were used for extrapolating the viscosity data as a function of concentration to infinite dilution:[21]

$$\frac{\eta_{sp}}{\gamma} = [\eta] + k'[\eta]^2 \gamma \qquad (3)$$

$$\frac{\ln \eta_r}{\gamma} = [\eta] - k''[\eta]^2 \gamma \qquad (4)$$

The viscosity average molar mass was determined using the Mark-Houwink equation relating to intrinsic viscosity:[21]

$$[\eta] = K_m M^a \qquad (5)$$

where K_m and a are the empirical viscometric constants specific to a polymer, solvent and temperature.

Preparation of polymer solutions for rheology

The blend systems studied are $\zeta_{CS/PVA}$, $\zeta_{CS/PVP}$ and $\zeta_{CS/PEO}$. For rheological studies, each polymer was dissolved in $\varphi = 1$ % aqueous acetic acid at room temperature and left overnight with continuous stirring to obtain a homogeneous $w = 2$ % solution. Ternary solution for each system was prepared by mixing the appropriate quantity of binary polymer solution in the mass ratio (ζ_{m_1/m_2}) as (0.25:0.75), (0.50:0.50) and (0.75:0.25).

Rheological measurements

The rheological measurements were performed on Haake cone and plate rheometer (RT-20) in CR mode (controlled rate mode) at a constant temperature of 25 ± 0.1 °C. A water bath (Julabo, FT-30) was connected to the rheometer to control the temperature. The sensor used for measurement was C 60/1° Ti with 0.052 mm gap between the cone and the plate. The Haake software package was used to operate and control the RT-20, and was also used for data evaluation and analysis.

Preparation of polymer films

Polymer films for FTIR study were prepared by casting the solution on a Petri dish. After solvent evaporation, films were allowed to dry at room temperature and then placed in a vacuum oven at about 40 °C for 24 h to remove the traces of moisture. After drying, the films were carefully peeled off and stored in an airtight glass container until further investigations.

Results and discussion

Characterization of chitosan for degree of deacetylation

The carbon and nitrogen content of CS was 42.43 % and 7.84 % respectively and thus degree of deacetylation on the basis of eq. (1) was determined to be 84.55 %.

Intrinsic viscosity

The neat polymers were characterized by their molecular weights listed in Table 1, on the basis of eq. (3). The intrinsic viscosities of neat polymers and blends in the solvent (1 % acetic acid) using eq. (2) are listed in Table 2. It is observed that the intrinsic viscosity of CS is higher than that of other synthetic polymers having molecular weights comparable to or higher than CS, which can be attributed to the fact that the backbone of CS is essentially composed of rigid cellulosic linkages which result in increasing the intrinsic viscosity of CS. Fig. 1 shows the intrinsic and reduced viscosity for CS as a function of concentration, the intercept corresponds to the intrinsic viscosity $[\eta]$. Similar plots for other polymers and blends were also made and the Huggin's plots are shown in Figs. 2a, 2b, 2c. The Huggin's and the Kraemer's coefficient, k' and k'', (eq. 3, 4) were determined and are listed in Table 2. Theoretically,[21] it is considered that for a polymer in a good solvent $k' + k''$ should be ≤ 0.5. In this work $k' + k''$ is shown to be almost less than

Table 1 – *Viscometric data in aqueous solutions*

Polymer	Solvent	$T/°C$	K_m mL g^{-1}	a	Mv g mol^{-1}
CS	0.2 mol L^{-1} NaCl 0.2 mol L^{-1} CH$_3$COOH	25	$1.81 \cdot 10^{-3}$	0.93	$3.56 \cdot 10^4$
PVA	distilled water	20	$64 \cdot 10^{-3}$	0.58	$2.32 \cdot 10^4$
PVP	distilled water	30	$12.5 \cdot 10^{-3}$	0.78	$5.65 \cdot 10^5$
PEO	distilled water	25	$300 \cdot 10^{-3}$	0.50	$1.28 \cdot 10^5$

Table 2 – *Intrinsic viscosities of neat polymers and blends in 1 % acetic acid at 25±0.1 °C*

Blend ζ_{m_1/m_2}	$[\eta]$ dL g^{-1}	k'	k''	$k' + k''$
CS	19.547	0.445	0.092	0.537
CS/PVA (3:1)	12.920	0.435	0.076	0.511
CS/PVA (1:1)	9.530	0.484	0.04	0.524
CS/PVA (1:3)	4.760	0.373	0.086	0.459
PVA	0.869	0.286	0.201	0.487
CS/PVP (3:1)	14.645	0.352	0.134	0.486
CS/PVP (1:1)	8.442	0.354	0.119	0.473
CS/PVP (1:3)	3.644	0.149	0.285	0.434
PVP	0.195	0.157	0.262	0.419
CS/PEO (3:1)	14.200	0.384	0.121	0.505
CS/PEO (1:1)	10.160	0.453	0.057	0.510
CS/PEO (1:3)	7.147	0.195	0.259	0.454
PEO	3.840	0.451	0.064	0.515

0.5 in most cases. In a way, $k' + k''$ also reflects the solubility of a polymer in a solvent. In other words, if there are favourable polymer-polymer interactions, this occurrence of physical interaction corresponds to a reduction of solubility; thus, $k' + k''$ should increase.[28] The quantity $k' + k''$ is found to increase with chitosan concentration in $\zeta_{CS/PVA} = 1 : 3$ to $\zeta_{CS/PVA} = 1 : 1$ with a minor dip in the value
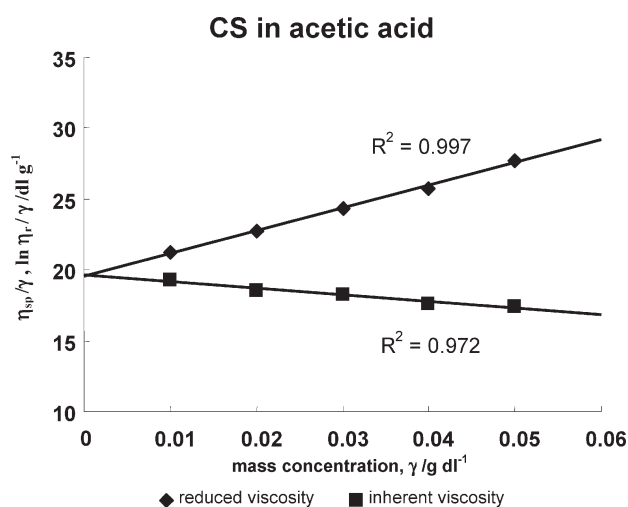

CS in acetic acid

Fig. 1 – η_{sp}/γ and $(\ln \eta_r)/\gamma$ vs. mass concentration, γ at 25 ± 0.1 °C
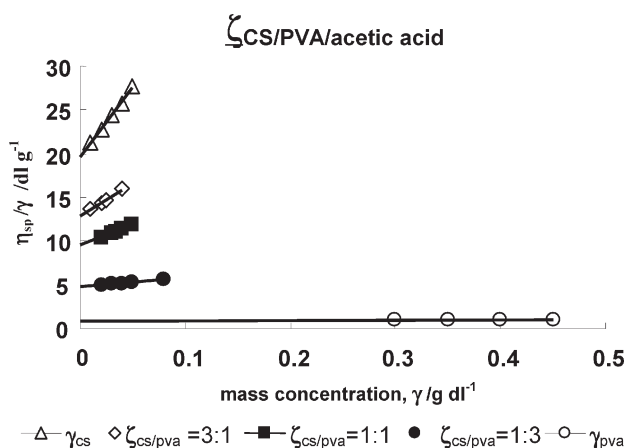
ζCS/PVA/acetic acid

F i g . 2 a – *Huggins plot (reduced viscosity in relation to the polymer mass concentrations) for CS, PVA and blends at 25 ± 0.1 °C*
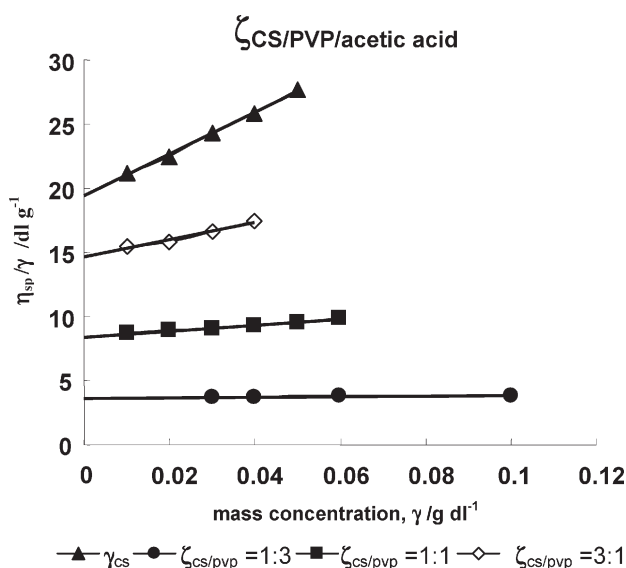
ζCS/PVP/acetic acid

F i g . 2 b – *Huggins plot (reduced viscosity in relation to the polymer mass concentrations) for CS and ζ$_{CS/PVP}$ blends at 25 ± 0.1 °C*
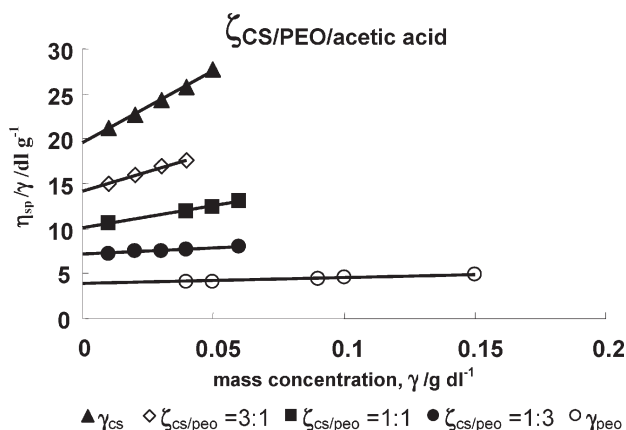
ζCS/PEO/acetic acid

F i g . 2 c – *Huggins plot (reduced viscosity in relation to the polymer mass concentrations) for CS, PEO and blends at 25 ± 0.1 °C*

at $\zeta_{CS/PVA}$ = 3 : 1 ratio. For $\zeta_{CS/PVP}$ blend there is an increase in $k' + k''$ from 0.434 to 0.486 as the blend mass ratio changes from $\zeta_{CS/PVP}$ = 1 : 3 to $\zeta_{CS/PVP}$ = 3 : 1 suggesting increased polymer-polymer interactions. However, in $\zeta_{CS/PEO}$ blend, no definite trend is observed. It is difficult to interpret the $k' + k''$ quantity in view of the typical behaviour of PEO as it is reported to induce crystallinity and phase segregation at intermediate compositions in some blend systems.[27] The specific viscosities (η_{sp}/γ) of all the blends lie in-between those of pure components suggesting possible miscibility.

Viscosity measurements

Miscibility between CS and PVA, PVP and PEO polymer-polymer blends was investigated by studying the molecular interactions by viscosity measurements of dilute polymer solution based on classical Huggins equation,[24] which expresses the specific viscosity, $(\eta_{sp})_i$ as a function of polymer concentration γ_i as:

$$\frac{(\eta_{sp})_i}{\gamma_i} = [\eta]_i + b_{ii}\gamma_{ii} \qquad (6)$$

where the interaction parameter, b_{ii} is related to the Huggins coefficient K_i by $b_{ii} = K_i[\eta]_i^2$, and $[\eta]_i$ is the intrinsic viscosity defined as:

$$[\eta]_i = \lim_{\gamma_i \to 0}\left(\frac{(\eta_{sp})_i}{\gamma_i}\right) \qquad (6a)$$

The plot of $(\eta_{sp})_i/\gamma_i$ vs. γ_i yields a straight line with intercept and slope respectively equal to $[\eta]_i$ and b_{ii}. Theoretically, intrinsic viscosity $[\eta]_i$ represents the effective hydrodynamic specific volume of an isolated polymer, and interaction parameter b_{ii} represents the binary interaction between polymer segments. Huggins equation when extended to a mixture of polymers in a common solvent (polymer 1/ polymer 2/ solvent) can be written as:

$$\frac{(\eta_{sp})_m}{\gamma_m} = [\eta]_m + b_m + \gamma_m \qquad (7)$$

where the subscript 'm' denotes 'mixture'. Here, the intrinsic viscosity of the mixture $[\eta]_m$ denotes the coil dimensions, which can be altered by contraction or expansion of the coil whether the interactions between unlike polymer segments are attractive or not. Likewise, the viscometric interaction parameter b_m represents the interaction between polymer segments in the mixture. The weighted average form of eq. (7) can be expressed as:

$$\frac{(\eta_{sp})_m}{\gamma_m} = \sum_i \frac{(\eta_{sp})_i}{\gamma_i} w_i \qquad (8)$$

where $w_i = \gamma_i / \gamma_m$ being the mass fraction of polymer i ($i = 1,2$). On combining eqs. (6) and (8) we get:[25]

$$\frac{(\eta_{sp})_m}{\gamma_m} = \sum_i [\eta]_i w_i + \gamma_m \left(\sum_i b_{ii}^{1/2} w_i \right)^2 \quad (9)$$

Comparison of eqs. (7) and (9) yields:

$$[\eta]_m = [\eta]_1 w_1 + [\eta]_2 w_2 \quad (10)$$

and

$$b_m = (\Sigma b_{ii}^{1/2} w_i)^2 = b_{11} w_1^2 + b_{22} w_2^2 + 2w_1 w_2 b_{11}^{1/2} b_{22}^{1/2} \quad (11)$$

Eq. (11) defines the global viscometric interaction parameter b_m^{id} between chains of both the polymers in the mixture. The ideal value of specific interaction parameter b_{12}^{id} is assumed to be geometric mean value of parameters corresponding to the interaction between like chain polymers[24] and expressed as:

$$b_{12}^{id} = b_{11}^{1/2} b_{22}^{1/2} \quad (12)$$

The slope of eq. (7) gives the experimental value b_m^{exp}. This experimental value, by analogy, can be defined as:

$$b_m^{exp} = b_{11} w_1^2 + b_{22} w_2^2 + 2 b_{12}^{exp} w_1 w_2 \quad (13)$$

Using eq. (6), parameters b_{11} and b_{22} can be determined from the binary system data obtained on polymer (1) and polymer (2) in the same solvent. In the polymer mixture the miscibility criteria as proposed by Krigbaum and Wall[24] is based on the comparison between experimental and theoretical value. A polymer mixture is miscible if $b_{12}^{exp} > b_m^{id}$ or $\Delta b_m = (b_m^{exp} - b_m^{id}) > 0$ and immiscible if $\Delta b_m < 0$. The value of $\Delta b_m > 0$ indicates the presence of attractive molecular interactions whereas $\Delta b_m < 0$ implies repulsive molecular interactions.

Another miscibility criterion proposed by Garcia et al.[25] is based on the difference between the experimental and ideal values of $[\eta]_m$, treating the intrinsic viscosity as an excess property similar to those of real solutions. The criterion states that miscibility exists, if $\Delta[\eta]_m = ([\eta]_m^{exp} - [\eta]_m^{id}) < 0$ and immiscible, if $\Delta[\eta]_m = ([\eta]_m^{exp} - [\eta]_m^{id}) > 0$. Chee[26] has also proposed a criterion for predicting the miscibility between two polymers, expressed as:

$$\mu = \left(\frac{\Delta B}{([\eta]_2 - [\eta]_1)^2} \right) \quad (14)$$

where ΔB is the arithmetic differential interaction parameter defined as

$$\Delta B = b_{12} - \left(\frac{b_{11} + b_{22}}{2} \right) \quad (15)$$

The criterion states that the polymer blend is miscible if $\mu \geq 0$, whereas, $\mu < 0$ indicates immiscibility.

Using the criteria as proposed by Krigbaum et al.,[24] Garcia et al.,[25] and Chee[26] the parameters Δb_m, $\Delta[\eta]_m$ and μ have been computed to establish the degree of miscibility in the polymer blends. From the values of Δb_m, $\Delta[\eta]_m$ and μ parameters listed in Table 3, it can be concluded that the blend systems studied are miscible over the entire composition range studied as $b_m^{exp} > b_m^{id}$, $[\eta]_m^{exp} < [\eta]_m^{id}$ and $\mu \geq 0$; the criterion for miscibility are satisfied.

T a b l e 3 – *Miscibility parameters for CS/PVA, CS/PVP and CS/PEO blends*

System $\zeta_{m_1/m_2/m_3}$	w_1	Δb_m (Garcia et al. 1999)	$\Delta[\eta]_m$ (Garcia et al. 1999)	μ (Chee 1990)	Remarks
CS(1)/PVA(2)/ Acetic acid	0.25	3.743	−1.389	0.2083	miscible
	0.5	39.916	−1.449	0.1293	miscible
	0.75	67.760	−0.069	0.0278	miscible
CS(1)/PVP(2)/ Acetic acid	0.25	1.287	−0.621	0.0059	miscible
	0.5	22.223	−1.534	0.0631	miscible
	0.75	65.703	−1.420	0.1808	miscible
CS(1)/PEO(2)/ Acetic acid	0.25	−18.991	−0.779	0.0558	miscible
	0.5	14.311	−0.678	0.2078	miscible
	0.75	53.971	−1.958	0.3493	miscible

However, at higher compositions of PEO in the $\zeta_{CS/PEO}$ blend = 1:3, the miscibility criterion fails to predict the miscibility. The presence of PEO is reported to induce crystallinity and phase segregation in some polymer blend systems at intermediate compositions.[27] This tendency of PEO could probably be responsible for the negative value of interaction parameter Δb_m.

Steady shear viscosity

The rheograms in Figs. 3a, 4a, 5a provide the correlation between the shear stress and the shear rate, and Figs. 3b, 4b, 5b show the viscosity
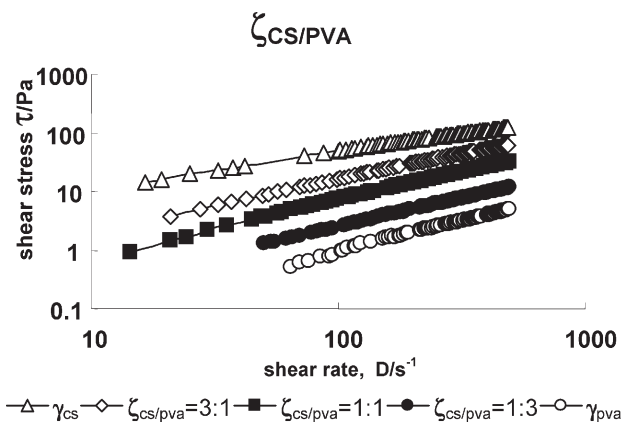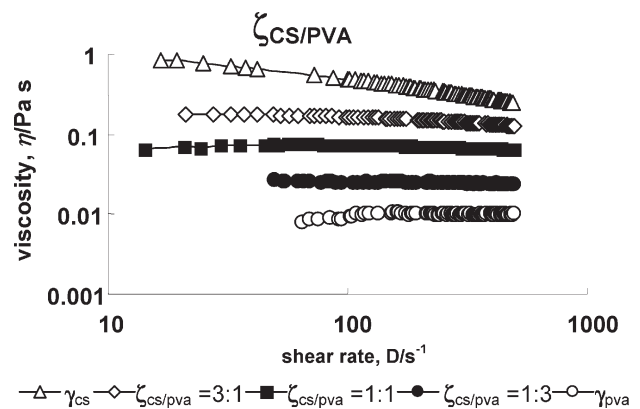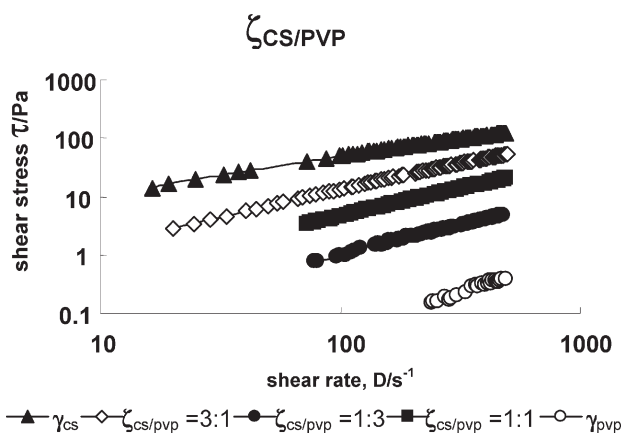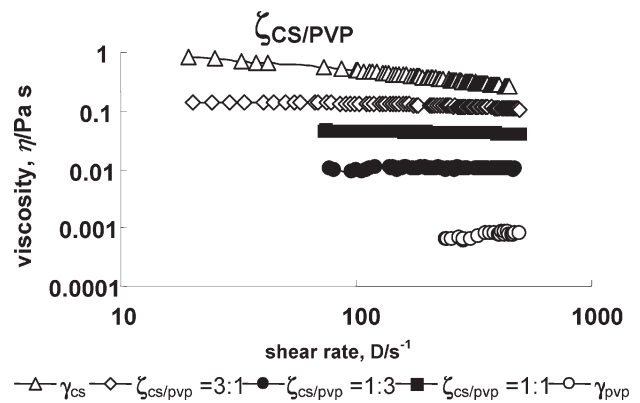
F i g . 3 a – *Rheogram for $\zeta_{CS/PVA}$ blends at 25 ± 0.1 °C*

F i g . 3 b – *Viscosity as a function of shear rate for $\zeta_{CS/PVA}$ blends*

F i g . 4 a – *Rheogram for $\zeta_{CS/PVP}$ blends at 25 ± 0.1 °C*

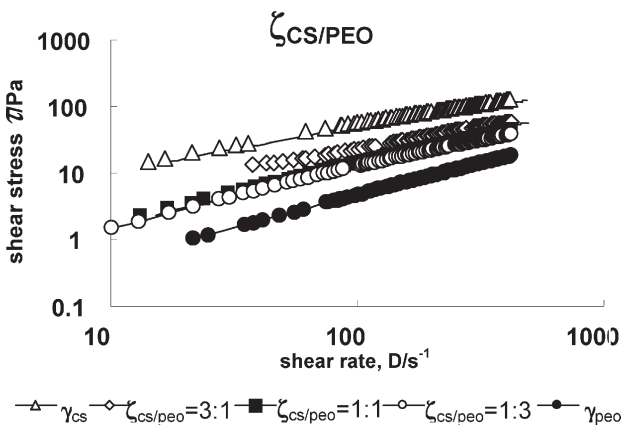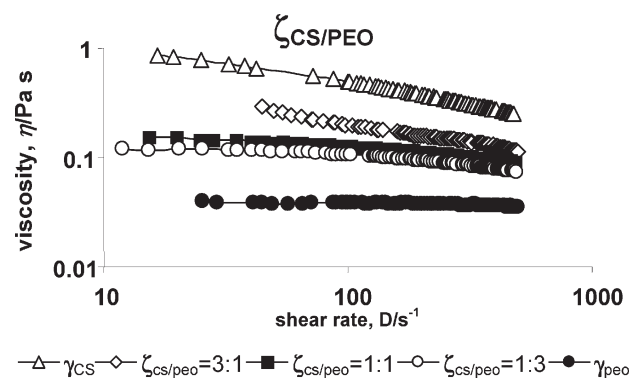F i g . 4 b – *Viscosity as a function of shear rate for CS, PVP and blends*

F i g . 5 a – *Rheogram for $\zeta_{CS/PEO}$ blends at 25 ± 0.1 °C*

F i g . 5 b – *Viscosity as a function of shear rate of CS, PEO and blends*

as a function of shear rate for neat as well as blend compositions. Both curves have been plotted over a log-log scale with shear rate ranging from 10 s^{-1} – 1000 s^{-1}. It is observed that the flow and viscosity curves are straight lines indicating that the Ostwald-de-Waele equation (Power law model) is a suitable model for the representation of the data. The power law model: $\tau = K\dot{\gamma}''$, where τ is the shear stress and $\dot{\gamma}$ the shear strain, was fitted to the observed rheological data (τ vs. $\dot{\gamma}$) and

the model parameters thus obtained are listed in Table 4.

Considering the values of 'n' of principal components, the index of flow behaviour, CS is highly pseudoplastic in nature with its flow index, n, as 0.586, indicating deviation from Newtonian behaviour due to the presence of entanglements. However, PVA, PVP and PEO with the molecular masses used in the present study, are nearly Newto-

T a b l e 4 – *Power Law parameters*

System ζ_{m_1/m_2}	K/Pa s^n	n
CS	3.3231	0.586
CS/PVA (3:1)	0.9595	0.662
CS/PVA (1:1)	0.3058	0.809
CS/PVA (1:3)	0.2134	0.839
PVA	0.0389	0.990
CS/PVP (3:1)	0.2716	0.853
CS/PVP (1:1)	0.0676	0.992
CS/PVP (1:3)	0.0134	0.954
PVP	0.0007	0.998
CS/PEO (3:1)	0.3493	0.841
CS/PEO (1:1)	0.1023	0.929
CS/PEO (1:3)	0.0300	0.963
PEO	0.0113	0.978

nian. It is observed that all the blend compositions exhibit non-Newtonian behaviour with pseudo-plasticity increasing with CS concentration (Table 4). Similarly, the consistency index 'K' of PVA, PVP and PEO indicates good polymer solvent interactions compared to CS in 1 % aqueous acetic acid solution. Rheograms of all the blends were found to lie between the rheograms of pure components over the entire compositional range (Figs. 3–5). Further, viscosity of all blend compositions was also found to lie between the viscosities of principal components of the blend.

Model fitting

The experimental measurements of the steady shear flow test were fitted using nonlinear regression technique to three and four parameter models. The typical nonlinear flow models that were used to describe the flow curves of non-Newtonian fluids are:

MODEL　　　MODEL EQUATIONS

Three parameter model

Sisko model　　$\eta = k_1 \dot{\gamma}^{n-1} + \eta_\infty$　　　(16)

Four parameter model

Cross model　$\eta = \eta_\infty + \dfrac{\eta_0 - \eta_\infty}{1 + [k_2 \dot{\gamma}]^m}$　　(17)

Standard deviation (SD) was calculated as:

$$SD = \sqrt{\frac{\Sigma(\text{calculated value} - \text{experimental value})^2}{N-1}} \quad (18)$$

where, N is the number of data points.

Tables 5(a, b), 6(a, b), 7(a, b) list the values of model parameters with SD. All the blend compositions are best described by the Cross model than the Sisko model as its SD values are lower. However, PVA and PVP do not follow the Cross model which could be due to the Newtonian character of these two polymers as compared to that of PEO.

T a b l e 5 a – *CS/PVA blend, Sisko model*

Model	System ζ_{m_1/m_2}	k_1/Pa s^n	n	η_∞/Pa s	SD
	CS	1.9535	0.6875	$0.98 \cdot 10^{-4}$	0.0341
	CS/PVA (3:1)	0.2993	0.8680	$0.72 \cdot 10^{-3}$	0.0028
Sisko	CS/PVA (1:1)	0.0951	0.9260	$0.64 \cdot 10^{-2}$	0.0008
	CS/PVA (1:3)	0.0248	0.9537	$0.51 \cdot 10^{-2}$	0.0004
	PVA	0.0423	0.0047	$0.98 \cdot 10^{-2}$	0.0002

T a b l e 5 b – *CS/PVA blend, Cross model*

Model	System ζ_{m_1/m_2}	η_∞/Pa s	η_0/Pa s	k_2/Pa s^m	m	SD
	CS	0.0959	1.1094	0.0169	0.7966	0.0064
	CS/PVA (3:1)	$0.23 \cdot 10^{-3}$	0.1901	$0.76 \cdot 10^{-3}$	0.7280	0.0004
Cross	CS/PVA (1:1)	$0.31 \cdot 10^{-2}$	$0.11 \cdot 10^2$	$0.10 \cdot 10^4$	0.4800	0.0009
	CS/PVA (1:3)	0.0238	6.9655	$0.99 \cdot 10^3$	0.7526	0.0004
	PVA		NA			

IR spectroscopy

CS/PVA blends

Figs. 6, 7 exhibit the FTIR spectra for CS and CS/PVA blended films in the range of 4000-500 cm^{-1}. Stretching vibration of hydroxyl groups (OH) appears around 3450 cm^{-1} in all CS and CS/PVA blended films spectra which overlaps with NH stretching in the same region. Stretching vibration spectra of the amide group of CS film (amide II) appears at 1585 cm^{-1} in pure CS and 1564 cm^{-1} in CS/PVA blends. The change in the characteristic

T a b l e 6 a – *CS/PVP blend, Sisko model*

Model	System ζ_{m_1/m_2}	k_1/Pa s^n	n	η_∞/Pa s	SD
	CS	1.9535	0.6875	$0.98 \cdot 10^{-4}$	0.0341
	CS/PVP (3:1)	0.2441	0.8712	$0.17 \cdot 10^{-3}$	0.0016
Sisko	CS/PVP (1:1)	0.0467	0.9200	$0.13 \cdot 10^{-1}$	0.0005
	CS/PVP (1:3)	0.0081	0.9697	$0.34 \cdot 10^{-2}$	0.0003
	PVP			NA	

T a b l e 6 b – *CS/PVP blend, Cross model*

Model	System ζ_{m_1/m_2}	η_∞/Pa s	η_0/Pa s	k_2/Pa s^m	m	SD
	CS	0.0959	1.1094	0.0169	0.7966	0.0064
	CS/PVP (3:1)	$0.37 \cdot 10^{-2}$	0.4193	0.6695	0.1825	0.0017
Cross	CS/PVP (1:1)	0.0410	$0.41 \cdot 10^2$	$0.10 \cdot 10^4$	0.7750	0.0007
	CS/PVP (1:3)			NA		
	PVP			NA		

F i g . 6 – *FTIR spectra of pure CS film*

T a b l e 7 a – *CS/PEO blend, Sisko model*

Model	System ζ_{m_1/m_2}	k_1/Pa s^n	n	η_∞/Pa s	SD
	CS	1.9535	0.6875	$0.98 \cdot 10^{-4}$	0.0341
	CS/PEO (3:1)	2.5669	0.3882	0.0583	0.0160
Sisko	CS/PEO (1:1)	0.2654	0.8352	$0.38 \cdot 10^{-4}$	0.0030
	CS/PEO (1:3)	0.21780	0.8359	$0.22 \cdot 10^{-3}$	0.0031
	PEO	0.0336	0.9227	0.0151	0.0003

T a b l e 7 b – *CS/PEO blend, Cross model*

Model	System ζ_{m_1/m_2}	η_∞/Pa s	η_0/Pa s	k_2/Pa s^m	m	SD
	CS	0.0959	1.1094	0.0169	0.7966	0.0064
	CS/PEO (3:1)	0.1182	1.2037	0.076	1.2675	0.0084
Cross	CS/PEO (1:1)	$0.27 \cdot 10^{-4}$	0.1661	$0.14 \cdot 10^{-2}$	0.6218	0.0006
	CS/PEO (1:3)	0.0333	0.1260	$0.25 \cdot 10^{-2}$	0.9560	0.0004
	PEO	0.0349	$0.15 \cdot 10^2$	$0.99 \cdot 10^3$	0.7246	0.0004

—— $\zeta_{CS/PVA} = 3:1$, ... $\zeta_{CS/PVA} = 1:1$,   – · – $\zeta_{CS/PVA} = 1:3$
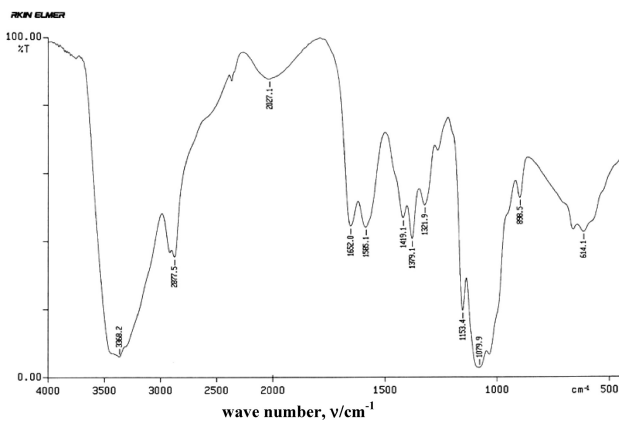
F i g . 7 – *FTIR spectra of CS/PVA blends*

shape of CS spectrum as well as peak shifts to lower frequency range suggests increased hydrogen bonding between OH of PVA and NH$_2$ of CS in the blended films.
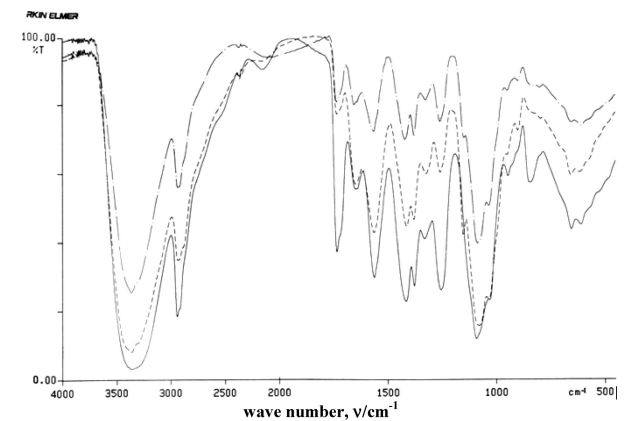
CS/PVP blends

Analysis of CS/PVP blend spectra indicates that interaction exists between these polymers, which can be attributed to the hydroxyl group in CS and carboxyl group in PVP. As observed in Fig. 8, the OH absorption spectrum for CS in the blend is observed to shift downwards in frequency (from about 3450 to 3406 cm^{-1}) with increase in PVP concentration. Also, the C=O absorption for PVP shifts downwards from 1670 cm^{-1} to 1661 cm^{-1} in blends. Both effects indicate hydrogen bonding.

CS/PEO blends

The FTIR spectra of CS/PEO blends indicate that interaction between CS and PEO occurs for all the blends. Fig. 9 shows the OH absorption peak in
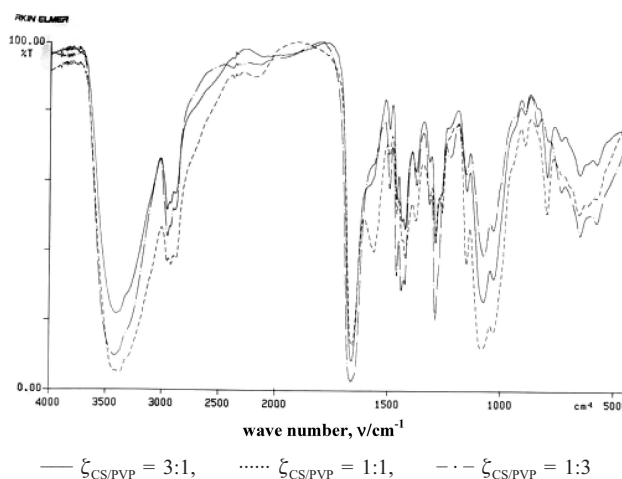
— $\zeta_{CS/PVP} = 3:1$,   ⋯⋯ $\zeta_{CS/PVP} = 1:1$,   — · — $\zeta_{CS/PVP} = 1:3$

F i g . 8 – *FTIR spectra of CS/PVP blends,*

— $\zeta_{CS/PEO} = 3:1$,   ⋯⋯ $\zeta_{CS/PEO} = 1:1$,   — · — $\zeta_{CS/PEO} = 1:3$
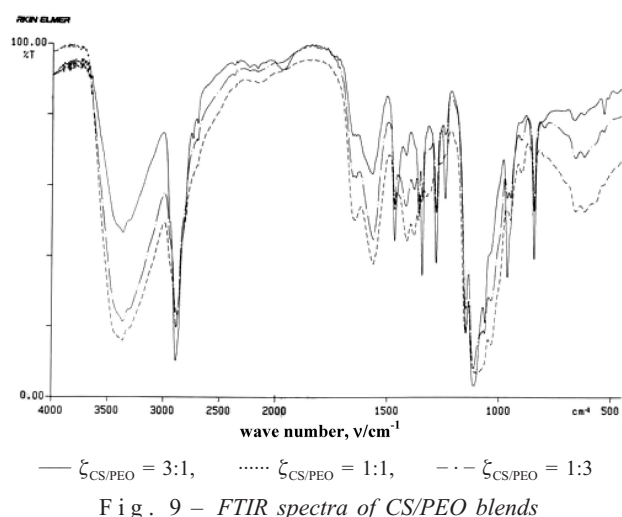
F i g . 9 – *FTIR spectra of CS/PEO blends*

all the CS/PEO blends shifts to lower frequencies (from about 3450 cm^{-1} in CS to about 3364 cm^{-1} in blends), indicates some hydrogen bonding interaction, possibly between the hydroxyl of CS and ether groups in PEO.

Conclusions

Blends of CS with PVA, PVP and PEO were miscible over the entire composition range as analyzed by dilute solution viscosity measurements and duly supported by FTIR spectroscopy. The rheological behaviour of CS, PVA, PVP, PEO and blends has been studied. CS exhibits pronounced shear thinning behaviour. The flow index behaviour of all the blends 'n' is < 1, indicating pseudoplasticity, which increases with CS concentration in the blend. Rheograms of all the blends were found to lie between the rheograms of pure components over the entire compositional range, which seems to be the characteristic property of a miscible polymer-polymer blend.

The experimental results reported in this work suggest that the rheological characterization of polymer blends offers an effective means to study the interactions between polymers for establishing miscibility between them.

List of symbols

a – empirical viscometric constant

b_m – viscometric interaction parameter

ΔB – arithmetic differential

D – shear rate, s^{-1}

k – viscometric coefficient, Pa s^m

K – empirical viscometric constant, Pa s^m

M – molar mass, g mol^{-1}

n – amount of substance, mol

N – number of data point

r – mole ratio, n_1/n_2

R^2 – correlation coefficient

w – mass fraction, %

γ – mass concentration, g dL^{-1}

ζ – mass ratio, $m_1 : m_2$

η – viscosity, Pa s

$[\eta]$ – intrinsic viscosity, Pa s

ν – wave number, cm^{-1}

τ – shear stress, Pa

φ – volume fraction, %

References

1. *Kumar, M. N. V. R.*, React. and Func. Polym. **46** (1) (2000) 1.
2. *Montembault, A., Viton, C., Domard, A.*, Biomaterials **26** (2005) 933.
3. *Agnihotri, S. A., Mallikarjuna, N. N., Aminabhavi, T. M.*, J. Control. Rel. **100** (2004) 5.
4. *Gupta, K. C., Jabrail, F. H.*, Carbohydrate Res. **341** (6) (2006) 744.
5. *Anal, A. K., Stevens, W. F., Lopez, C. R.*, Intern. J. Pharmaceu. **312** (1–2) (2006) 166.
6. *Zhao, L., Xu, L., Mitomo, H., Yoshii, F.*, Carbohydrate Polymers **64** (3) (2006) 473.
7. *Chen, C., Dong, L., Cheung, M. K.*, Eur. Polym. J. **41** (2005) 958.
8. *Khoo, C. G. L., Frantzich, F., Rosinski, A., Sjostrom, M., Hoogstraate, J.*, Eur. J. Pharmaceu. and Biopharm. **55** (2003) 47.
9. *Risbud, M. V., Hardikar, A. A., Bhat, S. V., Bhonde, R. R.*, J. Control. Rel. **68** (2000) 23.
10. *Hejazi, R, Amiji, M.*, J. Control. Rel. **89** (2003) 151.
11. *Sakurai, K., Maegawa, T., Takahashi, T.*, Polymer **41** (2000) 7051.

12. *Abou Aiad, T. H. M., Abd-El-Nour, K. N., Hakim, I. K., Elsabee, M. Z.*, Polymer **47** (2006) 379.

13. *Smitha, B., Sridhar, S., Khan, A. A.*, J. of Power Sources **159** (2) (2006) 846.

14. *Devi, D. A., Smitha, B., Sridhar, S., Aminabhavi, T. M.*, J. Membr. Sci. **280** (1–2) (2006) 45.

15. *Devi, D. A., Smitha, B., Sridhar, S., Aminabhavi, T. M.*, J. Membr. Sci. **280** (1–2) (2006) 138.

16. *Hwang, J. K., Shin, H. H.*, Korea-Australia Rheology J. **12** (3/4) (2000) 175.

17. *Roberts, G. A. F., Domzy, J. G.*, Intern. J. of Biolog. Macromolecules **4** (6) (1982) 374.

18. *Montembault, A., Viton, C., Domard, A.*, Biomacromolecules **6** (2005) 653.

19. *Skelland, A. H. P.*, Non-Newtonian Flow and Heat Transfer, John Wiley and Sons, New York, 1967, pp 120.

20. *Alovarez Lorenzo, C., Concheiro, A., Dubovik, A. S., Grienberg, N. V., Burovo, T. V., Grienberg, V. Y.*, J. Control. Rel. **102** (2005) 629.

21. *Billmeyer, F. W. Jr.*, Text book of Polymer Science, 3rd edition, John Wiley and Sons, New York, 2002, pp 209-210.

22. *Wanchoo, R. K., Sharma, P. K.*, Eur. Polym. J. **39** (2003) 1481.

23. *Wanchoo, R. K., Rohini, Thakur, A.*, J. Polym. Mater. **23** (4) (2006) 437.

24. *Krigbaum, W. R., Wall, F. T.*, J. Polym. Sci. **5** (1950) 505.

25. *Garcia, R., Melad, O., Gomez, C. M., Figueruelo, J. E., Campos, A.*, Eur. Polym. J. **35** (1999) 47.

26. *Chee, K. K.*, Eur. Polym. J. **26** (1990) 423.

27. *Mishra, R., Rao, K. J.*, Eur. Polym. J. **35** (1999) 1883.

28. *Cho, J., Heuzey, M., Bégin, A., Carreau, P. J.*, J. Food Eng. **74** (2006) 500.