Miscibility Studies of Xanthan Gum with Gelatin in Dilute Solution

K. C. Basavaraju, J. Jayaraju, S. K. Rai, T. Damappa

Department of Polymer Science, Sir. M.V.P.G. Center, University of Mysore, Karnataka 571402, India

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ABSTRACT: Miscibility of polysaccharide-based natural polymer, xanthan gum with gelatin in 0.1*M* NaCl medium was investigated using viscosity, ultrasonic, and refractive index technique. The effect of temperature on the miscibility was studied at 30 and 40°C. The interaction parameters ''μ'' and ''α'' were calculated based on the Chee (Eur Polymer J 1990, 26, 423) and Sun et al. (Eur Polym J 1992, 28, 1259) approach. The obtained values indicated that the blend is miscible when the xanthan gum is 70% (V/V) or more at 30°C, and 40% (V/V) or more at 40°C. The corresponding variation of refractive index and ultrasonic velocity also supports the Sun et al. approach. The compatibility between these two polymers was further confirmed by SEM and FTIR. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 109: 2491–2495, 2008

Key words: xanthan gum; gelatin; blend; compatibility; polysaccharide; SEM; FTIR

INTRODUCTION

Xanthan gum is an anionic extracellular polysaccharide produced by the bacterium *Xanthomonas campestris*. Its main chain is based on a linear backbone of 1,4-linked β-D-glucose (Fig. 2)[1]; at the C (3) position of every alternate glucose residue there is a charged trisaccharide side chain containing a glucuronic acid residue between two mannose units. The terminal β-1,4 of the glucuronic acid which, in turn, is linked at α-(1,2) to α-D-mannose. Approximately one half of the terminal mannose residue consisting of a pyruvic acid moiety is joined by a ketal linkage to the O (4) and O (6) positions. Acetate groups are present as substituents at the O (6) position of the nonterminal mannose. Xanthan gum has many industrial applications like thickener, stabilizing suspensions, and emulsions in the paper and textile industries.[2] It is also frequently employed in the food industry because of its solubility in hot or cold water, high viscosity at low concentrations, low variation in temperature, and stability in acid systems. It also shows excellent suspending properties owing to its high yield value and ability to provide good freeze–thaw stability.[3,4] Gelatin is a biodegradable hydrophilic polymer having many applications in the medical and food industry. Gelatin contains many glycine (almost 1 in 3 residues, arranged every third residue), proline, and 4-hydroxyproline residues (Fig. 1).[5] Xanthan gum forms a thick solution or gel at low concentration. Its rheological properties depend on its average molecular weight and acetate[6] and pyruvate content.[1,7] A high level of acetylation and pyruvulation increases the viscosity of its water solution because of intermolecular associations.[7]

Viscometric analysis of polymer–polymer miscibility in dilute solution is based on the Huggins equation, which reflects the relationship between specific viscosity and polymer concentration. Since xanthan gum is anionic in nature, we could not apply the Huggins equation to the xanthan gum in water solution,[8] so in this study we have blended xanthan gum with gelatin in 0.1*M* NaCl for viscosity studies.

Polymer blends are physical mixtures of structurally different polymers or copolymers, which interact with secondary forces with no covalent bonding such as dipole–dipole forces, H-bonding, and charge transfer complexes for homopolymers.[9–12] The miscibility of polymer blends is generally studied by various techniques such as dynamic mechanical measurement, neutron scattering, inverse gas chromatography, electron microscopy, etc.[12] All these techniques, though sophisticated are costly and time consuming. Hence simple, low cost, and rapid techniques have been used in recent studies. Chee[8] and Sun et al.[13] suggested viscometry for polymer–polymer miscibility. Paladhi and Singh[14,15] showed that the variation of ultrasonic velocity and viscosity with blend composition is linear for miscible and nonlinear for immiscible blends. VaradaRajalu et al.[16,17] have used viscosity, ultrasonic, and refractive index measurements to study the miscibility of sodium alginate and polyvinyl alcohol. Therefore, in

Correspondence to: T. Damappa (damappa@rediffmail.com).

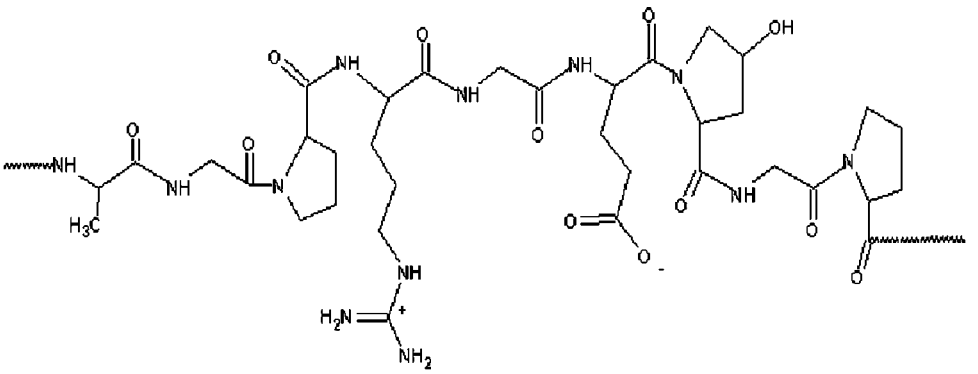

Figure 1 Chemical structure of gelatin.

this research we have adopted a solution blending method for miscibility studies.

EXPERIMENTAL

Xanthan gum was received from Pankaj Sales Agency (Mumbai, India). Gelatin (research grade, Merk). Dilute solution of 0.2% of xanthan gum and of gelatin were prepared and blended in NaCl solution with different compositions such as 10/90, 20/80, 30/70, 40/60, 50/50, 60/40, 70/30, 80/20, and 90/10. Viscosity, ultrasonic velocity, and refractive index were determined at 30 and 40°C. The required temperature was maintained in a thermostat bath with a thermal stability of ±0.5°C. The ultrasonic experimental cell has a double-walled jacket, and thermostated water was circulated in it. The frequency was 2 MHz and velocity measurements maintained at an accuracy of ±0.5%. The refractive indices of the blend solutions were measured with an Abbe's refractometer, and the accuracy of the refractive index measurements was maintained at ±0.02%.

Xanthan gum, gelatin, and different blend compositions in 0.1*M* NaCl solution were dried at 60°C under vacuum and conditioned for 48 h in a desiccator. Highly brittle film like flakes were crushed to make powder, and mixed with KBr to make a disc for FTIR analysis. The blended solutions (without NaCl) of 10/90 (immiscible) and 80/20 (miscible) compositions were poured over glass plates and dried at room temperature to get the thin films for SEM analysis.

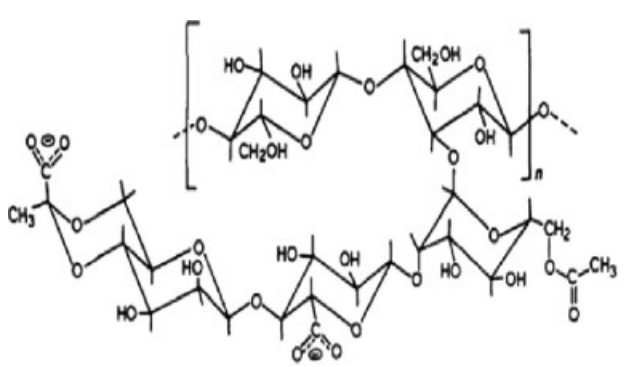

Figure 2 Chemical structure xanthan gum.

RESULTS AND DISCUSSION

Reduced viscosities of xanthan gum and gelatin blended for different compositions of 10/90, 20/80, 30/70, 40/60, 50/50, 60/40, 70/30, 80/20, and 90/10 were measured at 30 and 40°C, and are presented in the Tables I and II. Figures 3 and 4 show the Huggins plots for the pure polymers and their blends at 30 and 40°C, respectively. From the figure, it is clearly observed that the Huggins plots are composed of two regions with varying slopes for the blends. The change in the slope may be attributed to the mutual attraction of the macromolecules in solution, which favor miscibility. Similar observations were obtained by Haiyang et al.[18] and Raviprakash and Rai[19] in the case of PVC/polycaprolactone and sodium alginate/polyethylene glycol, respectively. The calculated ''μ'' and ''α'' values are presented in Table III. The results clearly indicated that the interaction parameter ''μ'' is negative for all the compositions at both 30 and 40°C. However, α values are positive when gelatin content is up to 30% (v/v) at 30°C and up to 60% (v/v) at 40°C. To quantify the miscibility of the polymer blends, Chee[8] suggested the general expression for the interaction parameter when the polymers are mixed in weight fraction W_1 and W_2 as follows:

$$\Delta B = \frac{b - \bar{b}}{2W_1W_2} \tag{1}$$

where $\bar{b} = W_1b_{11} + W_2b_{22}$, where b_{11} and b_{22} are the slopes of the viscosity curves for the components,

TABLE I
Reduced Viscosity Data for Xanthan Gum/Gelatin and Their Blends in 0.1*M* NaCl Solution at 30°C

	η_{sp}/C (dL/g) at 30°C										
			Xanthan/gelatin blend								
Concentration (g/dL)	Xanthan	Gelatin	90/10	80/20	70/30	60/40	50/50	40/60	30/70	20/80	10/90
0.02	20.60	0.45	16.25	15.62	12.80	10.30	8.90	6.87	5.00	3.75	2.50
0.04	24.06	0.50	17.18	14.06	11.56	10.00	8.13	6.20	4.37	2.81	1.87
0.06	29.30	0.60	21.30	16.66	13.54	11.45	9.16	6.04	4.70	2.60	1.66
0.08	32.80	0.65	25.00	18.59	15.31	12.40	9.84	6.98	5.40	2.98	1.71
0.10	36.25	0.65	26.80	21.00	17.12	13.60	10.75	7.71	5.50	3.22	1.87
0.12	42.29	0.90	29.89	23.85	19.27	14.90	11.60	8.22	5.93	3.54	1.97
0.14	46.07	1.22	32.10	25.89	20.98	16.07	12.32	8.93	6.25	4.01	2.14
0.16	50.00	1.47	34.76	27.96	22.66	17.18	13.28	9.51	6.71	4.20	2.34
0.18	55.64	1.56	37.50	30.55	24.65	18.40	14.23	10.23	7.01	4.37	2.36
0.20	58.13	1.59	40.00	32.62	26.25	19.75	15.18	11.00	7.50	4.60	2.50

TABLE II
Reduced Viscosity Data for Xanthan Gum/Gelatin and Their Blends in 0.1*M* NaCl Solution at 40°C

	η_{sp}/C (dL/) at 40°C										
			Xanthan/gelatin blend								
Concentration (g/dL)	Xanthan	Gelatin	90/10	80/20	70/30	60/40	50/50	40/60	30/70	20/80	10/90
0.02	17.39	0.72	18.20	15.00	12.31	9.50	8.30	7.00	4.80	3.40	2.17
0.04	21.37	0.72	17.40	14.10	11.23	8.33	7.20	6.32	4.00	2.90	1.81
0.06	26.32	0.75	20.12	16.18	13.00	9.83	8.00	6.10	4.20	2.80	1.20
0.08	30.79	0.90	22.50	18.21	15.03	11.23	9.05	6.88	4.71	3.07	1.44
0.10	34.20	0.95	25.15	20.50	17.00	12.90	10.28	7.53	5.21	3.33	1.59
0.12	38.64	1.08	27.58	22.58	18.89	14.00	11.11	7.93	5.31	3.38	1.93
0.14	43.37	1.10	30.18	24.72	20.72	15.70	12.00	8.83	5.90	3.41	2.00
0.16	47.41	1.17	32.71	26.92	22.32	17.26	13.50	9.20	6.28	3.71	2.17
0.18	52.71	1.28	35.23	29.17	24.28	18.53	14.91	10.12	6.86	4.26	2.19
0.20	56.59	1.30	37.42	31.08	26.23	20.00	16.81	11.30	7.42	4.34	2.10

TABLE III
Refractive Index, Ultrasonic Velocity, μ and α at 30 and 40°C in 0.1*M* NaCl Solution

	Refractive index		Ultrasonic velocity		μ		α	
Blend composition	At 30°C	At 40°C	At 30°C	At 40°C	At 30°C	At 40°C	At 30°C	At 40°C
90/10	1.3455	1.3400	1469.8	1472.5	−14.63	−15.92	+0.01	+0.01
80/20	1.3455	1.3400	1469.8	1472.5	−7.38	−8.04	+0.18	+0.08
70/30	1.3455	1.3400	1469.8	1472.6	−5.00	−5.41	+0.32	+0.24
60/40	1.3465	1.3400	1470.2	1472.6	−3.91	−4.23	−0.23	+0.81
50/50	1.3464	1.3400	1470.2	1472.6	−3.26	−3.51	−0.44	+0.05
60/40	1.3468	1.3400	1470.4	1472.6	−2.85	−3.05	−0.42	+0.83
30/70	1.3456	1.3394	1470.0	1472.0	−2.58	−2.75	−1.48	−0.83
20/60	1.3445	1.3415	1470.3	1473.0	−2.42	−2.57	−0.42	−1.79
10/90	1.3469	1.3406	1470.0	1473.1	−2.50	−2.58	−6.18	−6.83

and b is related to the Huggins coefficient K_H as follows:

$$b = K_H[\eta]^2 \tag{2}$$

for tertiary system, it is also given by

$$b = W_1^2 b_{11} + W_2^2 b_{22} + 2W_1 W_2 b_{12} \tag{3}$$

where b_{12} is slope for the blend solution.

However, Chee's theory fails because experimental data is in conflict with theoretical predictions. In such cases, Chee has defined a more effective parameter to predict the compatibility as follows:

$$\mu = \frac{\Delta B}{\{[\eta]_2 - [\eta]_1\}^2} \tag{4}$$

where $[\eta]_1$ and $[\eta]_2$ are the intrinsic viscosities for the pure polymer solutions.

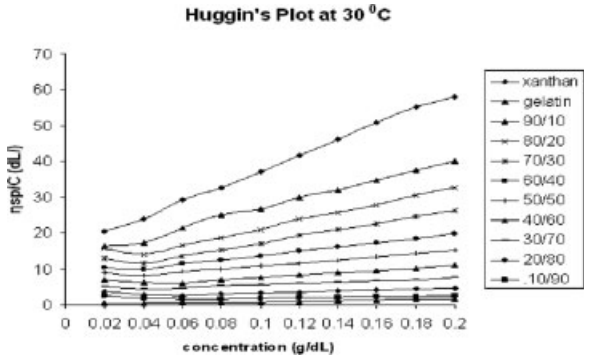

Figure 3 Huggins plot for 0.2% (w/v) xanthan gum/gelatin blend at 30°C.

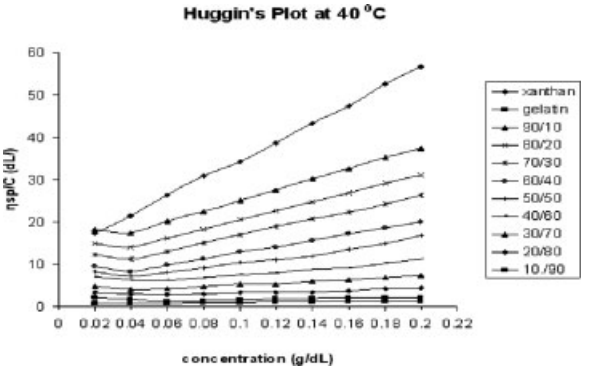

Figure 4 Huggins plot for 0.2% (w/v) xanthan gum/gelatin blend at 40°C.

The polymer blend is miscible if $\mu \geq 0$ and immiscible when $\mu < 0$. Recently, Sun et al.[13] suggested a more satisfactory equation for the determination of polymer miscibility as follows:

$$\alpha = K_m - \frac{K_1[\eta]_1^2 W_1^2 + K_2[\eta]_2^2 W_2{}^2 + 2\sqrt{K_1 K_2[\eta]_1[\eta]_2 W_1 W_2}}{\{[\eta]_1 W_1 + [\eta]_2 W_2\}^2} \quad (5)$$

where K_1, K_2, and K_m are the Huggins constants for individual components 1, 2, and blend, respectively. The long-range hydrodynamic interactions are considered while deriving the equation. The polymer blend is miscible if $\alpha \geq 0$ and immiscible when $\alpha < 0$. The long-range hydrodynamic interactions or secondary interactions are considered while deriving the eq. (5). Hence, it can be concluded that xanthan gum and gelatin blend is miscible when xanthan gum content is 70% or more at 30°C and 40% or more at 40°C. Gelatin consists of both crystalline and randomly oriented amorphous regions. This may be the reason for which results in the phase separation as gelatin content in blend composition.

To confirm the correct nature of the blend under consideration, ultrasonic velocities, refractive index of the xanthan gum–gelatin blend at various compositions at different temperatures were measured. The results are given in Table III. Ultrasonic velocity and refractive index are useful techniques for investigating the miscibility of polymer blend in solution. The variation of ultrasonic velocity/refractive index versus blend compositions is linear for compatible blends and nonlinear for noncompatible blends. Figures 5 and 6 show semicompatible nature of the xanthan gum/gelatin blend. FTIR studies were also carried out for further confirmation of semicompatibility of the blend, xanthan gum, gelatin, and different blend compositions. The band shifts (1650–1643 cm^{-1}) in 60/40 blend composition confirmed the involvement of the carboxylic groups of xanthan gum and peptide bond moieties of gelatin, but there is no shift in the 20/80 blend composition (Fig. 9). The FTIR spectrum supports the viscosity results and semicompatibility nature of blend under consid-

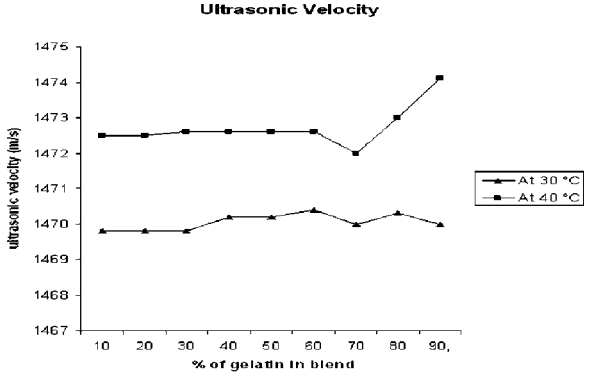

Figure 5 Variation of ultrasonic velocity with composition of 0.2% w/v of xanthan gum/gelatin blend at 30 and 40°C.

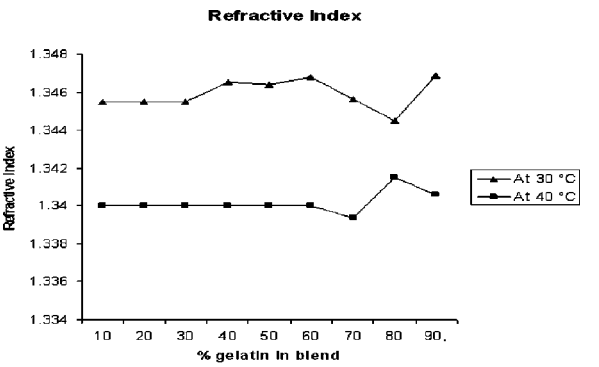

Figure 6 Variation of refractive index with composition of 0.2% w/v xanthan gum/gelatin blend at 30 and 40°C.

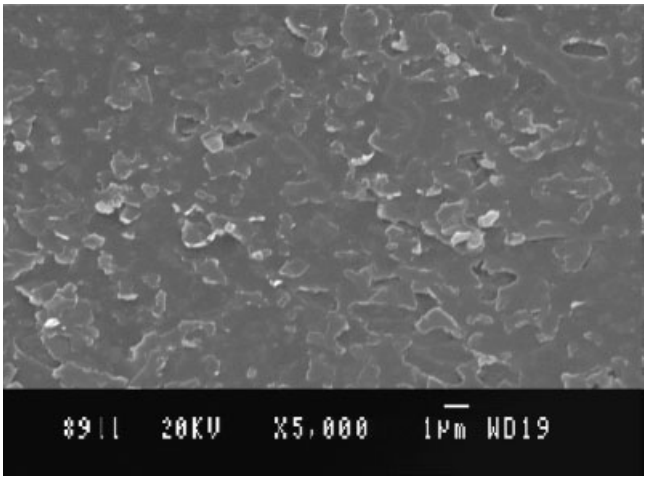

Figure 7 SEM photo of 10/90 blend of xanthan gum/gelatin film.

eration. The semicompatible nature of the blend is further confirmed by the SEM analysis. Figure 7 (10/90 composition) shows nonuniform/phase separation indicating the immiscible nature, and Figure 8 (80/20 composition) shows single phase indicating miscible nature.

CONCLUSIONS

Based on viscosity, ultrasonic velocity, and FTIR, the polymer blend of xanthan gum and gelatin was miscible when xanthan gum content is 70% or more at 30°C and 40% or more at 40°C. As gelatin content increases in blend composition, the compatibility decreases. This is because of the crystalline nature and nonlinearity of gelatin, and also because of the intra molecular H-bonding and ionic force of attraction present in the gelatin molecules. Miscibility windows are increased as the temperature increases. The semicompatible nature of the blend was further confirmed by SEM.

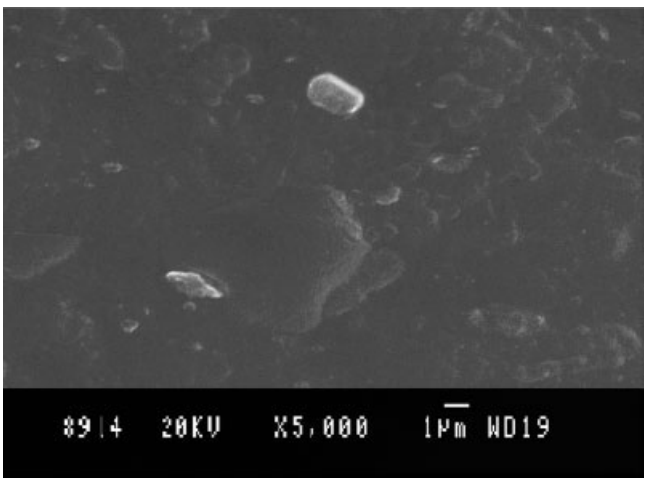

Figure 8 SEM photo of 80/20 blend of xanthan gum/gelatin film.

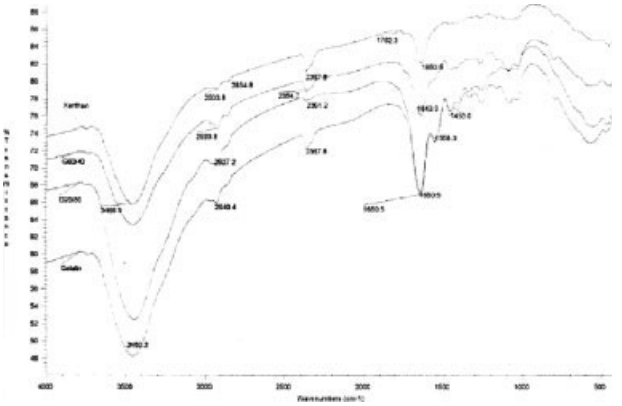

Figure 9 FTIR spectra of xanthan gum, gelatin, and blend.

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