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Miscibility studies of polysaccharide Xanthan gum and PEO (polyethylene oxide) in dilute solution

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Abstract

Compatibility of polysaccharide based natural polymer Xanthan gum with synthetic polymer polyethylene oxide have been investigated using viscosity, ultrasonic and refractive index technique in 0.1 M NaCl solution at 30 and 40 °C. Using viscosity data, the interaction parameter μ and α, based on Chee and Sun et al. approaches were determined. The values indicated that the blend is miscible, when the Xanthan gum is 40% (v/v) at both the temperatures. The variation of refractive index and ultrasonic velocity with blend composition also supports the Sun et al approach. FT-IR studies also carried out for further conformation of compatibility.

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Keywords: Xanthan gum; Polyethylene oxide; Blend; Compatibility; Polysaccharide; FT-IR

1. Introduction

Xanthan gum is an anionic extra cellular polysaccharide produced by the bacterium *Xanthomonas campestris*. Its main chain is based on a linear back bone of 1, 4-linked β-D-glucose; 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 to the glucuronic acid which, in turn, is linked α-(1, 2) to α-D-mannose. Approximately one half of the terminal mannose residues 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 non-terminal mannose (Fig. 1) (Kkang & Pettit, 1993). Xanthan gum has got many industrial applications like thickener, stabilizing the suspensions and the emulsions in the paper mill and textile industries (Kennady & Bradshaw, 1984). It is also frequently employed in the food industry because of its solubility in hot or cold water, high viscosity at low concentrations, little variation change in temperature and stability in acid systems. It also shows excellent suspending properties owing to high yield value and also and ability to provide good freeze–thaw stability (Margaritis & Zajic, 1978; Rinado & Milas, 1978). Polyethylene oxide (PEO) is a biodegradable hydrophilic polymer having many application in medical and food industry. Xanthan gum even though soluble in water, it form thick solution or gel at low concentration. The rheological properties change with polymer nature, which depends on average molecular weight and acetate (Tako & Nakumara, 1984), and pyruvate content (Kkang & Pettit, 1993; Peters, Suh, Schumpe, & Deckwer, 1993). Xanthan gum with high level of acetylation and especially, pyruvulation degree increases the viscosity of its water solutions because of intermolecular associations are favored (Peters et al., 1993).

Viscometric anylysis of polymer–polymer miscibility in dilute solution is based on the Huggins equation, which reflects the relationship between specific viscosity and polymer concentration. In this study, the polysaccharide Xanthan gum is blended with polyethylene oxide in different compositions and at different temperatures in 0.1 M NaCl solution. Since Xanthan gum is anionic in nature, we could not apply Huggins equation to the Xanthan gum in water solution, so the solution was made in 0.1 M NaCl for viscosity studies.

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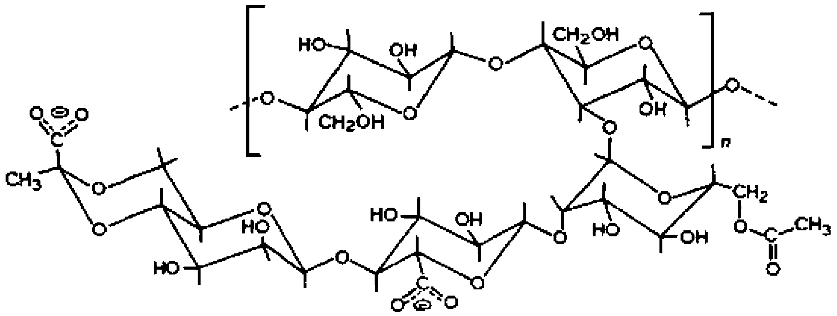

Fig. 1. Chemical structure of Xanthan gum.

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 homopolymer (Olabisi, Robenson, & Sham, 1979; Varnell & Coleman, 1981; Varnell, Runt, & Coleman, 1983 Woo, Barlow, & Paul, 1986). The miscibility of polymer blends is generally studied by number of techniques such as dynamic mechanical measurement, neutron scattering, inverse gas chromatography, electron microscopy etc. (Olabisi et al., 1979).

All this techniques though sophisticated are costly and time consuming. Hence simple, low cost and rapid techniques are of great importance in recent years. Chee (Chee, 1990) and Sun (Sun, wang, & Fung, 1992), suggested viscometry for polymer–polymer miscibility. Paladhi and Singh (Paladhi & Singh, 1994a, 1994b) showed that the variation of ultrasonic velocity and viscosity with blend composition is linear for miscible and nonlinear for immiscible blends. Varada Rajalu (VaradaRajalu et al., 2000, VaradaRajalu, Lakshminarayana Reddy, & Siddaramaiah, 1998) have used viscosity, ultrasonic and refractive index measurements to study the miscibility of sodium alginate/polyvinyl alcohol.

2. Experimental

Xanthan gum was received from Pankaj Sales Agency, Mumbai. Polyethylene oxide (PEO) research grade Merk Make and NaCl were used in this study. A dilute solution of 0.2% of homopolymer was prepared and the blended in different compositions like 10/90, 20/80, 30/70, 40/60, 50/50, 60/40, 70/30, 80/20 and 90/10 in NaCl solution. Viscosity, ultrasonic velocity and refractive index were determined at 30 and 40 °C. The required temperature was maintained in thermostat bath with a thermal stability of ±0.5 °C. Ultrasonic experimental cell has a double-walled jacket and thermostated water was circulated in it. The experimental frequency was 2 MHz and the velocity measurements were accurate to better than ±0.5%. Refractive indices of the blend solutions were measured with an Abbe's refractometer and the accuracy of the refractive index measurements is ±0.02%.

3. Results and discussion

Reduced viscosities for different compositions 10/90, 20/80, 30/70, 40/60, 50/50, 60/40, 70/30, 80/20 and 90/10 at 30 and 40 °C of Xanthan gum and PEO were measured. The Figs. 2 and 3 show the Huggins plots for the pure components and their blends at 30 and 40 °C, respectively. From the graph it is clear 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 macromolecules in solution which favor the miscibility. Similar observations were also made by Haiyang (Haiyang, Pingping, Shiquiang, & Qipeng, 1998) and Raviprakash (Raviprakash & Rai, 2004) in case of PVC/Poly caprolactone and sodium alginate/polyethylene glycol, respectively, and reported that both the systems having miscibility windows.

The evaluated values of the interaction parameter μ and α are presented in the Table 1. It is clearly evident from the Table 1 that the interaction parameters μ is negative for all the compositions at both 30 and 40 °C. However, α values are positive when the Xanthan gum content is up to 40% and then negative beyond this value at both temperatures.

In order to quantify the miscibility of the polymer blends, Chee (Chee, 1990) suggested the general expression for the interaction parameter when the polymers are mixed

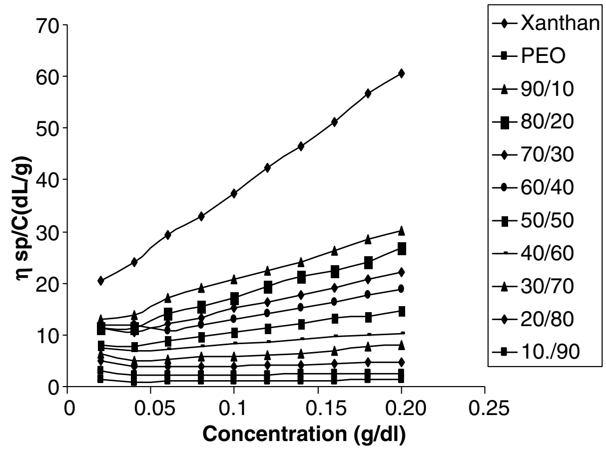

Fig. 2. Huggins plot for 0.2% w/v, Xanthan gum/PEO blend in 0.1 M NaCl at 30 °C.

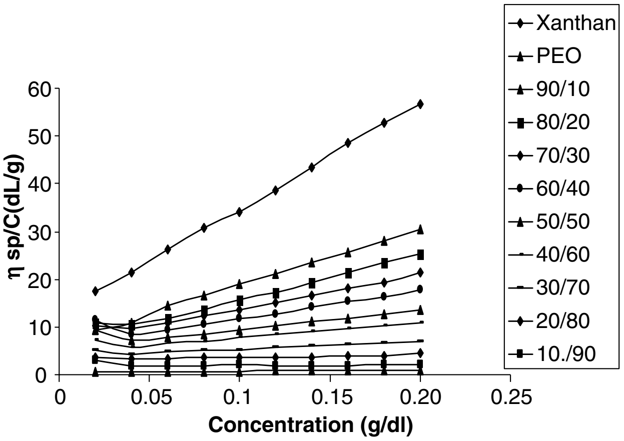

Fig. 3. Huggins plot for 0.2% w/v, Xanthan gum/PEO blend in 0.1 M NaCl at 40 °C.

in weight fraction W_1 and W_2 as

$$\triangle B = \frac{b - \overline{b}}{2W_1W_2} \tag{1}$$

where $\overline{b} = W_1b_{11} + W_2b_{22}$, in which b_{11} and b_{22} are the slopes of the viscosity curves for the components and b is related to Huggins coefficient K_H as

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

for tertiary system, it is also given by

$$b = W_1^2b_{11} + W_2^2b_{22} + 2W_1W_2b_{12} \tag{3}$$

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

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

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

where $[\eta]_1$ and $[\eta]_2$ are the intrinsic viscosities for the pure component solutions. The polymer blend is miscible if $\mu \geqslant 0$ and immiscible when $\mu < 0$. Recently Sun et al. suggested a most satisfactory new equation for the determination of polymer miscibility as

$$\alpha = K_m - \frac{K_1[\eta]_1^2W_1^2 + K_2[\eta]_2^2W_2^2 + 2\sqrt{K_1K_2[\eta]_1[\eta]_2W_1W2}}{\{[\eta]_1W_1 + [\eta]_2W_2^2\}} \tag{5}$$

where K_1, K_2 and K_m are the Huggins constants for individual components 1, 2 and blend, respectively. The polymer blend is miscible if $\alpha \geqslant 0$ and immiscible when $\alpha < 0$. The long-rang hydrodynamic interactions or secondary interactions are considered while deriving the Eq. (5). Hence, it

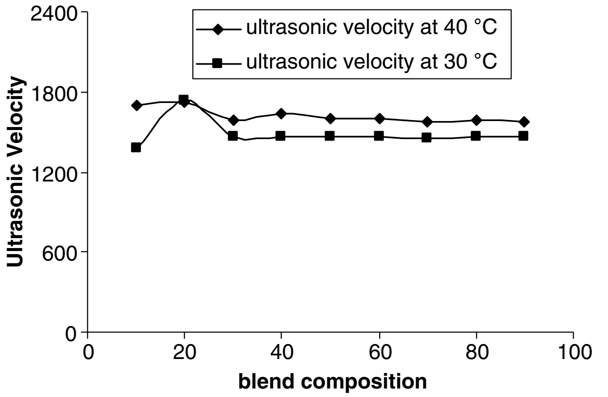

Fig. 4. Variation of ultrasonic velocity with composition of Xanthan gum/PEO in 0.1 M NaCl at 30 and 40 °C.

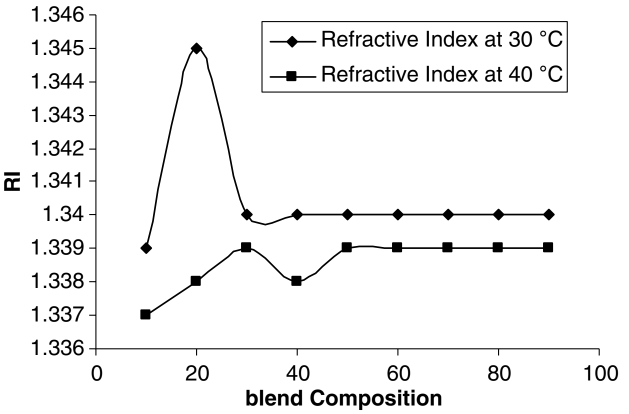

Fig. 5. Variation of refractive index with composition of Xanthan gum/PEO in 0.1 M NaCl at 30 and 40 °C.

Table 1
Refractive index, ultrasonic velocity, μ and α at 30 and 40 °C in 0.1 M NaCl solution for Xanthan gum/PEO blend

Blend Composition	Refractive index		Ultrasonic velocity		μ		α	
	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	1.340	1.339	1463	1580	−15.86	−16.52	+0.01	+0.86
80/20	1.340	1.339	1466	1592	−7.96	−8.33	+0.33	+1.14
70/30	1.340	1.339	1450	1580	−5.35	−5.65	+0.28	+0.85
60/40	1.340	1.339	1466	1596	−4.13	−4.32	+0.24	+0.77
50/50	1.340	1.339	1463	1597	−3.40	−3.57	+0.20	+0.32
40/60	1.340	1.338	1460	1640	−2.88	−3.09	+0.04	+0.44
30/70	1.340	1.339	1466	1591	−2.63	−2.77	−0.10	−0.71
20/80	1.345	1.338	1734	1725	−2.45	−2.55	−0.02	−2.09
10/90	1.339	1.337	1380	1700	−2.35	−2.47	−0.20	−4.64

can be defined as Xanthan gum and PEO blend is miscible when Xanthan gum content is 40% and more at both 30 and 40 °C. From the Figs. 3 and 4, it is clear that the reduced viscosity decreases as the temperature increases, but there is no effect of temperature on miscibility.

In order to confirm the correct nature of the blend under consideration, ultrasonic velocity, refractive index of the Xanthan gum/PEO at various compositions at different temperatures were measure and the values are given in the Table 1. The ultrasonic sound waves offer a useful technique for investigating the miscibility of polymer blend in solution, the variation of ultrasonic velocity versus blend compositions is linear for compatible blends and nonlinear for non-compatible. It has been established that refractive index measurement of blend compositions is a simple and useful technique for prediction of compatibility, the refractive index versus blend composition is linear for compatible and nonlinear for non-compatible. The Figs. 4 and 5 reveals semi-compatible nature of the Xanthan gum/PEO blend (see Fig. 6).

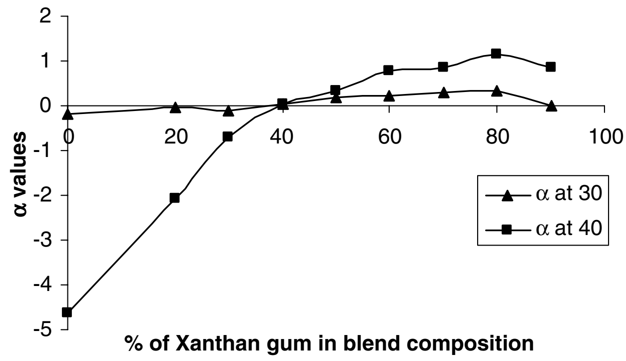

Fig. 6. Variation of α value with Xanthan gum content in blend composition at 30 and 40 °C.

For further confirmation, FT-IR analysis also carried out. Xanthan gum, PEO and different blend compositions in 0.1 M NaCl solution were dried at 60 °C under vacuum and conditioned for 48 h under dessicator. The highly brittle film like flaks were crushed to make powder, and mixed with KBr to make disc for FT-IR analysis. The FT-IR spectra of Xanthan gum, PEO and Xanthan gum/PEO: 80/20, 60/40 and 20/80 presented in the Fig. 7 in the spectrum of PEO, —O—H stretching at 3448 cm^{-1}; —C—H stretching of methylene groups at 2920 cm^{-1}; and —C—H stretching, bending and rocking vibrations at 1472, 1360 and 952 cm^{-1}, respectively; and —C—O bands at 1110 cm^{-1} is observed. In the Xanthan gum spectrum, absorption bands characterizing intermolecular hydrogen bonding due to —OH and —NH is observed at 3466 cm^{-1}; and —C=O, —COOH and —C—H at 1650, 1762 and 2933 cm^{-1}, respectively. In case of blends,

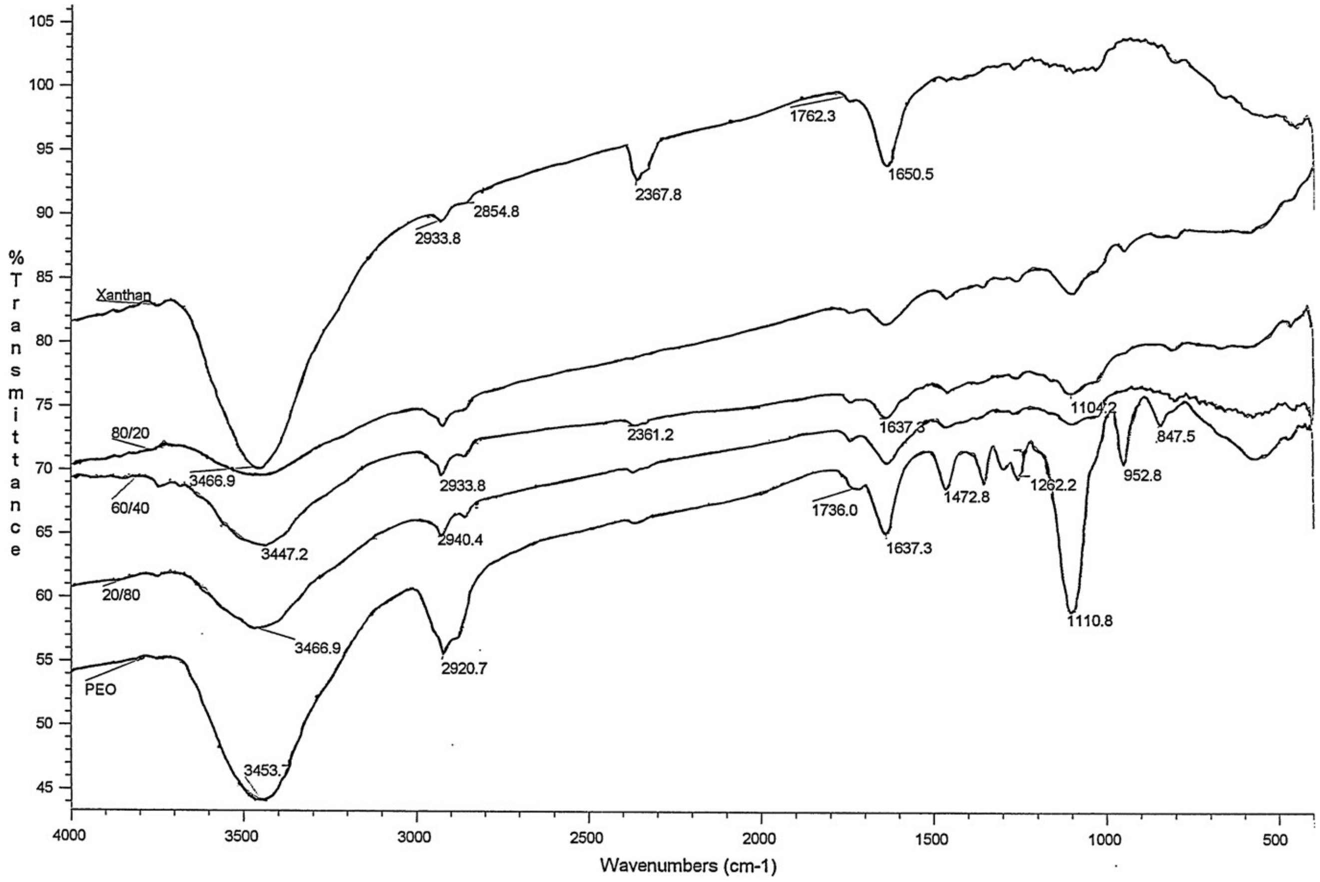

Fig. 7. FT-IR Spectrum of xanthan gum, PEO and Xanthan gum/PEO blends composition (80/20, 60/40, 20/80).

broadening of bands at 3466 and 1645 cm^{-1} can be attributed to inter-molecular H-hydrogen bonding between Xanthan gum and PEO, which favours the miscibility.

4. Conclusion

Based on viscosity, ultrasonic velocity and refractive index methods, the polymer blend of Xanthan gum/PEO is found to be miscible only when the polysaccharide Xanthan gum content is 40% and above and there is no effect of temperature on the miscibility of the blend system. FT-IR spectrum reveals that the possibilities of intermolecular H-bonding between Xanthan gum and PEO. Hence, Xanthan gum/PEO blend in 0.1 M NaCl solution is found to be semi-compatible in nature both at 30 and 40 °C.

References

Chee, K. K. (1990). *European Polymer Journal, 26*, 423.

Haiyang, Y., Pingping, Z., Shiquiang, W., & Qipeng, G. (1998). *European Polymer Journal, 34*, 463.

Kennady, J. F., & Bradshaw, I. J. (1984). Production, properties and applications of Xanthan. *Progress Industrial Microbiology, 19*, 319–371.

Kkang, F. S., & Pettit, D. J. (1993). Xanthan, gellan, welan, and rhamsan. In R. L. whistler & J. N. BeMiller (Eds.), *Indusrial gums. Polysaccharides and their derivatives* (3rd ed., pp. 341–399). San Diego, USA: Academic press.

Margaritis, A., & Zajic, J. E. (1978). *Biotechnology and Bioengineering, 20*, 939–1001.

Olabisi, O., Robenson, L. M., & Sham, M. T. (1979). *Polymer–Polymer Miscibility*. New York: Academic.

Paladhi, R., & Singh, R. P. (1994a). *Journal of Applied Polymer Science, 51*, 1559.

Paladhi, R., & Singh, R. P. (1994b). *European Polymer Journal, 30*, 251.

Peters, H.-U., Suh, I. S., Schumpe, A., & Deckwer, W. D. (1993). *Biotechnology Letter, 15*, 565–566.

Raviprakash, S. D., & Rai, S. K. (2004). *International Journal of Plastics Technology, 8*, 334.

Rinado, M., & Milas, M. (1978). *Biopolymer, 17*, 2663–2678.

Sun, Z., wang, w., & Fung, Z. (1992). *European Polymer Journal, 28*, 1259.

Tako, M., & Nakumara, S. (1984). Rheological properties of deacetylated Xanthan in aqueous media. *Agricultural Biochemistry, 48*, 2987–2993.

VaradaRajalu, A., & Lakshminarayana Reddy, R. (2000). *Journal of International Polymer Materials, 47*, 469.

VaradaRajalu, A., Lakshminarayana Reddy, R., & Siddaramaiah (1998). *Journal of Applied Polymer Science, 70*, 1823.

Varnell, D. F., & Coleman, M. M. (1981). *Polymer, 22*, 1324.

Varnell, D. F., Runt, J. P., & Coleman, M. M. (1983). *Polymer, 24*, 37.

Woo, E. M., Barlow, J. M., & Paul, D. R. (1986). *Journal of Applied Polymer Science, 32*, 3889.