Miscibility of Blends of *Aeromonas* Gum or *Erwinia* Gum with Other Polysaccharides

GUANG YANG,[1] LINA ZHANG,[1] WENFAN FENG,[1] HIDEKI IIJIMA,[2] HIROMICHI TSUCHIYA[3]

[1] Department of Chemistry, Wuhan University, Wuhan 430072, China

[2] Chemicals Technology Department IV, Asahi Chemical Industry Co., Ltd., Miyazaki 882-0847, Japan

[3] Fourth Specialty Chemical Department, Asahi Chemical Industry Co., Ltd., Tokyo 100-8840, Japan

ABSTRACT: *Aeromonas* (A) gum and *Erwinia* (E) gum are acidic heteropolysaccharides, which exist in water as expanded chains caused by the electrostatic repulsion between the charged groups. A modified approach, which was suggested to estimate miscibility of stiff polymer in our previous study, was used to determine miscibility parameter μ for blends between A gum or E gum with other polysaccharides, by using viscometry in aqueous 0.1M NaCl solution. When weight ratios of E gum/pectin were in the range of $3 : 7 \sim 7 : 3$, the blends in aqueous solution are miscible. The blends of A gum/xanthan, A gum/pectin, and E gum/xanthan in aqueous solution are obviously immiscible. When the weight fraction (w_2) of A gum or E gum in the mixture solution is 0.7, the μ predicts that the miscibility of blend films was on the order of E gum/pectin > E gum/xanthan > A gum/pectin > A gum/xanthan. These results are in good agreement with those observed by scanning electron microscopy and Fourier transform IR. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 73: 1387–1395, 1999

Key words: miscibility; viscometry; *Aeromonas* gum; *Erwinia* gum; scanning electron microscopy; IR

INTRODUCTION

Polysaccharides have been widely used as thickening and gelling agents for many applications in the food, cosmetics, and building products industries. Synergistic effects for polysaccharides blends are of commercial interest because they offer the prospect of generating novel functionality, or of producing given rheological or textural characteristics using reduced levels of polysaccharides, and possibly reduced cost. Much effort has been devoted to the study of polysaccharide blends and the factors that have an effect on their miscibility.[1]

Aeromonas (A) gum and *Erwinia* (E) gum are the extracellular polysaccharides produced by strains of *Aeromonas nichidenii* 5797 and *Erwinia mituyensis* 5796,[2] respectively. A gum is composed of xylose, mannose, galactose, glucose, and mannuronic acid, and E gum contains fucose, galatose, glucose and glucuronic acid.[3,4] The various extracellular polysaccharides produced from *Aeromonas solmvnicida* and *Erwinia chrysanthemi* have been reported[5,6]; however, studies relating to miscibility are rarely published. It is well known that xanthan and pectin are normally used as additives for foods and cosmetics. Xan-

Figure 1 Huggins and Kraemer plots of *Aeromonas* gum in water (○) and in 0.1*M* (●), 0.2*M* (■) and 0.5*M* (▲) NaCl aqueous solution at 25°C.

vents. Recently, a modified approach based on Chee's method was suggested to determine blend miscibility of stiff polymer/stiff polymer,[10] and was proved to be reliable by other results from blend films in our laboratory.[11]

In this paper, the miscibility of blends of A gum and E gum with xanthan and pectin was studied by an improved viscosity method. The miscibility and interaction of the blends were measured by SEM and IR.

(a)

(b)

Figure 2 Huggins and Kraemer plots of xanthan gum (a) and pectin (b) in water (■) and 0.1*M* NaCl aqueous solution (●) at 25°C.

than, produced extracellularly by the plant pathogen *Xanthomonas campestris,* is a water-soluble ionic polysaccharide, whose dilute solution has exceedingly high viscosity and is an industrially important. Its main chain consists of $(1 \rightarrow 4)$-β-D-glucose residues, and each cellobiose unit carries a trisaccharide side with carboxyl groups. Xanthan dissolves in 0.1*M* aqueous NaCl as a double-helical dimer.[7] Pectin is a natural polysaccharide from various sources such as fruit and vegetable. Its chemical structure is a $(1 \rightarrow 4)$-α-D-galacturonic acid, including polygalactose and polyarabnose.

Miscibility is an important parameter governing morphologies and properties of multicomponent polymers. It can be detected by differential scanning calorimetry, dynamic mechanical analysis, neutron scattering, and scanning electron microscopy (SEM), etc. Chee[8] proposed that a simple and inexpensive method based on dilute-solution viscometry could be used to study the miscibility of polymer blends. Moreover, Danait[9] has reported a novel method based on the intrinsic viscosity of polymers in pure and "mixed" sol-

and washed with isopropanol, then dried at reduced pressure. The amount of 0.4 wt % aqueous solution of the E gum was prepared, and centrifuged at 10,000 rpm to remove the water-insoluble gum. Acetone as a precipitant was used for preparation and purification under the same process. The samples of xanthan and pectin were provided by Wuhan Food Resource Co. (importation from Japan), which were not further purified. The apparent weight average molecular weights of A gum and E gum in $0.5M$ NaCl aqueous solution were measured by light scattering to be 7.9×10^6 due to the aggregate[4] and 7.83×10^5, respectively.

(a)

(b)

Figure 3 Huggins and Kraemer plots of *Aeromonas* gum/xanthan (a) and *Aeromonas* gum/pectin (b) in $0.1M$ NaCl aqueous solution at 25°C. (■) $w_2 = 0.2$; (●) $w_2 = 0.3$; (▲) $w_2 = 0.5$; (○) $w_2 = 0.7$; and (□) $w_2 = 0.8$.

EXPERIMENTAL

Materials

A gum and E gum were provided by Fourth Specialty Chemicals Department, Asahi Chemical Industry Co., Ltd. The A gum was dissolved in water to a polymer concentration of 0.56 wt %, then centrifuged at 10,000 rpm to remove the water-insoluble gum. To prepare the samples, isopropanol as a precipitant was added at room temperature until no new precipitate took place, and the precipitated product was obtained by filtration

(a)

(b)

Figure 4 Huggins and Kraemer plots of *Erwinia* gum/xanthan (a) and *Erwinia* gum/pectin (b) in $0.1M$ NaCl aqueous solution at 25°C. (■) $w_2 = 0.2$, (●) $w_2 = 0.3$, (▲) $w_2 = 0.5$, (○) $w_2 = 0.7$, and (□) $w_2 = 0.8$.

Table I   The $[\eta]$, b, and Miscibility Parameter μ of Blend Systems for *Aeromonas* Gum and *Erwinia* Gum with Other Polysaccharides

w_2/w_3	10 : 0	8 : 2	7 : 3	5 : 5	3 : 7	2 : 8	0 : 10
A gum/xanthan							
$[\eta] \times 10^{-2}$	9.16	9.92	11.05	12.20	12.98	13.60	14.8
$b \times 10^{-5}$	3.20	3.40	3.75	4.45	5.15	5.50	6.20
μ		-0.38	-0.32	-0.23	-0.059	-0.058	
A gum/pectin							
$[\eta] \times 10^{-2}$	9.16	7.28	6.80	5.38	4.83	4.17	3.06
$b \times 10^{-5}$	3.20	2.20	1.75	1.07	0.86	0.68	0.15
μ		-0.038	-0.15	-0.14	-0.11	-0.023	
E gum/xanthan							
$[\eta] \times 10^{-2}$	3.015	5.40	6.65	8.78	11.66	13.18	14.80
$b \times 10^{-5}$	0.299	1.10	1.90	3.10	4.90	6.20	6.20
μ		-0.088	-0.037	-0.012	-0.05	-0.25	
E gum/pectin							
$[\eta] \times 10^{-2}$	3.015	3.080	3.048	2.900	2.691	3.005	3.064
$b \times 10^{-5}$	0.299	0.154	0.353	0.306	0.263	0.393	0.15
μ		-253.1	46.16	90.85	42.25	-538.9	

Characterization of Miscibility

Based on Chee's method,[8] a modified approach has been suggested to determine miscibility parameter μ of stiff polymer/stiff polymer by viscometry in aqueous solution as follows[10]:

$$\mu = \frac{(b - b_{22})/([\eta] - [\eta]_2) - (b_{33} - b_{22})/([\eta]_3 - [\eta]_2)}{2([\eta]_3 - [\eta])} \tag{1}$$

Here, $[\eta]_2$, $[\eta]_3$, and $[\eta]$ represent the intrinsic viscosity of polymer 2, polymer 3, and the mixture of the two polymers 2 and 3, respectively, and are estimated from Huggins and Kraemer plots. The coefficients b, b_{22}, and b_{33} are obtained from plots of $[(\eta_{sp}/c) - [\eta]]/c$ vs c for the mixture of two polymers, polymer 2 and polymer 3, respectively, which are based on the following equation:

$$\frac{\eta_{sp}/c - [\eta]}{c} = b + Ac \tag{2}$$

The miscibility parameter μ can predict miscible and immiscible blends. When μ is more than zero, the blend of two polymers is miscible. The $\mu - w_2$ (weight fraction of polymer 2) relation was used as prediction of blend miscibility for various ratios of polymer 2/polymer 3.

Viscosity Measurements

Viscosity of the polysaccharide solutions was measured using a Ubbelodhe capillary viscometer at $25 \pm 0.1°C$. Water, $0.1M$ NaCl, $0.2M$ NaCl, and $0.5M$ NaCl aqueous solutions were used as solvents. Huggins and Kraemer plots were used to estimate the intrinsic viscosity $[\eta]$ of the polysaccharides. The kinetic energy was negligible.

A gum, E gum, xanthan, and pectin were dissolved in $0.1M$ NaCl aqueous solution, respectively, to prepare a polymer concentration of 0.1 wt %. A series of mixture solutions of A gum/xanthan, A gum/pectin, E gum/xanthan, and E gum/pectin, with various ratios (8 : 2, 7 : 3, 5 : 5, 3 : 7, and 2 : 8 by weight), were prepared.

Characterization of Blends

The mixture solutions of 0.5 ∼ 1 wt % polymer concentration were cast on the sample plate of the SEM, then dried at room temperature. The surface was coated with gold and observed by Hitachi S-570 SEM. IR spectra of the samples were recorded with a Nicolet FT-IR Spectrometer.

(a)

(b)

Figure 5 Plots of $\{(\eta_{sp}/c) - [\eta]\}/c$ vs c of *Aeromonas* gum/xanthan (a) and *Erwinia* gum/xanthan (b). (■) w_2 = 0.2, (●) w_2 = 0.3, (▲) w_2 = 0.5, (○) w_2 = 0.7, and (□) w_2 = 0.8.

RESULTS AND DISCUSSION

Viscosity Behavior

Figure 1 shows Huggins and Kraemer plots of A gum in water and 0.1, 0.2, and 0.5M NaCl aqueous solution at 25°C. The $[\eta]$ of the A gum in water exhibited an excessive value, and decreased sharply with increase of the salt concentration. Figure 2 shows Huggins and Kraemer plots of xanthan and pectin in water and 0.1M NaCl aqueous solution at 25°C. These polysaccharides in water revealed unusual behavior caused by the electrostatic repulsion between charged groups,

but normal solution behavior was observed in 0.1M NaCl aqueous solution. It is suggested that the electrostatic repulsion effects were inhibited. Figures 3 and 4 show Huggins and Kraemer plots of mixture solutions for A gum with xanthan and pectin, and for E gum with xanthan and pectin, respectively. The $[\eta]$ values obtained from extrapolation of the curves of η_{sp}/c vs c and ln η_r/c vs c plots are listed in Table I. By changing the weight fraction (w_2) of A gum or E gum in the mixture solutions, the plots of $\{(\eta_{sp}/c) - [\eta]\}/c$ vs c of the mixture solution for A gum/xanthan and E gum/ xanthan were obtained and are shown in Figure 5. By extrapolating these lines to the intercept,

(a)

(b)

Figure 6 Dependence of μ on w_2 in the blend system of *Aeromonas* gum (a) and *Erwinia* gum (b) at 25°C.

Aeromonas gum /xanthan(7:3)   Aeromonas gum /xanthan(3:7)

Aeromonas gum / pectin (7:3)   Aeromonas gum / pectin (3:7)

Figure 7   SEM of blends of *Aeromonas* gum with xanthan and pectin.

the b values were obtained. For the others (A gum/pectin and E gum/pectin), the b values were directly obtained from the slope of these straight lines of η_{sp}/c vs c. The μ was calculated from eq. (1), and the values of b and μ are summarized in Table I.

Miscibility

The plots of μ vs w_2 are shown in Figure 6. The empirical $\mu - w_2$ relation indicate that the blends of E gum/pectin ($0.3 < w_2 < 0.7$) are miscible. Figure 7 and 8 show SEM of blend films of A gum and E gum with xanthan and pectin, respectively. The blend films of E gum/pectin ($w_2 = 0.7$) display smooth surfaces, which is a result of blend homogeneity. In contrast, the blend films of A gum/xanthan ($w_2 = 0.3$ or 0.7), A gum/pectin ($w_2 = 0.3$ or 0.7), E gum/xanthan ($w_2 = 0.2$ or

0.7), and E gum/pectin ($w_2 = 0.2$) all appear to have surfaces of globules or particles, suggesting phase separation in the blend. These results agree basically with those predicted by viscometry. When w_2 of A gum or E gum is 0.7, the μ values predict that the miscibilities of blend films were on order of E gum/pectin > E gum/xanthan > A gum/pectin > A gum/xanthan.

Miscibility is closely related with intercomponent specific interactions, such as ion–ion or ion–dipole interactions and hydrogen bonding. Fourier transform IR (FTIR) is an effective method to identify hydrogen bonding between compositions. IR spectra of the films for A gum, A gum/xanthan (7 : 3), xanthan, A gum/pectin (7 : 3), pectin, E gum, E gum/xanthan (7 : 3), and E gum/pectin (7 : 3) are shown in Figure 9. For A gum, pectin, and their blend films, the bands at $1724 \sim 1752$ cm^{-1} are

Erwinia gum /xanthan(7:3)

Erwinia gum /xanthan(2:8)

Erwinia gum /pectin(7:3)

Erwinia gum /pectin(2:8)

Figure 8   SEM of blends of *Erwinia* gum with xanthan and pectin.

assigned to carbonyl stretching vibration of A gum and pectin. The bands at $1604 \sim 1625$ cm^{-1} are attributed to —COO$^-$. Except for E gum/pectin, the blend films [Fig. 9(b, d, g)] show the bands of the pure components, indicating there are no special interactions between A gum/xanthan, A gum/pectin, and E gum/xanthan, leading to immiscibility for these blends. In addition, the immiscibility of A gum with pectin may be correlated with its higher molecular weight than E gum. The blends of xanthan with either A gum or E gum were immiscible. This can be explained by the strong intermolecular hydrogen bonds existing in xanthan, which sustain the double-strand chains of xanthan in aqueous solution, resulting in a reduction of the intermolecular interaction of xanthan with other polysaccharides.

Figure 10 shows the FTIR spectra of E gum/pectin blend when changing the ratios of E gum and pectin to 10 : 0, 7 : 3, 5 : 5, 3 : 7, 2 : 8, and 0 : 10. The carbonyl stretching vibration of pectin is at 1752 cm^{-1}; however, the band of the blends of pectin with E gum shifts to low wavenumber and this tendency becomes more pronounced with an increase of the content of E gum. Moreover, the intensity of the band at 1604 cm^{-1} for E gum/pectin (7 : 3) was significantly larger than for the mixture from powder of E gum and pectin (7 : 3) by a mechanical method (Fig. 10 "mix"). The shifts of C=O stretching vibration to lower frequency are widely considered to be the "acid test" of the formation of hydrogen bonds,[12] implying an intermolecular interaction between the carbonyl groups of pectin and the hydroxyl groups of E gum. Therefore, the experimental results proved that the strong intermolecular interaction between E gum and pectin formed when the content of E gum was in the range of $0.3 \sim 0.7$,

resulting in good miscibility for E gum/pectin (7 : 3) in aqueous solution.

CONCLUSIONS

Aeromonas gum and *Erwinia* gum exhibited unusual viscosity behavior in water, owing to chain expanding caused by the electrostatic repulsion, and their plots of η_{sp}/c vs c in $0.1M$ NaCl aqueous solution displayed curves rather than straight lines. A modified approach to determine stiff polymer/stiff polymer miscibility by viscometry in

Figure 9   FTIR spectra of blends: (a) *Aeromonas* gum; (b) *Aeromonas* gum/xanthan (7 : 3); (c) xanthan; (d) *Aeromonas* gum/pectin (7 : 3); (e) pectin, (f) *Erwinia* gum; (g) *Erwinia* gum/xanthan (7 : 3); (h) *Erwinia* gum/pectin (7 : 3).

Figure 10   FTIR spectra of *Erwinia* gum/pectin. "7 : 3 (Mix)" means mixture from powder of *Erwinia* gum and pectin (7 : 3) by mechanical method.

aqueous solution was satisfactorily used to predict miscible and immiscible blends of the *Aeromonas* gum and *Erwinia* gum with other polysaccharides, and the predicted results are in good agreement with those by SEM and FTIR. When the weight content of *Erwinia* gum for *Erwinia* gum/pectin were in the range of $0.3 \sim 0.7$, the miscibility parameter μ obtained by viscometry was more than zero, indicating that the blends were miscible. The E gum/pectin (7 : 3) blend had stronger interaction caused by the hydrogen bonds than other blends. The μ values predicted that the blends of *Aeromonas* gum with xanthan, pectin, and *Erwinia* gum with xanthan are immiscible.

REFERENCES

1. David, D. J. Adv Polym Technol 1996, 15, 315.
2. Tanaka, S. Jpn Kokai Tokyo Koho 1989, 89-13360, 8.
3. Tanaka, S.; et al. Jpn Kokai Tokyo Koho 1989, 89-206971, 3.
4. Zhang, L.; Xu, X.; Jiang, G.; et al. Polym J 1999, 31, 150.
5. Gray, J. S. S.; Koermer, T. A. W.; et al. Carbohydr Res 1995, 226, 153.
6. Ramon, B.; Dolores, S. D. M.; et al. Appl Environ Microbiol 1993, 59, 2437.
7. Zhang, L.; Liu, W.; Norisuye, T.; Fujita, H. Biopolymers 1987, 26, 333.
8. Chee, K. K. Eur Polym J 1990, 26, 423.
9. Danait, A.; Deshpaned, D. D. Eur Polym J 1995, 31, 1121.
10. Zhang, L.; Zhou, D.; Cheng, S. Eur Polym J 1998, 34, 381.
11. Zhang, L.; Zhou, D.; Wang, H.; Cheng, S. J Membrane Sci 1997, 124, 195.
12. Sun, Y.; Shao, Z.; Hu, P.; Yu, T. J Polym Sci B Polym Phys 1997, 35, 1405.