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Complexation and blending of starch, poly(acrylic acid), and poly(*N*-vinyl pyrrolidone)

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Abstract

Starch is often modified to improve its end-use properties. In this work, we sought to improve the properties of starch through non-covalent means, viz., the blending of starch with poly(acrylic acid), poly(*N*-vinyl pyrrolidone), and poly(*N*-vinyl pyrrolidone)-iodine. An emphasis was placed on the rheological and gel forming properties. Starch was found to form a synergistic mixture with poly(acrylic acid). It has no effect on poly(vinyl pyrrolidone) but produces a gel with poly(vinyl pyrrolidone)-iodine. The addition of a small amount of a third polymer caused either increased viscosity (at low addition levels) or gel formation (at higher levels). Through gel formation, a large quantity of starch can be incorporated in the interpolymer complex. These observations are rationalized on the basis of specific interactions among the polymers. Several specific compositions of these blends may find applications as thickeners and encapsulating agents.

Keywords: Starch; Poly(acrylic acid); Poly(*N*-vinyl pyrrolidone); Poly(*N*-vinyl pyrrolidone)-iodine; Viscosity; Complexation and blending

1. Introduction

Starch is a well-known, versatile, and inexpensive agricultural material used for a variety of industrial applications. In addition to being a major food item, it is currently used industrially as coatings and sizing in paper, textiles and carpets, as binders and adhesives, as absorbants, and as encapsulants (Stephen, 1995; Whistler & BeMiller, 1993). Often it is modified to improve its end-use properties, e.g., oxidation, hydrolysis, and substitution with an ether, an ester or a quaternary amine (Whistler & BeMiller, 1993). In our desire to seek further applications that will add value to starch, we look at novel blends of starch with other commercial polymers. Two polymers known for the formation of interpolymer complexes are poly(acrylic acid) (PAA) and poly(*N*-vinyl pyrrolidone) (PVP) (Elgingy & Elegakey, 1981; Gupta, Garg, & Khar, 1994; Kaczmarek, Szalla, & Kaminska, 2001; Lau & Mi, 2002; Maunu, Kinnunen, Soljamo, & Sundholm, 1993; Takayama & Nagai, 1987; Tan, Peh, & Al-Hanbali, 2000, 2001). It is of interest to study the mixtures of these water-soluble polymers, observe their interactions (or lack thereof), and monitor their rheological and gel forming properties.

In addition, poly(*N*-vinyl pyrrolidone)-iodine (PVPI) is frequently used for its anti-microbial properties (Barabas, 1989; Digenis & Ansell, 1983). Iodine is known to associate not only with PVP, but also with starch (Lauterbach & Ober, 1995; Morawetz, 1975). It is informative to include the PVPI in this study to observe the added effect of iodine.

2. Experimental

2.1. Samples

Two unmodified starches were used in this work: "Textra® Plus" (Starch 1), and "Mira-sperse 623" (Starch 2),

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from National Starch and Chemical Company, Bridgewater, NJ, and A.E. Staley, Decatur, IL, respectively. All vinyl polymers came from Sigma–Aldrich Company. PVP has an average molecular weight of 55,000, and PAA has an average molecular weight of 450,000. PVP-I has an estimated molecular weight of 40,000; the monomer:iodine molar ratio is 10:1.

2.2. Rheology

Brookfield viscosity was measured on a Brookfield programmable rheometer, Model DV-III, equipped with the UL adapter 304 s/s and using a YULA-15 spindle. The polymer solutions were placed in a cylindrical cell, and the shear rate was progressively increased while the viscosity reading was taken. Each Brookfield viscosity was taken in triplicate, and the average value was reported. The reproducibility in each measurement was about 5%.

2.3. Fourier transform infrared (FTIR)

A model system consisting of soluble starch (Textra Plus), PVP, and PAA was prepared and tested by FTIR spectrometry. Calibration samples were prepared by mixing soluble starch, PVP and PAA in distilled water at 5% concentration and held at 30 °C for 4 h to allow the polymers to precipitate and interact completely. The precipitates formed immediately as white gels that were then freeze-dried and pulverized under liquid nitrogen (−196 °C) to give a fine powder that was used to obtain the test spectra. Pure soluble starch, pure PVP and pure PAA dispersions were each freeze dried and pulverized separately as above to prepare standard spectra as the sum of the three pure polymer spectra. A semi-quantitative chemometric technique, based on iterative combination of the pure polymer spectra, was used to estimate the concentrations of starch, PVP and PAA in the precipitated gels. Estimates were substantiated by comparison with spectra of precipitated gels having known concentrations of the polymers.

Samples of the test starch/PVP/PAA gels and the pure polymers were pulverized with KBr and pressed into transparent disks for analysis by FTIR spectrometry. A test sample (100 mg) was pulverized at liquid nitrogen temperature in a sealed stainless steel vial containing a stainless steel ball bearing for 15 s on a Wig-L-Bug amalgamator (Crescent Dental Manufacturing, Lyons, IL). KBr (100 mg) was added to the vial and the sample was hand mixed for 15 s. From this 200 mg mixture 50 mg was removed and pulverized as above in another stainless steel vial under liquid nitrogen for 10 s. The vial was allowed to warm to room temperature before KBr (450 mg) was added. The KBr/sample mixture was shaken in the same vial without the ball bearing on the amalgamator at room temperature for 10 s. From this 500 mg mixture 50 mg was removed and shaken at room temperature in another stainless steel vial without a ball bearing for 10 s. The vial was again allowed to warm to room temperature before 300 mg of the 1000 mg KBr/sample mixture was transferred to a KBr die (Perkin-Elmer Corp., Norwalk, CT) and pressed under vacuum at 110 MPa on a laboratory press (Fred S. Carver, Menominee Falls, WI).

FTIR spectra were measured on an FTS 6000 spectrometer (Digilab, Cambridge, CT) equipped with a DTGS detector. The absorbance spectrum (4000–400 cm^{-1}) for each sample was acquired at 4 cm^{-1} resolution and signal-averaged over 32 scans. Interferograms were Fourier transformed using triangular apodization for optimum linear response. Spectra were baseline corrected and scaled to adjust for small differences in sample weights.

2.4. NMR

The NMR spectra were obtained on a Bruker AMX400 spectrometer, operating at 100.625 MHz for 13C, 2H lock (on D_2O), with a delay time of 7–10 s between pulses. T_1 measurements were achieved with a standard inversion recovery experiment (Hornak, 2005; Sanders & Hunter, 1993).

3. Results and discussion

The rheological behavior of starch in aqueous solutions is well known (Carriere, 1998; Kar & Misra, 1996; Whistler, BeMiller, & Paschall, 1984). As a baseline for our studies, we first obtained the Brookfield viscosity of a 5% starch solution (Table 1). The data gave the typical shear-thinning behavior of starch, ranging from 140 cps at low shear rate to about 70 cps at higher frequencies. Because the viscosity of a starch solution tended to decrease with time, a fresh solution was made prior to each measurement in this work.

3.1. Two-component blends

We first took the polymers two at a time and mixed the two solutions. The viscosity results for starch and PAA mixtures are summarized in Table 2. The data reflected the results of two starch samples in two concentrations. In both cases, a mildly synergistic interaction occurred between starch and PAA such that the Brookfield viscosity exhibited a maximum at a specific starch:PAA ratio. For Starch 1 at 5% solution, the maximum occurred at about

Table 1
Dependence of Brookfield viscosity (BV) of starch solution on shear rate

Shear rate (Hz)	BV (fresh)[a]	BV (aged)[b]
0.7	–	140
1.8	120	86
3.7	102	79
7.3	91	70

[a] 5% solution of starch 1, freshly prepared.

[b] 5% solution of starch 1, after 2 days.