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

Atanu Biswas [a,*], J.L. Willet [a], Sherald H. Gordon [a], V.L. Finkenstadt [a], H.N. Cheng [b,*]

[a] *Plant Polymer Research Unit, National Center for Agricultural Utilization Research, USDA, Agricultural Research Services, 1815 N. University Street, Peoria, IL 61604, USA*
[b] *Hercules Incorporated Research Center, 500 Hercules Road, Wilmington, DE 19808-1599, USA*

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.
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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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* Corresponding authors.
  E-mail addresses: biswasa@ncaur.usda.gov (A. Biswas), hcheng@herc.com (H.N. Cheng).

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$_2$O), 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.

Table 2
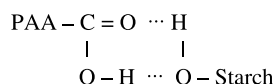Brookfield viscosity (BV) of starch:PAA solution blends

Starch (wt%)	PAA (wt%)	BV	
		Starch 2[a]	Starch 1[b]
100	0	3.5	86
80	20	10.0	200
60	40	9.6	230
40	60	9.4	184
20	80	9.0	144
0	100	8.5	90

[a] BV done on 2% solutions at room temperature at a shear rate of 85 Hz.
[b] BV done on 5% solutions at room temperature at a shear rate of 0.37 Hz.

60:40 weight ratio. For Starch 2 at 2% solution, the maximum was closer to 80:20 weight ratio.

The appearance of this maximum is intriguing. Perhaps fortuitously, it occurs at approximately 50:50 molar ratio of glucose and acylic acid residues, and the result suggests a possible 1:1 specific interaction, on the average, between the relevant functional groups of the two polymers. One possibility is illustrated below. The broad maxima observed in Table 2 suggest the lack of a ladder-like structure; indeed, the interaction is more likely to be scrambled in view of the highly branched nature of starch.

$$PAA - C = O \cdots H$$
$$| \qquad |$$
$$O - H \cdots O - Starch$$

A different picture was found when starch and PVP were added together in solution. In this case, no specific interaction was observed. The Brookfield viscosities for PVP and two starch samples (in two concentrations) are shown in Table 3. In both cases, the viscosity decreased monotonically as the composition changed.

Yet another situation was encountered when 5% PVP and PAA solutions were added together. In this case, an insoluble gel was found. Indeed PAA and PVP are known to form an interpolymer complex, due to very strong hydrogen bonds between the carbonyl groups of PVP and the hydroxyl groups of PAA (Elgingy & Elegakey,

Table 3
Brookfield viscosity of starch:PVP solution blends

Starch (wt%)	PVP (wt%)	BV	
		Starch 2[a]	Starch 1[b]
100	0	3.5	69
80	20	2.8	45
60	40	2.1	26
40	60	1.8	13
20	80	1.6	6
0	100	1.4	4

[a] BV done on 2% solutions at room temperature at a shear rate of 85 Hz.
[b] BV done on 5% solutions at room temperature at a shear rate of around 8 Hz.

1981; Gupta et al., 1994; Kaczmarek et al., 2001; Lau & Mi, 2002; Maunu et al., 1993; Takayama & Nagai, 1987; Tan et al., 2000, Tan, Peh, & Al-Hanbali, 2001).

3.2. Three-component blends

In view of the two-component results given above, two particular modes of blend formation might be of interest. First, we started with a 5% solution of starch:PVP blend (in a weight ratio of 80:20, although other ratios could also be used), and added a small amount of PAA. Even at 0.1% PAA, gel particles were found corresponding to the formation of an interpolymer complex involving these three polymers. Interestingly, at 1% concentration of starch:PVP blend, no gel was observed with the addition of PAA. Since many drug and organic dye molecules are known to complex with PVP (Barabas, 1989; Digenis & Ansell, 1983), this complex formation may find application in the encapsulation of drugs or dyes. Similarly, PVP is known to interact with proteins (Matsudo, Ogawa, & Kokufuta, 2003; Sionkowska, 2003), and this may be a novel way to form a starch/protein complex.

A second possibility of blend formation was to start with a 5% solution of starch and PAA at 60:40 weight ratio. As PVP was added (at 0.1–1.0%), we observed the appearance of gel particles, and the amount of gel increased as more PVP was added. This situation would be particularly useful for the encapsulation of molecules carrying cationic charges, which might be retained by PAA through coulombic interactions.

Quantitative information on the gel formation is given in Table 4. Samples 1–3 refer to the starch:PVP (80:20) blend where PAA is added at three increments (0.04, 0.20, 0.40 g). Likewise, Samples 4–6 refer to the starch:-PAA with three incremental additions of PVP. The gel formed in each case was washed with DI water in a test tube until the supernatant became clear. The gel was then dried and its weight obtained. As indicated in Table 4, the weight of the dry gel increases as the third polymer (PAA or PVP) is added. The second series (Samples 4–6) give more gel because more PAA (0.80 g) is present. Note that the solid content of the gel (Table 4, last column) is higher in the second series, suggesting that the gels in Samples 4–6 are denser and tighter in structure.

A detailed study was carried out by FTIR of the composition of the gels (Table 5). The analysis revealed the insoluble gels consisted of soluble starch entrapped in the interpolymer complex of PVP and PAA. Soluble starch appeared from the FTIR spectra to be physically entrapped in the gel matrix and not significantly hydrogen bonded as the precipitated PVP:PAA complex. As indicated above, the total amount of PVP:PAA complex formation varied with the amount of PVP and PAA added to the reaction mixture. Hence, the amount of the interpolymer complex, as well as the entrapped starch, also varied in the separated gel. Note that the data in Table 5 all indicate a PVP:PAA weight ratio of approximately 1.0:1.25. This corresponds to

Table 4

Gravimetric data on two modes of gel formation: the addition of PAA to 5% solution blends of starch:PVP (80:20), and the addition of PVP to 5% solution blends of starch:PAA (60:40)

Sample number	Total wt (g) dry polymer[a]	3rd polymer added (g)	Liquid wt (g, obsd)	Gel wt (g, by diff.)	Dried gel wt (g, obsd)	Gel, solid content (%)
80:20 starch:PVP blend; 3rd polymer = PAA						
17263-50-1	2.0[b]	0.04	35.2	4.8	0.08	1.6
17263-50-2	2.0[b]	0.20	33.4	6.8	0.13	1.9
17263-50-3	2.0[b]	0.40	31.5	8.9	0.26	2.9
60:40 starch:PAA blend; 3rd polymer = PVP						
17263-50-4	2.0[c]	0.04	36.9	3.1	0.05	1.6
17263-50-5	2.0[c]	0.20	33.7	6.5	0.31	4.8
17263-50-6	2.0[c]	0.40	27.7	12.7	0.70	5.5

[a] Each blend was dissolved in 40 g water (5% solution).
[b] This contains 1.60 g starch and 0.40 g PVP.
[c] This contains 1.20 g starch and 0.80 g PAA.

Table 5

Composition[a] of gel obtained by FTIR

Sample no.	Polymers added (wt%)			Gel composition (wt%)		
	Starch	PVP	PAA	Starch	PVP	PAA
17263-50-1	78.4	19.6	2.0	22.0	37.0	41.0
17263-50-2	72.7	18.2	9.1	28.6	31.4	40.0
17263-50-3	66.6	16.7	16.7	34.0	29.0	37.0
17263-50-4	59.0	2.0	39.0	9.7	38.7	53.3
17263-50-5	54.5	9.1	36.4	6.7	40.0	53.3
17263-50-6	50.0	16.7	33.3	12.5	37.5	50.0

[a] Estimated by iterative combination of the pure polymer spectra.

an approximate VP:AA molar ratio of 1:2. It is of interest that when PAA is added to PVP (Sample 1–3), we obtained a looser gel (from gravimetric data) and also entrapped more starch (up to 34% by weight). However, when PVP is added to PAA and with PAA in excess (Samples 4–6), we observed a tighter gel, with less starch incorporated. Since a looser gel can better accommodate the entrapped starch, the above findings are not unexpected.

FTIR spectra of pure starch, pure PVP, and pure PAA are shown overlaid in Fig. 1. The strong absorption peaks at 1681 and 1713 cm^{-1}, due to carbonyl groups in PVP and PAA respectively, are separated by only 32 cm^{-1}. Because of the great heights of the two peaks this difference is not large enough to produce two discernible peaks when the pure polymers are measured in the infrared beam simultaneously. This is shown in Fig. 2 where an average of the two carbonyl absorptions from PVP and PAA with soluble starch, mixed cryogenically to prevent intermolecular interaction, appears as a single skewed peak at 1685 cm^{-1}.

The FTIR spectra of the dried gels from the starch/PVP/PAA solution mixtures were found to be markedly different from those of the cryogenic mixtures of the pure polymers. As seen in Fig. 3, the carbonyl peak of the precipitate is split into a doublet with the PAA absorption shifted higher to 1730 cm^{-1} and the PVP absorption shifted lower to 1637 cm^{-1}. This difference in the FTIR spectrum of the precipitate indicates the PVP:PAA complex formation, as such large carbonyl peak shifts are characteristic of strong
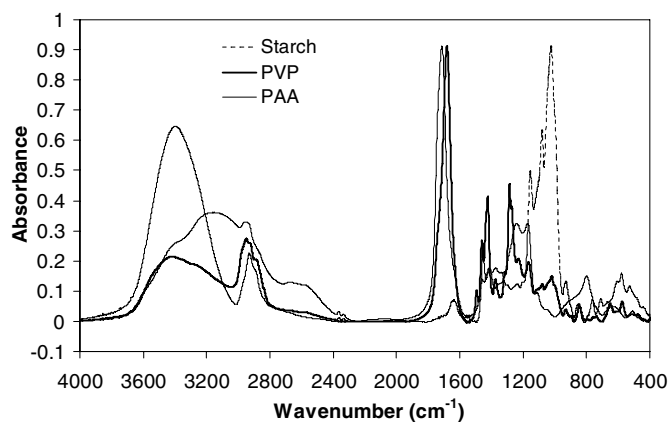

Fig. 1. Overlaid FTIR spectra of pure starch, pure PVP and pure PAA.

hydrogen bonding. The shift in the carbonyl peak from 1681 to 1637 cm^{-1} in PVP is attributed to the formation of the intermolecular hydrogen bonds in the PVP:PAA complex, while the carbonyl peak shift from 1713 to 1730 cm^{-1} is attributed to concomitant disruption of intramolecular hydrogen bonding in PAA as the two polymers merge and interact. The absence of an expected intermediate fraction, which would appear in Fig. 3 as a third carbonyl peak between the two at 1730 and 1637 cm^{-1}, suggests the isolated gels consisted mainly of that fraction of the solution mixture in which the PVP:PAA complex formation had reached virtual completion.
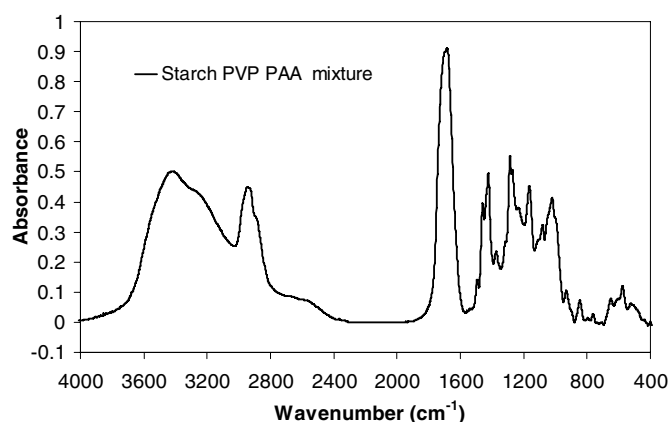
Fig. 2. FTIR spectrum of a cryogenically prepared dry mixture of pure starch, pure PVP, and pure PAA.
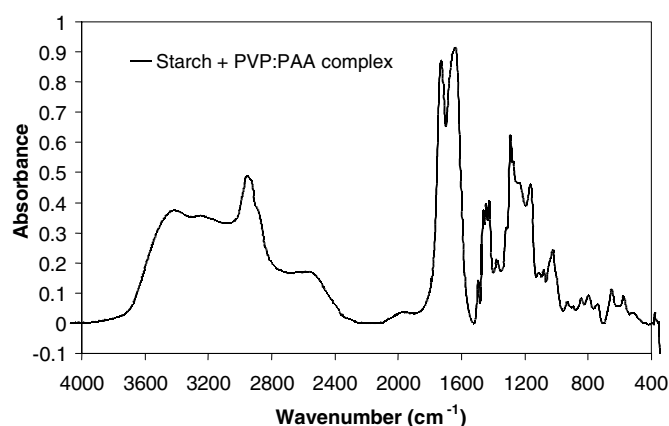

Fig. 3. FTIR spectrum of the dried precipitate from a mixture of starch, PVP, and PAA in aqueous solution.

3.3. Two-component blends involving PVPI

It was seen earlier that starch and PVP in solution showed no specific interactions. The situation was different when starch and PVPI solutions were added together. In this case, a large increase in viscosity was observed at a starch:PVPI ratio of 80:20 (Fig. 4). Interestingly, the viscosity at higher PVPI concentrations (greater than 60%)
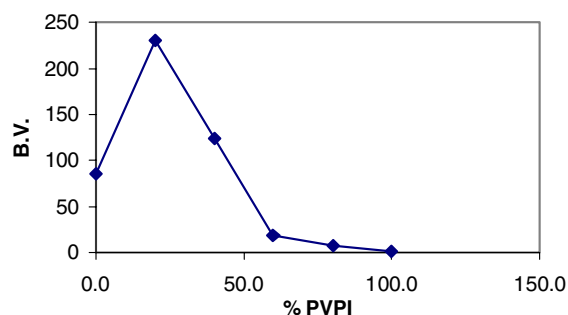
was very low. Thus, the interactions between starch and PVPI are rather specific in nature. It is likely that at high starch concentrations PVPI serves as a "crosslinker" that joins different starch chains together, thereby increasing the viscosity. However, at higher PVPI concentrations, each starch molecule is surrounded by PVPI, with minimal "crosslinking" and no apparent viscosity increase.

Since PAA and PVP form an interpolymer complex, we would expect PAA and PVPI to do likewise. Indeed, when 5% PAA and PVPI solutions were added together at any proportion, they formed numerous gel particles. Since we expect such complexation to decrease with decreasing concentrations, we repeated the experiment at 1% and at 0.5%. In both cases, no gel was visibly observed. The Brookfield viscosity data gave smooth curves (Fig. 5). Thus, in the approximately 0.5–1.0% range, we can avoid gel formation, thereby providing us with a working solution window when we need to formulate products.

3.4. Three-component blends involving PVPI

Since we made gels from the three-component blends of starch, PAA, and PVP, we would expect a blend of starch, PAA, and PVPI to form gels as well. This was indeed observed. However, we also made a more detailed study of these blends in order to gain a better understanding of these multicomponent systems.

We saw earlier that the starch:PAA mixture showed a maximum viscosity at 60:40 ratio. Accordingly, we made a 5% solution of starch:PAA at 60:40 ratio and added PVPI incrementally as a dry powder directly to the solution. At 0.1% PVPI the effect on viscosity was negligible (Fig. 6). With increasing PVPI, the viscosity increased rapidly, until a maximum was reached at 0.4% PVPI (to 876 cps). Beyond this concentration of PVPI, gel formation was abundant, and the Brookfield viscosity decreased because some of the polymers precipitated out as gel particles.

A slightly different situation was encountered when we added PAA to the starch:PVPI solution. We started with

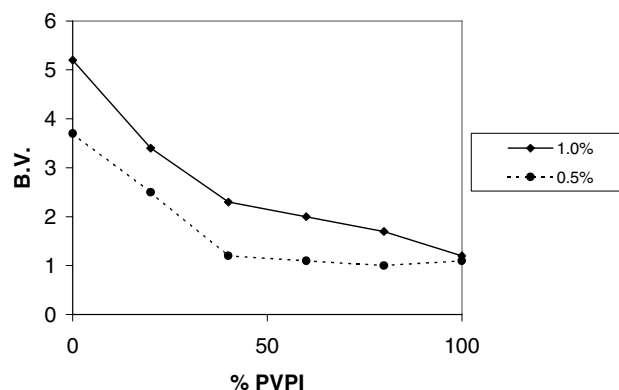Fig. 4. Brookfield viscosity of starch/PVPI solutions at 5% (w/w) concentration.

Fig. 5. Brookfield viscosity of PAA/PVPI solutions at 0.5 and 1.0 (w/w) concentrations.
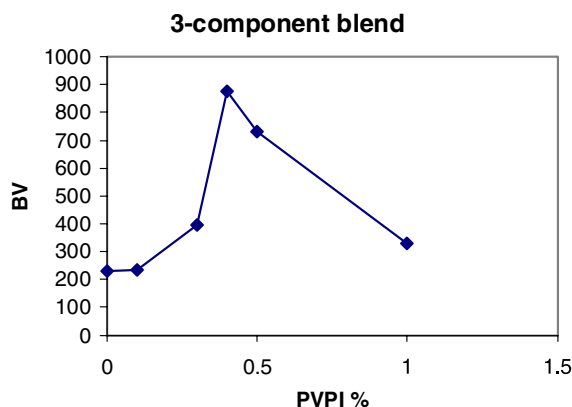
Fig. 6. Brookfield viscosity of 5% starch/PAA (64:40) solution with different amounts of PVPI added.

a 5% solution of 80:20 starch:PVPI. PAA was added as a dry powder to the solution, and the viscosity data were obtained (Fig. 7). At low PAA concentrations (ca. 0.2%), the viscosity actually *decreased*. As more PAA was added, the viscosity increased again until a maximum (460 cps) was reached at about 0.6%. Further addition of PAA caused visible gel formation, and the viscosity decreased as some polymer gels separated out from the solution.

The observed viscosity behavior can be rationalized in a qualitative way. As indicated earlier, in the starch/PVPI mixture PVPI serves effectively as a "crosslinker" for starch. Since PAA and PVPI have a strong tendency to complex with each other, the addition of PAA deprives starch of PVPI, and the viscosity drops as a result. As more PAA is added, the ternary interactions of PAA–PVPI– starch set in, and the viscosity increases again, until gel formation occurs.

A NMR relaxation study was carried out in order to gain additional perspectives. First, the ^{13}C NMR spectra of separate starch, and PAA solutions (at 5% concentrations) were obtained and T_1 of all relevant carbons determined. Then a solution containing 5% of both starch and PAA was made up and 0.4% of PVPI added. The ^{13}C
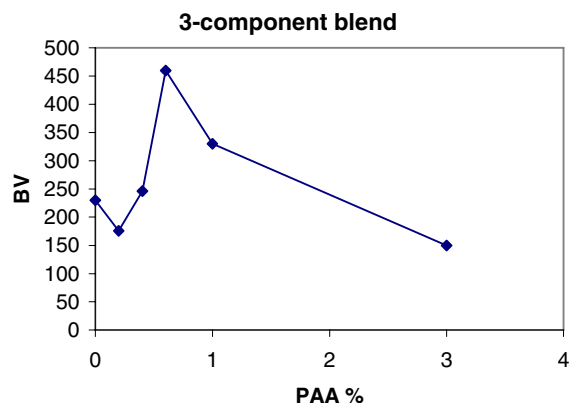
Table 6
NMR T_1 values (in seconds) for 5% polymer solutions alone, and for the three-component blend (starch:PAA = 60:40, with 0.4% PVP-I[a])

PAA	COOH		CH		CH$_2$
Alone	1.8		0.4		0.2
Blend	1.8		0.3		0.2
Starch	C1	C4	C3	C2	C5	C6
Alone	0.3	0.3	0.3	0.3	0.3	0.2
Blend	0.4	0.5	0.5	0.5	0.5	0.2

[a] Owing to its low concentration, the T_1 values for PVP-I were not obtained.

NMR spectrum of the resulting solution gave somewhat broader resonances, corresponding to restrictions in low-frequency motion (such as complex formation). However, the T_1 values for starch and PAA stayed roughly the same, suggesting the lack of high-frequency chemical exchange (Table 6). This result is reminiscent of the T_1 data observed for PVPI in different solvents (Cheng, Smith, & Vitus, 1985).

4. Conclusions

In this work, we studied the viscosity and gel formation in the tricomponent system, starch/PAA/PVP. Starch and poly(acrylic acid) at 5% aqueous solution formed a synergistic mixture at 60:40 ratio. The addition of a small amount of PVP caused the formation of a gel that entraps starch. In contrast, starch and PVP in solution showed no significant interactions between them; yet, the addition of PAA also caused gel formation.

The corresponding data for PVPI were also obtained. The addition of PVPI to a starch:PAA solution first increased the solution viscosity; further addition of PVPI caused gel formation. Similarly, starch and PVPI at 5% aqueous solution formed a synergistic mixture at 80:20 ratio; the addition of a small amount of PAA first caused a decrease in viscosity and then an increase. These observations are consistent with the formation of interpolymer complexes and specific interactions among the polymers.

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Fig. 7. Brookfield viscosity of 5% starch/PVPI (80:20) solution with variable amounts of PAA added.

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