Biocompatible Polymer Blends: Effects of Physical Processing on the Molecular Interaction of Poly(vinyl alcohol) and Poly(vinyl pyrrolidone)

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ABSTRACT: Blending is a very effective method for manufacturing new polymeric materials; however, the process used to combine two polymers can influence the physicochemical properties of the final product. As such, the aim of this study was to investigate how the rapid removal of a solvent from a composite by the spray drying of partially hydrolyzed poly(vinyl alcohol) (PVA)/poly(vinyl pyrrolidone) (PVP) altered the solid-state properties of the material compared to casting the blend within a film. Although thermal analysis showed that PVP acted as a plasticizer, reducing the melting point of PVA, spray drying the product rather than using a film-casting procedure improved its solid-state stability (increasing the glass transition) and resulted in the formation of a second crystalline phase within the material. Spectroscopic studies suggested that the manufacturing-induced variance in the solid-state properties of the PVA/PVP blends originated from structural differences in the composite caused by the processing method employed to form the blend. Although blending should still be considered a viable method of generating novel polymeric material, this study illustrated that through careful manipulation of the actual manufacturing process, the solid-state properties of the product can be altered. This could open a whole range of novel applications for traditionally used polymer composites. © 2005 Wiley Periodicals, Inc. J Appl Polym Sci 98: 2290–2299, 2005

Key words: blending; biopolymers; solid-state structure; thermal properties

INTRODUCTION

Water-soluble polymers can be derived from synthetic, semisynthetic, or natural sources.[1] As with many macromolecules, the differing stereochemistry of these high-molecular-weight compounds results in multiple arrays of primary, secondary, and tertiary/quaternary composites within their structure.[2] However, regardless of their inherent structural complexity, water-soluble polymers are commonly biocompatible and, in most cases, biodegradable. Their low environmental burden means that they are typically used for a wide range of applications within the textile, food, health care, paper, adhesive, waste treatment, oil recovery, film, and warp sizing industries.[1,3]

Blending is one of the most effective methods of manufacturing new polymeric materials.[4] Blends can be produced that have properties independent of either the original homopolymers or a structurally similar copolymerized macromolecule.[5] However, mixing polymers to produce novel materials is typically only possible if the two compounds are miscible. It is important to relate the chemical structure of polymers to their physical properties, as miscibility is often a result of a physical or chemical interaction between two materials.[6] The advantages of combining polymers within a blend is twofold. First, as the composite is completely miscible, the physical properties of the material will be dependent not only on the constituent polymers but also on their interaction. As such, the solid-state stability of the composite can be manipulated, and the material's key physical properties, such as its glass-transition temperature (T_g) and melting/decomposition regions, can be altered, depending on the molecular organization of the two polymers in the blend.[7,8] Second, the mixing of two polymers adds a second functionality with which the blend can form chemical or physical interactions. A polymer composite can act in a similar manner to a mixed surfactant/polymer system, which can be used to enhance the interactions of incompatible compounds or bridge immiscible environments.[9]

Poly(vinyl alcohol) (PVA) and poly(vinyl pyrrolidone) (PVP) are two water-soluble polymers that are known to interact to form a miscible composite.[5] The production of a novel PVA/PVP polymer blend can be an effective method for expanding the applications

of these materials; however, it is only commercially useful if the macromolecules can be combined reproducibly to form a product with predictable physicochemical properties. Preliminary studies, such as those by Cassu and Felisberti,[5] that have examined the interaction of PVA and PVP within blends with differential scanning calorimetry (DSC) are essential in determining if the two polymers interact. However, the technique of slow film casting, which is used frequently to combine the polymers in experimental studies,[5,10–12] has questionable relevance to industrial manufacturing procedures. Within industry, polymer blending is combined with large-scale techniques, such as melt mixing,[13] melt extrusion,[14,15] and liquid blending followed by rapid casting or spray drying, to produce granules or powders.[16–18] At present, there have been few published studies designed to investigate the effect of the processing conditions on the formation of polymer composites, and therefore, it is unknown whether the data obtained from analytical methods using polymers cast within films can be correlated with those obtained from polymer composites manufactured on an industrial scale. If a disparity does exist and the robustness of the polymer blending methods is poor, the commercial viability of industrially manufacturing certain materials may be unacceptable.

The aim of this study was to investigate the effects of the manufacturing process on the physical, chemical, and structural characteristics of blended polymers, with PVA/PVP composites as a model. The polymers were combined with two contrasting processing methods: spray-drying, which forces polymer composites to combine in a high-velocity, elevated-temperature environment, and film casting (at room temperature), which allows the polymers to combine in a less time-dependent manner. A range of polymer grades, varying in physicochemical properties, were used in the study so that the relationship between the manufacturing method and the type of polymer composite could be investigated. It was expected that changes in the polymers could have been either chemical or physical, and therefore, both the raw and blended materials were analyzed with a batch of analytical techniques, including Fourier transform infrared (FTIR) spectroscopy, NMR spectroscopy, and modulated differential scanning calorimetry (MDSC).

EXPERIMENTAL

Materials

The PVA was provided in a variety of grades by two suppliers. Seventy percent hydrolyzed PVA [Gohsenol NK-05; weight-average molecular weight (M_w) = 28,000, as quoted by the supplier] was supplied by Nippon Gohsei (Osaka, Japan), whereas 80% hydro-

lyzed PVA (M_w = 9,000–10,000), 87–89% hydrolyzed PVA (M_w = 13,000–23,000), 87–89% hydrolyzed PVA (M_w = 124,000–186,000), and 98% hydrolyzed PVA (M_w = 13,000–23,000) were sourced from Sigma Aldrich (Gillingham, UK). PVP K15 (M_w = 10,000) and poly(vinyl acetate) (M_w = 140,000) were supplied by Sigma Aldrich. The deuterated solvents dimethyl sulfoxide (DMSO) D6 (99.9%) and chloroform (99.8%) used for NMR were supplied by Cambridge Isotope Laboratories (Andover, MA).

Preparation of the polymer blends

Each of the individual polymers and the polymer composites (70% hydrolyzed PVA/PVP and 98% hydrolyzed PVA/PVP in ratios of 1 : 2, 1 : 1, and 2 : 1) were all processed into films and spray-dried particles. The films were cast on a glass Petri dish from 20% w/v aqueous solutions that were heated to 90°C to facilitate polymer blending and dried at room temperature. Once manufactured the films were stored at room temperature under silica desiccation. The spray-dried polymers were processed with a 191 laboratory scale machine (Buchi, Flawil, Switzerland) set with an inlet temperature of 180°C, a flow rate of 4 mL/min, a nozzle airflow of 800 mL/min, an aspiration rate of 70%, and an outlet temperature that varied between 89 and 105°C. The feedstock was a 1% w/v polymer solution, and the product was collected and stored under silica desiccation at room temperature.

FTIR

Absorption IR spectra of the polymer films were recorded at room temperature with a PerkinElmer FTIR 1720X spectrometer (PerkinElmer, Berkshire, UK) fitted with a DurasamplIR attenuated reflectance unit (SensIR Technologies, Warrington, UK). The machine was calibrated with a polystyrene standard as per the manufacturer's instructions. The films were pressed directly onto the attenuated reflectance crystal with the sampling unit. Sixty-four scans of each sample were run at a 4-cm^{-1} resolution over the 400–4000-cm^{-1} range. Approximately 2 mg of spray-dried samples were pressed into 300-mg KBr discs (KBr was supplied by Sigma Aldrich and was dried in a 150°C oven) with 9 tons of force for 60 s and analyzed directly on a PerkinElmer FTIR 1600 series (PerkinElmer, Berkshire, UK) (calibrated as mentioned previously). Again, 64 scans of each sample were run at a 4-cm^{-1} resolution over the 400–4000-cm^{-1} range.

MDSC

Thermograms were produced with a TA 2920 modulated differential scanning calorimeter (TA Instruments Ltd., Crawley, UK). The films, raw material,

and spray-dried samples were each analyzed in a sealed pan containing a pinhole with a 1 mm diameter in the roof. A double-heating method was employed. The first temperature cycle heated the sample to 110°C, where it remained isothermal for between 15 and 60 min to remove the remaining water in the samples. The sample was then cooled to 20°C before it was immediately reheated to 350°C. The heating/cooling rate was set at 5°C/min, and the modulation was set at ±2°C. Oxygen-free nitrogen was used as the purge gas set at a flow rate of 110 mL/min. Calibration of the equipment was performed with Indium as per the manufacturer's instructions. The T_g of the samples was taken as the midpoint of the stepwise deviation in the heat-flow curves during the second heating of the polymers. The melting temperature (T_m) of the polymers was taken as the maximum of the endothermic peak, and the enthalpy of fusion (ΔH_f) was taken as the integrated area of this peak.

Thermogravimetric analysis (TGA)

The samples were heated at 5°C/min up to 200°C, and the volatile content of each sample was defined as the percentage weight loss of the sample as it was heated from 30 to 140°C.

NMR

^{13}C-NMR and ^{1}H-NMR measurements were performed with a Bruker spectrometer (Bruker, Coventry, UK) operating at 500 and 125 MHz for the two respective nuclei. All spectra were recorded at 300 K with a digital resolution of 0.57 Hz, an acquisition time of 0.871 s, and a pulse delay of 0.001 s. Two dimensional (2D) heteronuclear and homonuclear correlation spectroscopy (COSY) experiments were performed to confirm the peak assignments in the one dimensional (1D) spectra for both raw and spray-dried PVA (70 and 98% hydrolyzed) and PVP K15. In addition, 2D nuclear Overhauser effect spectroscopy (NOSY) experiments investigated the spatial arrangements and interactions of PVA (with both 70 and 98% hydrolyzed) and PVP after spray drying. The PVA samples were dissolved within a 10% w/v deuterated DMSO solution for the ^{13}C, ^{1}H, and 2D COSY NMR measurements, and the PVP K15 was dissolved at the same concentration in chloroform. However, the 2D NOSY experiments were performed in 1 : 1 deuterated DMSO/deuterated chloroform (with tetramethylsilane) to allow direct comparison of the raw and combined polymers.

Gel filtration chromatography (GFC)

Liquid chromatography was performed with an integrated Waters Millennium system consisting of a 660E system controller, an inline 410 differential refractometer and a 717 autosampler (Waters, Elstree, UK). Filtered (0.45-μm nylon filter paper, Whatman, Maidstone, UK) and degassed 0.1M phosphate buffer (Sigma Aldrich), adjusted to pH 7.5 with sodium hydroxide (Sigma Aldrich) was used as the mobile phase. The samples (100 μL) were eluted from the column with mobile phase (1 mL/min), and the injection syringe was washed with HPLC-grade methanol (Merck, Darmstadt, Germany) between each injection. The column employed was a TSKgel G2000 SW column, with a 7.5-mm inner diameter and a 30-cm length (Phenomenex, UK). The validation of this method has been described previously.[19]

RESULTS AND DISCUSSION

Thermal analysis of PVA

During the MDSC heating sequence, PVA showed no signs of depolymerization (i.e., breakdown of the polymer chain) at temperatures up to 250°C. The GFC retention times of two PVA samples heated to 100 and 250°C, respectively, were not significantly different compared to the original material [Fig. 1 inset; $p > 0.05$, with an analysis of variance (ANOVA)]. Conversely, when PVA was heated to 275°C, it was poorly soluble in the phosphate buffer, and no response was detected in the GFC assay indicating that the polymer had decomposed.

Figure 2 compares 98% hydrolyzed PVA with the MDSC heating methodology in both the MDSC and TGA apparatus. During the first heating cycle, the sample lost approximately 18% of its weight as a result of removal of the volatile components (the majority of which was water). During the second heating, no further weight was lost until the second endothermic peak in the MDSC trace, which led to a rapid reduction in weight. This experiment showed that the volatile components (which if present can act as a plasticizer for the polymer and shift the glass transition) were completely removed from the polymer before the second heating with the MDSC, and the second endothermic peak corresponded to the polymer decomposition.

PVA is a semicrystalline polymer, and the MDSC data indicated the presence of one crystalline (T_m = 170–220°C) and two amorphous phases (two glass transitions, $T_{g1} \approx$ 70°C and $T_{g2} \approx$ 116°C) within the partially hydrolyzed material (Fig. 1). All three phases were apparent both in the spray-dried and film-cast polymer samples (Table I). Previous work that employed a volume temperature method to analyze the thermal properties of PVA reported two glass transitions at approximately 85 and 120°C, accompanied by a melt around 210°C.[20] However, the second of the two glass transitions was relatively small, and several
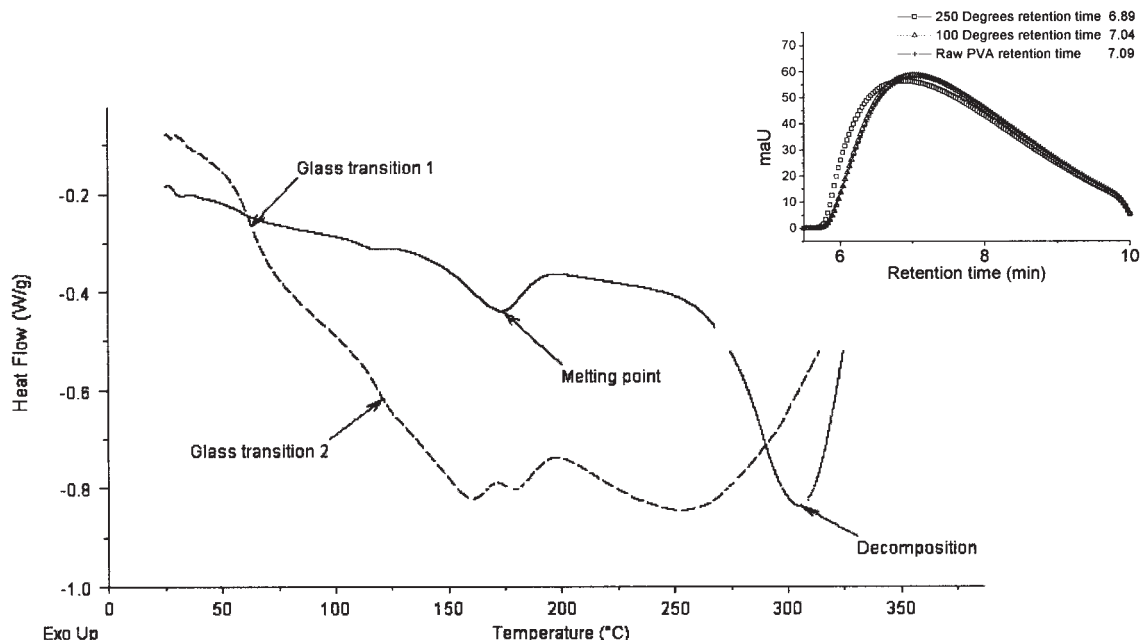
Figure 1 Typical MDSC trace of 70% hydrolyzed PVA. The solid line represents the heat flow, and the dashed line represents the reversing heat flow. The inset picture shows the effects of heating on the GFC profile of the same polymer. A sample was also taken at 275°C, but there was no result after injection onto the column (therefore, no profile is shown).

more recent studies with DSC have failed to detect it.[5,21,22]

Cassu and Felisberti[5] reported that increasing the percentage hydrolysis of PVA that is, reducing the number of bulky acetate molecules within the polymer, increased its crystallinity. Similarly, in this study,

regardless of whether the polymer was cast in a film or spray dried, T_m and ΔH_f increased as a function of the percentage hydrolysis of PVA (Table I). However, in addition, the thermal analysis in this study showed that T_{g1} displayed a linear relationship with the number of acetate groups per molecule in the polymer
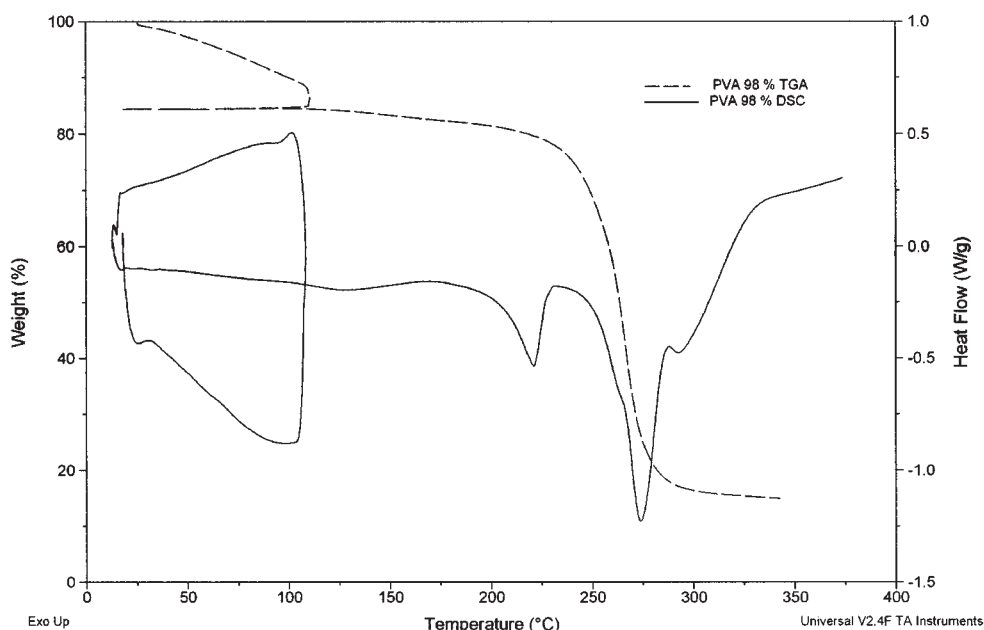
Figure 2 Comparison of a MDSC trace of 98% hydrolyzed PVA (M_w 13,000–23,000) prepared with a double-heating methodology to that of an identical TGA experiment. The solid line represents the heat flow; the dashed line represents the percentage weight change.

TABLE I
Effects of the Processing Conditions on the Thermal Properties of the Partially Hydrolyzed PVA Presented as Either Spray-Dried Particles or Cast Films

Polymer	Spray-dried particles				Cast films			
	T_{g1} (°C)	T_{g2} (°C)	T_m (°C)	ΔH_f	T_{g1} (°C)	T_{g2} (°C)	T_m (°C)	ΔH_f
70% hydrolyzed PVA	61.9 ± 1.4	117.5 ± 1.1	173.1 ± 0.4	27.8 ± 3.7	61.2 ± 0.8	121.2 ± 1.0	173.4 ± 0.3	23.4 ± 1.2
80% hydrolyzed PVA	68.5 ± 0.7	118.0 ± 0.5	180.6 ± 1.0	32.4 ± 1.9	65.4 ± 0.3	ND	186.3 ± 2.0	29.7 ± 0.6
87–89% hydrolyzed PVA	73.3 ± 0.3	ND	192.0 ± 1.7	42.4 ± 5.6	69.0 ± 0.9	ND	193.0 ± 0.4	32.4 ± 1.9
98% hydrolyzed PVA	78.5 ± 1.1	115.8 ± 0.0	221.5 ± 0.1	71.8 ± 1.0	71.8 ± 1.0	ND	221.2 ± 0.1	69.1 ± 2.8

ND, not detected.

(Table I). Therefore, not only did reducing the acetate groups increase the crystallinity of PVA, but it also restricted the chain mobility within the amorphous regions of the polymer. Changing the ratio of acetate to alcohol groups within PVA had little affect on T_{g2}, and this transition showed no change as a function of the percentage hydrolysis of PVA (Table I).

T_g of the pure poly(vinyl acetate) was 42 ± 1°C (Table II; $n = 3$, determined with the same DSC methodology as with the PVA and PVP samples). The fact that T_{g1} of PVA occurred in the region of 60–80°C, depending on the grade, and that there was no concentration-dependent depletion of the intensity of this transition even when the number of acetate groups fell from 30% (in 70% hydrolyzed PVA) to only 2% (in 98% hydrolyzed PVA), suggests that T_{g1} was probably not representative of a pure acetate phase of the polymer. It was likely that T_{g1} was a transition caused by the combination of the alcohol and acetate functional groups. The changes in T_{g1} were not simply due to the volume additivity of the two composite monomeric units of PVA, as there was not a linear relationship between the heat capacity of T_{g1} and the percentage hydrolysis (data not shown). Therefore, T_{g1} was likely to be a consequence of the intermolecular interaction

between the two monomeric units of PVA. Pritchard[20] previously defined T_{g2} as a secondary relaxation of the alcohol moiety, and MDSC analysis of the polymer did not produce any data to contradict this theory. T_{g2} was found to be in a similar position to that observed during the heating of the PVA homopolymer reported by Tubbs et al.[23] at about 120°C.

The processing conditions of PVA had little effect on the crystalline phase of the material, and both T_m and ΔH_f were identical, regardless of whether the polymer was spray-dried or cast within a film. However, spray drying did significantly increase T_{g1} ($p < 0.05$, ANOVA) in the 80, 87–89, and 98% hydrolyzed material compared to casting the PVA within a film (Table I). In addition, the stabilization of the amorphous region of the polymer induced by spray drying in comparison to that conferred by film casting was more pronounced with the highly hydrolyzed material, that is, 98% hydrolyzed PVA. The T_{g1} values for the spray-dried 98% hydrolyzed PVA and film-cast material were 78.5 ± 1.1°C and 71.8 ± 1.0°C, respectively, whereas for 80% hydrolyzed PVA, they were 68.5 ± 0.7°C and 65.4 ± 0.3°C, respectively. The double-heating methodology employed during the MDSC analysis removed the thermal history of the material,

TABLE II
Influence of the Processing Conditions on the Thermal Properties of PVA and PVP Blends

Polymers	Spray-dried particles			Cast films		
	T_{g1} (°C)	T_{g2} or T_{m2} (°C)	T_m (°C)	T_{g1} (°C)	T_{g2} (°C)	T_m (°C)
70% hydrolyzed PVA	61.9 ± 1.4	117.5 ± 1.1[a]	173.1 ± 0.4	61.6 ± 0.8	121.2 ± 1.0	173.4 ± 0.3
70% hydrolyzed PVA2:1PVP K15	70.5 ± 1.0	116.8 ± 1.4[a]	159.3 ± 1.0	68.5 ± 3.8	ND	149.1 ± 16.0
70% hydrolyzed PVA1:1PVP K15	83.0 ± 1.5	118.0 ± 0.7[a]	ND	59.5 ± 2.0	123.6 ± 3.7	172.7 ± 0.6
70% hydrolyzed PVA1:2PVP K15	96.4 ± 1.2	ND	ND	91.1 ± 2.7	ND	ND
98% hydrolyzed PVA	78.5 ± 1.1	115.8 ± 0.0[a]	221.5 ± 0.1	71.8 ± 1.0	ND	221.2 ± 0.1
98% hydrolyzed PVA2:1PPVP K15	97.3 ± 0.3	254.2 ± 4.1[b]	217.9 ± 0.3	ND	ND	212.2 ± 0.5
98% hydrolyzed PVA1:1PVP K15	98.1 ± 1.6	268.0 ± 2.9[b]	211.6 ± 0.1	87.9 ± 1.1	ND	199.0 ± 2.2
98% hydrolyzed PVA1:2PVP K15	99.0 ± 0.8	271.3 ± 3.5[b]	168.8 ± 1.7	86.7 ± 1.6	ND	ND
PVP K15	135.1 ± 0.0	ND	ND	ND	ND	ND
PVAc	42.0 ± 1.0	ND	ND	ND	ND	ND

ND, not determined; PVAc, poly(vinyl acetate).
[a] T_{g2}.
[b] T_{m2}.

and therefore, the manufacturing-induced changes in T_g were not simply related to the rate of heating and cooling during the processing of the polymers. Krimm et al.[10] detailed changes in the crystallinity of PVA when the material was rapidly dried in a vacuum oven, but stabilizing the amorphous region of PVA via heating has not previously been reported. Spray-drying is an extremely rapid form of drying and is commonly used to enhance the interactions between drugs and excipients in amorphous solid dispersions.[24–26] In this case, the rapid evaporation of the aqueous solvent during the spray-drying process was likely to have induced changes in the acetate–alcohol interaction, which decreased the mobility of the polymer chain to improve its solid-state stability.

Thermal analysis of the PVA/PVP composites

PVA and PVP interacted to form a totally miscible composite regardless of the physical properties of PVA, both when spray dried and upon film casting. The T_g of PVP (135.1 $\pm$ 0.0°C) and the T_{g1} of PVA (~70°C) were replaced in the polymer blend by a single new transition, which was in the 68.5–99.0°C range (Table II). T_{g2} in PVA was difficult to detect in the majority of the blends due to the dilution of the polymer with PVP, but when detected, it was shown to not be affected by the blending of the two polymers. There was a nonlinear relationship between the heat capacity of T_{g1} and the percentage composition of the blends (data not shown), which implied that the changing T_g was not simply due to volume additivity. This was in agreement with the data produced by Cassu and Felisberti,[5] who determined that a strong interaction existed between PVA and PVP on the basis of the increasing width of the composite's glass transition and the variations in ΔH_f as the two polymers were combined.

Although blending PVP with PVA increased T_{g1} in all of the polymer composites, the quantity of PVP added to 98% hydrolyzed PVA appeared to have no significant ($p > 0.05$) ANOVA effect on this transition (Table II). In contrast, combining 70% hydrolyzed PVA with PVP resulted in a concentration-dependent rise in T_{g1}. The rapid increase of T_{g1} at very low concentrations of PVP suggested that 98% hydrolyzed PVA formed stronger interactions with PVP K15 compared to 70% hydrolyzed PVA. Jang and Lee[22] showed that fully hydrolyzed PVA (actually 99.8% hydrolyzed) appeared to interact more strongly with the plasticizer glycerin compared to the low-hydrolysis material. In that study, it was shown that the addition of the plasticizer to the highly hydrolyzed material caused the T_m of PVA to decrease more rapidly than that of the low-hydrolyzed PVA.[22] An identical trend was seen for the film-cast polymers in the this study (Table II). Blending increasing quantities of PVP K15

with 98% hydrolyzed PVA with the film-casting technique decreased the T_m by 23°C, whereas using the same technique to combine 70% hydrolyzed PVA with PVP resulted in a drop in T_m of less than 1°C over the same concentration range (Table II). Defining both the melting point and T_g for the film-cast 70% hydrolyzed PVA PVP K15 composites was problematic due to poor definition of the transitions within the thermal profile. This led to the high standard deviation ($\pm$16°C) for the 2 : 1 70% hydrolyzed PVA/PVP K15 material and the unusual T_g of 59.2 $\pm$ 2.0 °C with the 2 : 1 70% hydrolyzed PVA/PVP K15 material. Such phenomena were not observed with any of the other polymer composites.

When the polymers were combined in a physical mixture (Fig. 3), no T_m depression occurred; this implied that the plasticizing effect of PVP was probably a result of PVA/PVP bonding that occurred during blending, which disrupted the crystalline phase of PVA. The crystalline regions of PVA are more accessible to PVP without the presence of acetate moieties, and therefore, the PVA/PVP interactions were more readily formed as the extent of PVA's hydrolysis was increased.[22]

As with the raw material, a difference between the effects of blending PVA and PVP in cast films compared to spray drying was observed. In all but one of the polymer blends, the spray-dried T_{g1} was detected at a significantly higher temperature ($p < 0.05$, ANOVA) than T_{g1} in the cast film (Table II). However, the T_m depression of the spray-dried material induced by the addition of PVP was less compared to the film-cast material. As described by Kubo and Kadla,[27] a lower T_m depression suggests that there is a weaker interaction energy between the two polymers in the spray-dried material.

With this data, it is not possible to conclude whether the appearance of a second peak in the thermal profile of the spray-dried PVA/PVP composite (defined as T_{m2} in Table II) was as a result of the PVA/PVP interaction, due to a new PVA/PVA or PVP/PVP crystalline region, or was simply a new decomposition peak. Tracking the weight loss of the sample with TGA, we found it difficult discriminate the peak definitively, but the weight loss profile varied little from that shown in Figure 2 (data not shown), which inferred that it indeed may have been a second melt. Regardless of the origin, the appearance of a new peak in the thermal trace was again an indication that PVA and PVP interactions were apparently different within the spray-dried polymer composites than in the film-cast material.

Structural analyses of PVA, PVP, and their composites

The ^{13}C and ^{1}H spectra for both PVA and PVP contained several overlapping peaks, and 2D homo-
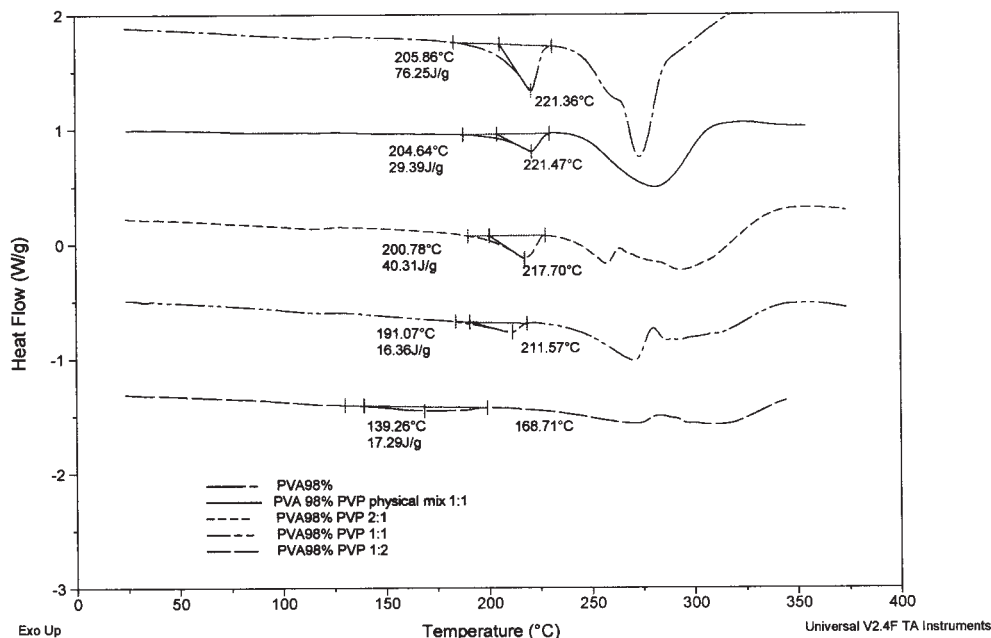
Figure 3 DSC trace detailing the effects of blending 98% hydrolyzed PVA and PVP K15 at different ratios on the melting point of the spray-dried composite.

nuclear and heteronuclear COSY experiments were required to assign all the peaks in the spectra. The proton and carbon peak assignments for these two polymers were identical to those described in previous articles[28,29] and, therefore, are not reported here. The number of broad, overlapping peaks also made the NOSY experiments difficult to interpret, and no significant through-space association between PVA and PVP could be discerned with this method (data not shown). Alexy et al.[30] reported that thermally induced degradation of PVA could be detected by the changing ratios of peaks in the CH_2 area of the NMR spectra and the appearance of a C=C peak (~130 ppm). In this study, PVA had an identical ^{13}C-NMR spectra whether in its original, spray-dried, or combined with PVP form (data not shown). Furthermore, no C=C peaks were identified in any of the carbon traces. Therefore, the ^{13}C-NMR traces did verify that no chemical changes had occurred during the spray-drying process.

The FTIR spectra recorded in this study for the alcohol moiety of PVA matched the assignments described in Krimm et al.'s[10] work. However, a comparison of spray-dried PVA and film-cast PVA showed an upfield shift of the OH stretching frequency (~3300 cm^{-1}) in the FTIR spectra (Fig. 4). Kubo and Kadla[27] studied the interaction of PVA with lignin and showed that the formation of intermolecular hydrogen bonds are commonly associated with a downward shift in the FTIR spectra. Therefore, the results in this study suggest that spray-drying weakened the intermolecular hydrogen bonds within the PVA polymer.

The magnitude of the wave number shift ($_{\Delta\nu}$OH = 132 cm^{-1}) was similar to that previously reported to occur when a strong hydrogen bond (−17.5 kJ/mol) between lignin and poly(ethylene oxide) is formed. Interestingly, Bjorklund et al.[31] performed a similar FTIR analysis of film-cast PVA before and after heating the polymer in a vacuum oven at 190°C, that is, the induction of dehydration in the polymer, but did not observe the same spectra changes. This suggests that it is the process of spray-drying, not just heating and dehydration, which influenced the structural changes
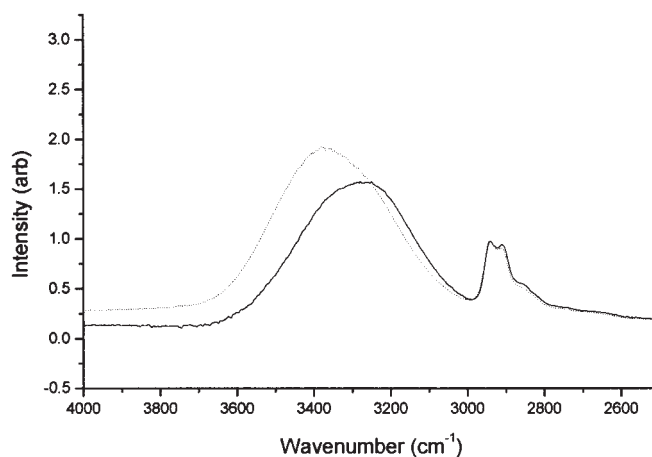
Figure 4 FTIR spectra of 98% hydrolyzed PVA either film-cast (solid line) or spray-dried (dashed line). The peaks of the film-cast OH stretch (ca. 3300) and CH_2 (ca. 2942) are shown.

observed in the polymers. The acetate monomer had a much greater hydrophobicity compared to the alcohol moiety of PVA,[32] and this difference in the physicochemical properties of the monomers within PVA may have been the driving force for the molecular rearrangement within the polymer that resulted from spray drying. Boury et al.[33] previously showed that the acetate groups are drawn to the surface of the air–liquid interface when PVA is in an aqueous solution. Rapid removal of the aqueous phase of the system may fix the polymer in this conformation, therefore altering the microstructure of the macromolecule. This process may have not been as prevalent within the polymer films, as the water evaporation occurred much more slowly and the molecules had chance to reequilibrate as the water was lost.

PVA is commonly regarded as an atactic polymer,[34] and its stereoregularity can be semiquantified with the ratio of the IR absorbances at 916 and 850 cm^{-1}. In contrast to the findings of Scholtens and Bijsterbosh,[35] the results obtained in this study demonstrated that the syndiotactic sequences (as determined with a previously described method[20]) decreased as the percentage hydrolysis of the material rose (data not shown). However, the stereoregularity was not affected by blending PVP with PVA or the processing conditions applied to the polymers.

In contrast to the investigation by Krimm et al.[10] where the IR spectral assignments were made, this study used partially hydrolyzed PVA, and an extra absorbance peak was observed in the IR spectra at about 1720 cm^{-1}, which corresponded to the ester carbonyl. Scholtens and Bijsterbosh[35] defined the carbonyl stretch as two independent modes that are displayed as two bands in the IR spectra at 1715 and 1735 cm^{-1}, which correspond to the hydrogen-bonded and non-hydrogen-bonded C=O, respectively. Although the 1715-cm^{-1} peak commonly occurs as a shoulder in the spectra, it was completely resolved with a second derivative function (Fig. 5). Interestingly, the ratio between the absorbances at 1715 and 1735 cm^{-1} increased as the hydrolysis of PVA rose. Scholtens and Bijsterbosh[35] also suggested that the 1715-cm^{-1} peak was associated with carbonyls in a random distribution in the polymer sequence, whereas the 1735-cm^{-1} peak was related to a blocky environment. Therefore, as the percentage hydrolysis rose, the FTIR analysis suggested that the positioning of the ester carbonyls became progressively more random and corresponded to the trends suggested by the results obtained from the thermal analysis of the polymers (Table I). Random acetate molecules would be less likely to disrupt the crystalline phase of the material. Therefore, the sudden exponential growth of the crystalline region in PVA when the acetate groups in PVA were reduced from 12 to 2% (as indicated by the results in Table I) could have been a consequence of a reduction

in both the number and blockiness of the disrupting acetate groups. Furthermore, the larger crystalline component of the 98% hydrolyzed PVA would cause the lone acetate groups within the amorphous regions of 98% hydrolyzed PVA to have less mobility compared to the groups of acetates found in 70% hydrolyzed PVA. Lower fluidity within the amorphous regions would increase the glass transition of the material, an effect that was previously shown by the thermal analysis of the polymers (Table I).

Spray-dried PVA exhibited a lower 1715/1735-cm^{-1} ratio compared to the polymer film (Fig. 5). In the absence of changes in the chemical structure of PVA (shown by the NMR results) or tacticity, the structural difference in the polymers induced by the two manufacturing processes must have been a result of a changing microenvironment of both the acetate and alcohol groups within PVA. The shift in the OH IR band (shown in Fig. 4) already provided some evidence that spray-drying weakened the intermolecular OH hydrogen bonds of PVA, but in addition, the changes that occurred in the 1715/1735-cm^{-1} IR band ratio suggested that spray-drying may also have had an influence on the carbonyl region of the molecule.

CONCLUSIONS

The physicochemical diversity of the various grades of PVA makes it an ideal macromolecule to use for a wide range of applications. However, the data produced in this study highlighted that variations in the percentage hydrolysis of PVA affects its solid-state properties, including its melting point and glass transitions. In addition, the structural features of PVA, such as its intermolecular bonding, the blockiness of the monomer sequence, and the stereoregularity of the polymer chain are influenced by the percentage hydrolysis of the material. Although the influence of the polymers thermal history has previously been shown to alter its physicochemical properties, this study also highlighted that the type of processing conditions used to manufacture the solid-state forms of this polymer can also influence its properties. Spray-drying the pure polymer altered its intermolecular hydrogen bonds, which improved its solid-state stability by increasing its T_g. These changes induced by physical processing may be vital if PVA is used to facilitate long-term storage.

PVA and PVP combined to form a totally miscible composite, and PVP was shown to act as a typical plasticizer, reducing the melting point and quantity of crystalline material within the composite. Spray-drying produced differences in both the solid-state and chemical properties of the blended material compared to that which resulted from film casting. Therefore, as with the pure PVA, the physical properties, structural

(a.)

(b.)
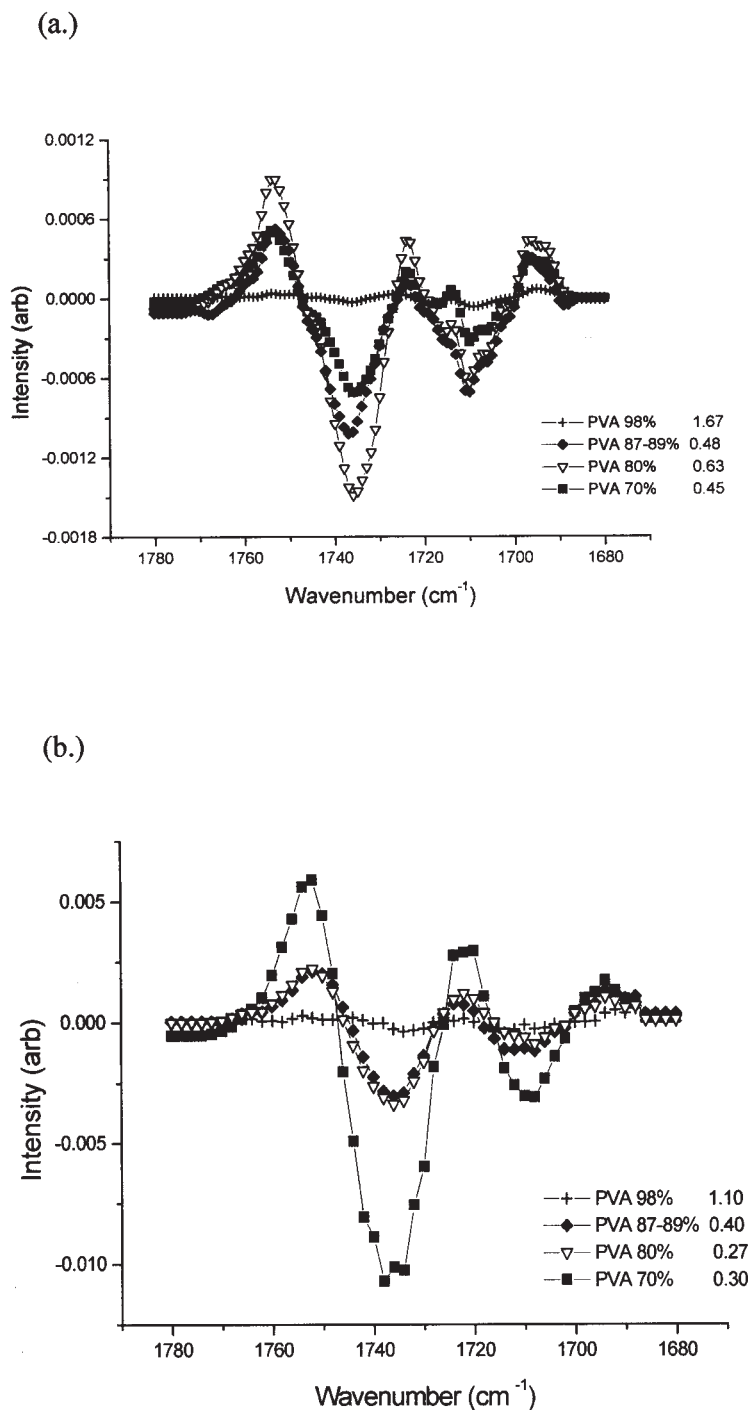
Figure 5 Second derivative absorbance FTIR spectra showing the influence of processing conditions on the free ($1735\ cm^{-1}$) and hydrogen-bonded ($1715\ cm^{-1}$) carbonyl moieties of different grades of PVA presented as (a) film-cast and (b) spray-dried polymers. The ratio of $1715/1735\ cm^{-1}$ is shown in the key.

makeup, and thermal history of the polymers in the blends influenced the physicochemical characteristics of the resultant composites, as did the method with which the polymers were combined.

This study has shown that although blending is a relatively simple method capable of producing novel polymeric materials, the manner in which the polymers are combined can influence the final composite.

Poor manufacturing robustness may affect the reproducibility of the final product and, hence, the quality of the final composite, which might lead to problems with the commercial viability of materials produced with the polymer blending process.

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