

Thermal Properties of Poly(Vinyl Alcohol)–Solute Blends Studied by TMDSC

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ABSTRACT: A thermal analysis study of blends of semicrystalline poly(vinyl alcohol) (PVA) with a pharmaceutical substance, buflomedil pyridoxal phosphate (BPP) is presented. Temperature-modulated DSC (TMDSC) was used to determine the T_g as well as the crystallinity of blends with various polymer to drug ratios, for different annealing procedures. Positive deviations from a simple expression for the composition dependence of the glass transition of the blend were found. This result, together with the increased thermal stability of PVA–BPP blends, evidenced by TGA analysis, indicates the existence of specific interactions between the

polar groups of the two components. The incorporation of dispersed BPP in the PVA matrix results in a composition-dependent lowering of the polymer's T_m and degree of crystallinity. In addition, we found that, while melting of pure PVA is predominantly reversing, its melting in the blends acquires an increasingly higher nonreversing component with increasing BPP content in the blend. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 93: 1151–1156, 2004

Key Words: temperature-modulated DSC; glass transition; poly(vinyl alcohol); blends; thermal properties

INTRODUCTION

The incorporation of organic solutes in polymers is of relevance in many applications, for example, dyeing of textiles and controlled drug delivery systems. Properties of pure polymer such as crystallinity, glass transition, and mechanical properties may be affected upon blending to an extent depending on the molecular interactions of the two species and the amount of the solute present in the blend. In particular, monolithic or matrix drug delivery devices are prepared by blending the drug with a swellable polymer. When the initially dry release system is contacted with a liquid solvent (usually water or aqueous buffer solution), drug release is activated by the ingress of the solvent. The effect of the incorporated drug on the crystallinity and the T_g of the polymer is of particular importance in such systems, as it may affect the stability of the matrix as well as the kinetics of drug release to the surrounding aqueous environment.^{1–4}

The effect of incorporated solute on the T_g of the polymer has been studied in many cases.^{5–8} In the absence of specific intermolecular interactions between polymer–solute molecules, a simple expression, based on free volume additivity, can be used to describe the composition-dependent glass transition of the blend⁵

$$\frac{1}{T_g} = \frac{w_1}{T_{g1}} + \frac{w_2}{T_{g2}} \quad (1)$$

where T_g , T_{g1} , and T_{g2} are the glass transition of blend, pure polymer, and pure solute, respectively, and w_1 and w_2 are the weight fractions of polymer and solute in the blend. In the case of specific interactions between polymer and solute, deviations from this relation may be observed. For example, Slark⁵ studied the effect of intermolecular forces on T_g in blends of a relatively high MW dye, disazoethiophene, with a series of amorphous polymers at a fixed dye : polymer ratio of 1 : 2 (w/w). Positive deviations from eq. (1) were observed for polymers exhibiting a high affinity for the dye, as expressed by the calculated average polar/hydrogen bonding solubility parameters. Other factors, such as molecular size and rigidity of the solute, may also determine the T_g of the polymer in the blend. For example, in a study of blends of both flexible and rigid amines in partly sulfonated polystyrene,⁸ IR data indicated in all cases proton transfer from the acid group of the polymer to the amines and H-bonding of the protonated amines to the sulfonate ion. On the other hand, the T_g of the polymer was decreased by addition of flexible amines but it was increased by rigid amines by 12 to 15°C.

The relatively recent temperature-modulated DSC (TMDSC) method has been used to study the crystalline structure of semicrystalline polymers and to provide additional information (not obtainable by conventional DSC) on melting and recrystallization processes related to the metastability of polymer

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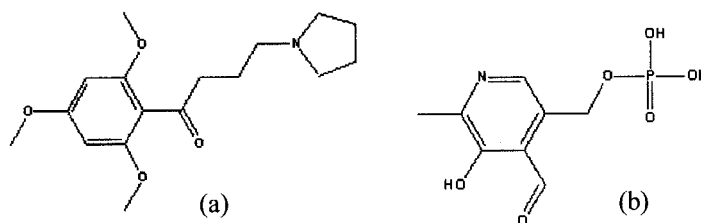


Figure 1 Molecular structure of (a) buflomedil and (b) pyridoxal phosphate. BPP is the ammonium salt of (a) with (b).

crystals.^{9–12} In this technique, the sample is subjected to a linear heating ramp with a superimposed low frequency temperature oscillation, resulting in modulation of the heating profile. The total heat flow (corresponding to the signal obtained from conventional DSC) is deconvoluted into a “reversing” heat capacity-related component (identifying heat effects that can be reversed within the temperature range of the modulated amplitude) and a nonreversing component. Glass transition and crystallization are present exclusively in the reversing and nonreversing signals, respectively, while melting may appear in both signals. In general, reversing endotherms are attributed to partial melting of crystal lamellae, which are then able to rapidly recrystallize on existing, not yet melted, crystals within the temperature modulation cycle of the experiment. The exothermic recrystallization process may be directly observed in the nonreversing signal,⁵ but one should note that exothermic and endothermic nonreversing effects may occur simultaneously, thus offsetting each other. Endothermic nonreversing events are attributed to complete melting of crystals that cannot recrystallize fast enough, since the nuclei are lost or the barrier to recrystallization is too high because of low undercooling. Thus, high quality crystals with T_m near its equilibrium value are expected to exhibit substantial nonreversing melting.^{9,11–13} Nonreversing endotherms may also be observed due to slow melting kinetics occurring even during the zero heating rate part of the temperature modulation cycle.¹³

Here we present a thermal analysis study of blends of poly(vinyl alcohol) (PVA) with a pharmaceutical substance, buflomedil pyridoxal phosphate (BPP). PVA is a biocompatible polymer used in controlled drug delivery systems. TMDSC was used to determine the T_g as well as the crystallinity of blends with various polymer to drug ratios, for different annealing procedures. In addition, by deconvolution of the total TMDSC signal, we examined the effect of the incorporated drug on the relative amounts of reversing and nonreversing melting endotherms.

EXPERIMENTAL

PVA in the form of powder was supplied by Aldrich (cat. no. 36313-8) with the following specifications:

98–99% hydrolyzed, $M_w = 31\text{--}50$ K. BPP (a product of Lisapharma SPA, Italy) was kindly provided by Kleva Pharmaceutical Industry, Greece. The molecular structure of BPP is shown in Figure 1.

Films of PVA with different contents of BPP were produced by the following procedure. PVA aqueous solutions (10%) were prepared by dissolving PVA powder in deionized water at 90°C for 6 h under magnetic stirring. After cooling to ambient temperature, the desired amount of BPP was added, under stirring, and then the solution was transferred to petri dishes. Evaporation of water at atmospheric conditions produced transparent films, which were further dried under vacuum at room temperature. Films of pure PVA were also prepared by the same procedure. All films were kept in a desiccator until further use.

TMDSC measurements were performed with Model MDSC 2920 of TA Instruments, using a heating ramp of 5°C/min and a temperature modulation of $\pm 0.80^\circ\text{C}$ every 60 s. The temperature modulation amplitude is small relative to the underlying heating rate, and the modulated profile was obtained by heating only. Usually, in semicrystalline polymers, T_m and the degree of crystallinity are determined during a first heating run up to the melting temperature range, and T_g is determined during a second heating run, after rapidly cooling the sample. This procedure is followed to erase any previous thermal history of the sample and to remove moisture that acts as a plasticizer, before the determination of T_g . For the polymer blends studied here, to avoid possible high temperature-induced morphological changes, T_g was also determined during the first heating run. Accordingly, moisture was removed from the highly hydrophilic PVA–BPP blends by annealing the samples, in most cases at 100°C for 3 h, before a single heating run was performed for the determination of T_g as well as of T_m and the degree of crystallinity. The latter two quantities were also determined in as-prepared, untreated samples. The onset temperature was used to determine T_g from the reversing TMDSC signal. All measurements were performed at least twice for each sample.

TGA scans (model 2050 TGA Analyser of TA Instruments) were also performed on BPP powder and on as-prepared film samples of pure PVA and of the

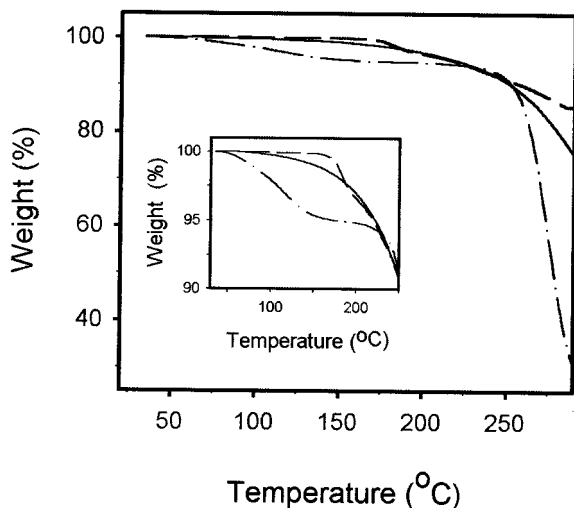


Figure 2 TGA thermograms of pure PVA (dot-dashed line), pure BPP (dashed line), and 55/45 w/w PVA-BPP blend (solid line).

55/45 w/w PVA-BPP blend, in a nitrogen atmosphere at a heating rate of 10°C/min.

RESULTS AND DISCUSSION

Thermogravimetric analysis

The thermal stability of pure components as well as of the 55/45 PVA/BBP blend, in the temperature range of subsequent DSC studies, was investigated by TGA. The corresponding TGA thermograms are shown in Figure 2. A ~ 5% weight loss observed around 100°C in pure PVA is attributed to moisture loss. The onset of degradation of pure PVA occurs at 240°C, in line with reported data.¹⁴ The thermogram of pure BPP is characterized by a 2.5% weight loss, occurring in the temperature range between 175 and 185°C, followed

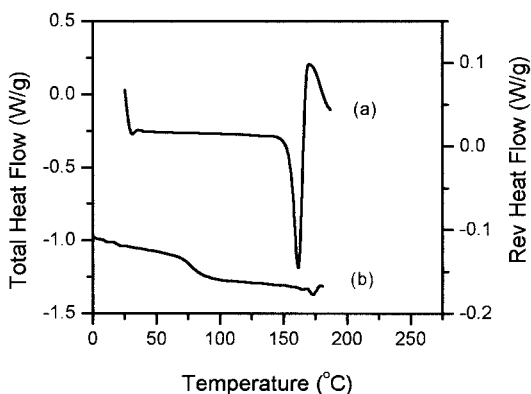


Figure 3 (a) Total TMDSC signal of pure as-received BPP; (b) reversing TMDSC signal of pure BPP, after heating the as-received sample to its melting point and rapidly quenching to ambient temperature.

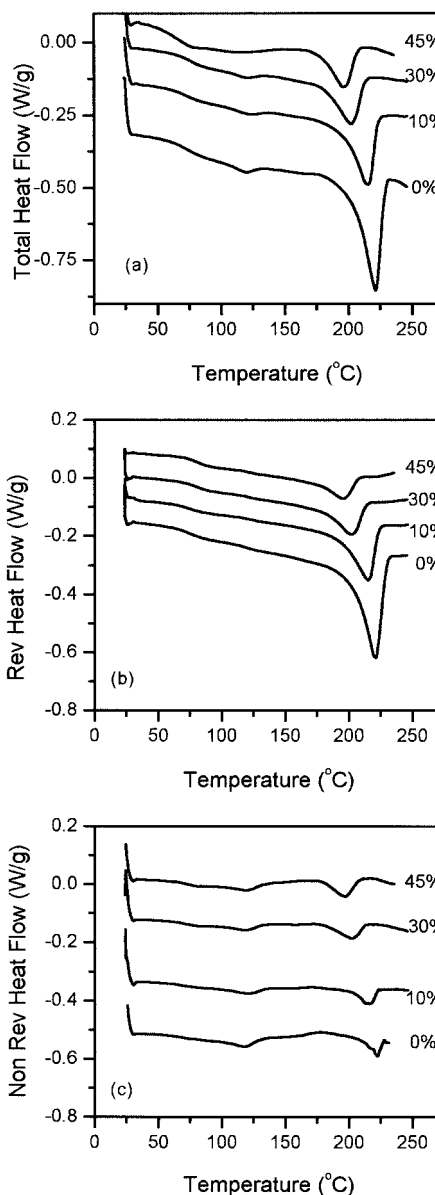


Figure 4 (a) Total, (b) reversing, and (c) nonreversing TMDSC signal of pure PVA and PVA-BPP blends. All samples were annealed for 3 h at 100°C. All data are plotted on the same relative scale but the curves have been shifted vertically for clarity. On each curve the BPP content of the blend (% w/w) is indicated.

by a slower degradation rate. The TGA thermogram of the blend suggests an increased thermal stability compared to pure components. For example, at 285°C the observed weight loss for pure PVA and pure BPP is ~ 70% and ~ 15.5%, respectively. If the blend's components behaved independently, a ~ 45% weight loss is expected for the 55/45 blend, whereas only a 25% loss is actually observed. In addition, the rather abrupt 2.5% weight loss observed for pure BPP around 180°C is absent in the blend, as clearly shown in the inset of Figure 2.

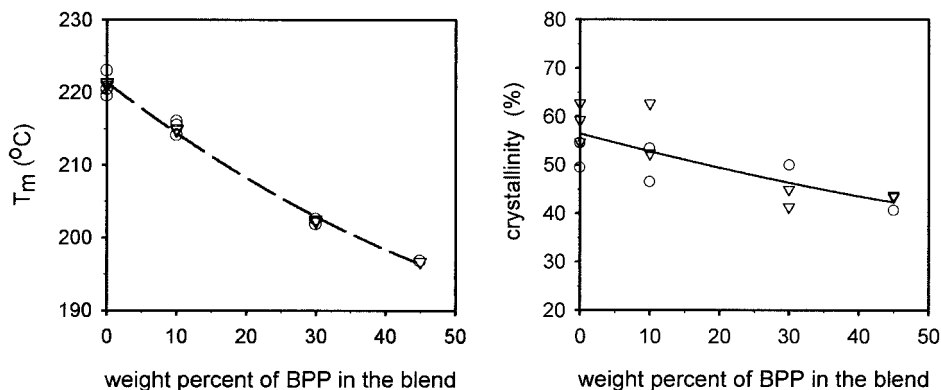


Figure 5 Effect of BPP content in the blend on (a) T_m and (b) the degree of crystallinity of the PVA fraction in the PVA–BPP blends. Untreated (○) and annealed for 3 h to 100°C (▽) samples. The crystallinity of the PVA fraction in the blend was calculated from the latent heat of melting, deduced from the endothermic peak of the total TMDSC signal, taking into account the corresponding value of 138.6 J/g reported for 100% crystalline PVA.¹⁶

Effect of BPP on the crystallinity of PVA

The total TMDSC signal of as-received pure BPP is presented in Figure 3, curve (a). A sharp endothermic peak is observed at 161°C, reflecting a highly crystalline structure. The exothermic peak at 175°C, following melting, may indicate partial decomposition of BPP, to be related with the small weight loss starting at the same temperature in the respective TGA thermogram (Fig. 2)

The total, reversing, and nonreversing signals of pure PVA, as well as of all the PVA–BPP blends annealed at 100°C for 3 h are presented in Figures 4(a–c), respectively. The total TMDSC signal of pure polymer [Fig. 4(a)] exhibits a broad endothermic peak at 221°C, indicative of its semicrystalline structure. A small endothermic peak present at 120°C in the total and nonreversing signal has been observed previously in conventional DSC studies¹⁴ and attributed to molecular motions of the disordered crystalline phase.¹⁵

The absence of melting endotherms around 160°C in the total TMDSC signals of all the PVA–BPP blends indicates that BPP is dispersed in the PVA matrix, even for the blend with the highest BPP content studied. This was also confirmed by optical examination of the films in a polarizing microscope. In addition, no evidence of exothermic events is observed around 175°C, in line with the increased thermal stability of the blends suggested from the TGA results. The small endothermic peak at 120°C mentioned above for pure PVA is also present in all blends. The endothermic peak in the vicinity of 200°C is assigned to melting of PVA. The data of Figure 4(a) indicate that, in the presence of increasing amounts of BPP in the blend, the melting endotherm of PVA (i) shifts to lower temperatures and (ii) becomes smaller and broader. These data are quantified in Figures 5(a) and (b), where T_m and the degree of crystallinity of the PVA fraction in the blend are plotted versus the BPP content in the

blend. Moreover these data show that the observed decrease in T_m and crystallinity with increasing BPP content was the same for both the untreated samples as well as for the samples annealed at 100°C for 3 h.

Deconvolution of the total TMDSC signals of Figure 4(a) in reversing [Fig. 4(b)] and non-reversing [Fig. 4(c)] components shows that melting of pure PVA is predominantly reversing, but one should take into account that the small degree of nonreversing melting observed may result from concurrent recrystallization and melting phenomena offsetting each other. Increasing amounts of BPP in the blend results in (i) progressive diminution of the reversing melting component, which is responsible for the observed reduction of the total melting endotherm of Fig. 4(a), and (ii) a small, but distinct increase of the nonreversing melting component. This is also clearly demonstrated in Figure 6 in which the nonreversing (ΔH_{NR}) and reversing (ΔH_R) heats of fusion per gram of PVA for all the annealed samples studied here are plotted versus the BPP content in the blend. As mentioned in the Introduction,

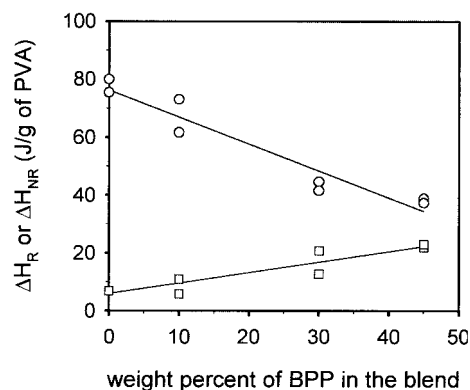


Figure 6 Reversing (ΔH_R , ○) and nonreversing (ΔH_{NR} , □) heat of melting of samples annealed for 3 h to 100°C, as a function of BPP content of the blend.

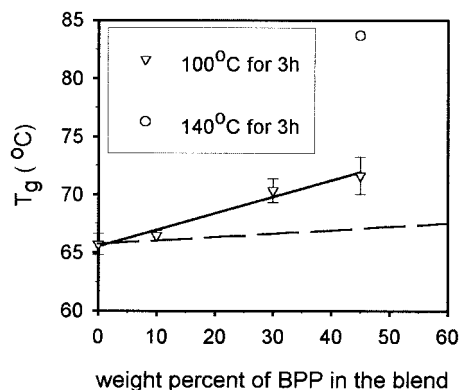


Figure 7 T_g of PVA-BPP blends as a function of BPP content of the blend. Samples annealed for 3 h at 100°C (∇) and at 140°C (\circ). The dashed line is calculated on the basis of eq. (1).

substantial nonreversing contribution to melting of pure polymers is typically expected for high quality crystals with T_m near their equilibrium value.^{9,11-13} For the blends studied here, the opposite trend is observed, since the lower the T_m of PVA in the blend, the higher the contribution of nonreversing PVA crystal melting. In semicrystalline polymers, crystallites are embedded in an amorphous matrix, and individual chains transverse consecutively amorphous and crystalline regions. For the blends studied here, the amorphous matrix involves the relatively bulky BPP molecules, which are capable of interacting with the polymer segments, and increase their rigidity, as evidenced by the observed increase in T_g (see below). Thus, it is reasonable to assume that, during the modulated heating cycle, both melting and recrystallization of crystal lamellae will be constrained, resulting in a higher nonreversing contribution to melting compared to pure PVA.

Glass transition temperature of blends

Due to its highly crystalline structure, pure as-received BPP displayed no glass transition, during the first heating run [Fig. 3, curve (a)]. After heating a sample to its melting point and quenching to ambient temperature, a T_g of 68.7°C was determined for pure BPP [Fig. 3, curve (b)]. The T_g of pure PVA, annealed at 100°C for 3 h, was found to be 65.7°C. On the basis of eq. (1), for all PVA/BPP blends a T_g value intermediate between the pure components' T_g is expected. However, positive deviations from this relation are observed, as shown in Figure 7, where the T_g versus blend composition for samples annealed for 3 h to 100°C is presented. More interestingly, we also found that increasing the annealing temperature resulted in a more pronounced increase in T_g . For example, annealing the 55/45 PVA-BPP blend for 3 h to 100 and

140°C, resulted in a T_g of 71 and 83°C, respectively. Taking into account that, as shown by TGA, no evidence of decomposition occurs at these annealing temperatures, the observed increase in T_g may be attributed to intermolecular bonding between the OH groups of PVA and the polar groups of BPP. This hypothesis may also explain the enhanced thermal stability of the blends compared to the pure components. Moreover, our data indicate that the said interactions are promoted by increasing the annealing temperature, possibly as a result of the corresponding increased segmental mobility of the polymer. As stated in the Introduction, antiplasticization effects have also been established in other polymer-solute blends. In the case of PVA, a similar behavior has been observed for blends of the polymer with lactose.¹⁴ In particular, DSC and WAXD studies showed that lactose could crystallize in the PVA matrix and the polymer's T_g was increased with increasing lactose content. This effect was attributed to hydrogen bonding between the hydroxyl groups of the two components. Moreover, the observed effect was found to be more pronounced for blends annealed for 1 h to 100°C than for the unheated samples.

CONCLUSION

The increased thermal stability of PVA-BPP blends as evidenced by TGA analysis as well as the observed positive deviations from a simple expression for the composition dependence of the glass transition of the blend indicate the existence of specific interactions between the polar groups of the two components. The increase of T_g became more pronounced upon increasing the annealing temperature of the blend, possibly due to the enhanced segmental mobility of the macromolecules facilitating molecular interactions. As expected, the incorporation of dispersed BPP in the PVA matrix disrupts the crystalline structure of the latter, resulting in a composition-dependent lowering of the polymer's T_m and degree of crystallinity. Deconvolution of melting endotherms in reversing and nonreversing components by TMDSC shows that, while melting of pure PVA is predominantly reversing, its melting in the blends acquires an increasingly higher nonreversing component with increasing BPP content in the blend.

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