

# Miscibility and Morphology of Chiral Semicrystalline Poly-(R)-(3-hydroxybutyrate)/Chitosan and Poly-(R)-(3-hydroxybutyrate-co-3-hydroxyvalerate)/Chitosan Blends Studied with DSC, $^1\text{H}$ $T_1$ and $T_{1\rho}$ CRAMPS

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**ABSTRACT:** The phase structure of poly-(R)-(3-hydroxybutyrate) (PHB)/chitosan and poly-(R)-(3-hydroxybutyrate-co-3-hydroxyvalerate) (P(HB-co-HV))/chitosan blends were studied with  $^1\text{H}$  CRAMPS (combined rotation and multiple pulse spectroscopy).  $^1\text{H}$   $T_1$  was measured with a modified BR24 sequence that yielded an intensity decay to zero mode rather than the traditional inversion-recovery mode.  $^1\text{H}$   $T_{1\rho}$  was measured with a 40-kHz spin-lock pulse inserted between the initial  $90^\circ$  pulse and the BR24 pulse train. The chemical shift scale is referenced to the methyl group of PHB as 1.27 ppm relative to tetramethylsilane (TMS) based on  $^1\text{H}$  liquid NMR of PHB. Single exponential  $T_1$  decay is observed for the  $\beta$ -hydrogen of PHB or P(HB-co-HV) at 5.4 ppm and for the chitosan at 3.7 ppm.  $T_1$  values of the blends are either faster than or intermediate to those of the plain polymers. The  $T_{1\rho}$  decay of  $\beta$ -hydrogen is bi-exponential. The slow  $T_{1\rho}$

decay component is interpreted as the crystalline phase of PHB or P(HB-co-HV). The degree of crystallinity decreases with increasing wt % of chitosan in the blend. The fast  $T_{1\rho}$  of  $\beta$ -hydrogen and the  $T_{1\rho}$  of chitosan in the blends either follow the same trend as or faster than the weight-averaged values based on the  $T_{1\rho}$  of the plain polymers. Together with the observation by differential scanning calorimeter (DSC) of a melting point depression and one effective glass transition temperature in the blends, the experimental evidence strongly suggests that chitosan is miscible with either PHB or P(HB-co-HV) at all compositions. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 86: 1253–1258, 2002

**Key words:** differential scanning calorimetry; miscibility; nuclear magnetic resonance

## INTRODUCTION

Polymers are present in a wide variety of materials, and can be tailored for many diverse applications. Polymers are widely accepted because of their durability, ease of processability, and cost-effectiveness to provide advanced materials to enhance quality of life. However, the high usages of nonbiodegradable polymeric materials have contributed to serious waste management problems. As a result, biodegradable polymers have become a common interest all over the world.

Bacteria synthesized poly(3-hydroxybutyrate) (PHB) is a chiral stereoregular biodegradable thermoplastic polyester. It has the physical properties and thermal processability of conventional thermoplastics, and yet are fully biodegradable when disposed of in a microbially active environment.<sup>1–5</sup> To improve its impact resistance and processability, a series of copolymers containing 3-hydroxyalkanoate units other than the 3-hydroxybutyrate unit were biosynthesized by bacterial fermentation.<sup>6</sup> For example, poly(3-hydroxybutyrate-co-3-hydroxyvalerate) [P(HB-co-HV)] and poly(3-hydroxybutyrate-co-3-hydroxyhexanoate) [P(HB-co-HHx)] show a wide range of mechanical and physical properties depending on the HV or HHx content.<sup>7–9</sup>

So far, many blends containing PHB have been studied, including binary blend and ternary blend systems;<sup>1–4</sup> however, not all of them are totally biodegradable. Chitosan [poly- $\beta$ (1–4)-D-glucosamine] is a chiral material suitable for asymmetric separation of racemic mixtures, and for biomedical applications.<sup>10,11</sup> Chitosan is brittle, and if it is used as artificial actuator and as tissue scaffold, it is usually blended with other polymers to modify its properties. The polymers should ideally be biocompatible if the blends are used as artificial muscles or tissues. Polyhydroxyalkanoates

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(PHAs), especially the copolymers such as P(HB-*co*-HV) and P(HB-*co*-HHx), are elastomers, and so they may serve well as biocompatible natural plasticizers to reduce the stiffness of chitosan. Because chitosan has functional groups like hydroxyls, amines, and amides, which can be chemically modified, PHB and P(HB-*co*-HV) are probably miscible with chitosan on blending.<sup>12,13</sup>

The objective of this work is to shed light on the miscibility and phase behavior of PHB/chitosan and P(HB-*co*-HV)/chitosan blends. We investigate the miscibility and phase behavior with both differential scanning calorimetry (DSC) and <sup>1</sup>H high-resolution solid-state NMR spectroscopy (CRAMPS).

## EXPERIMENTAL

### Materials

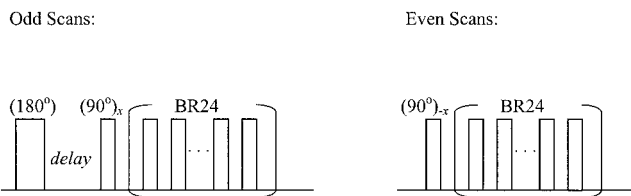
Biosynthesized PHB and P(HB-*co*-HV) were purchased from Fluka, a Sigma-Aldrich company (product #81329 and 27819, respectively). P(HB-*co*-HV) (7 : 3) stands for the copolymer with a molar ratio HB : HV = 7 : 3. The molecular weight  $M_w$  of PHB and of P(HB-*co*-HV) are 400–700 kDa, according to the supplier. Chitosan coarse powder from crab shells was purchased from Aldrich Chemical Company Inc. (product #41,941-9). Both powders were used without further purification. A mutual solvent, 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP) (99.5+%) was purchased from Acros Organics Company.

### Preparation of blends

The dissolve-drying method was used for the preparation of all polymer blend samples in this study. PHB, P(HB-*co*-HV) and chitosan were dissolved in HFIP separately before blending. The polymer concentration of each solution was 10 g/L. After the chitosan solutions were well homogenized, they were mixed with PHB solutions and P(HB-*co*-HV) solutions. Thin films of PHB/chitosan and P(HB-*co*-HV)/chitosan blends (weight ratios of 100/0, 80/20, 60/40, 50/50, 40/60, 20/80, and 0/100) were prepared by casting from hexafluoroisopropanol (HFIP) with 1% acetic acid by slow evaporation at ambient temperature for 24 h. The blends were then dried under vacuum at 60°C to constant steady-state weight. All samples were kept dry in a desiccator.

### Differential scanning calorimetry

DSC analysis was performed to study miscibility and thermal behavior of the blends, on a Mettler DSC 30 differential scanning calorimeter under a dry nitrogen atmosphere. The instrument was calibrated with indium and zinc standards. For all plain polymers and their blends, samples as casting films were first heated



**Figure 1** The odd scan is just an inversion-recovery sequence with BR24 to decouple <sup>1</sup>H-<sup>1</sup>H dipolar interactions. Together with the even scan, the effective accumulated signal decays to zero. It is now a two-parameter fit for single  $T_1$  instead of a three-parameter fit for traditional inversion recovery.

from 25 to 250°C at a heating rate of 20°C min<sup>-1</sup>. Samples at 250°C were waited for 2 min then quenched to -50°C using liquid nitrogen, and then scanned to 250°C at a heating rate of 5°C min<sup>-1</sup>. The midpoint of stepped change in the heat capacity of the sample during the second heating scan was taken as the glass transition temperature ( $T_g$ ).

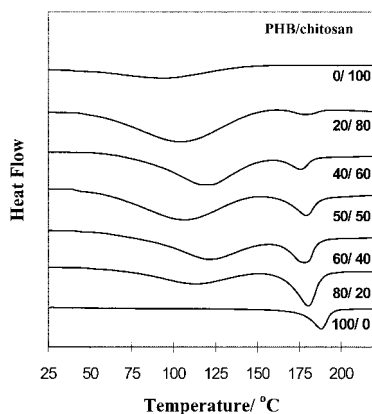
### Nuclear magnetic resonance

<sup>1</sup>H  $T_1$  and  $T_{1\rho}$  were measured using 5-mm glass CRAMPS (combined rotation and multiple pulse spectroscopy) rotors spun at 2 kHz. The 90° pulse width was 1.5  $\mu$ s, and  $\tau$  in the BR24 pulse train was 3.5  $\mu$ s. The predelay recycle time was 6 s. The number of spectral data points was 512, and the number of transients taken for signal averaging was either 4 or 8. Based on <sup>1</sup>H liquid NMR of PHB, the chemical shift scale is referenced to the methyl group of PHB as 1.27 ppm relative to tetramethylsilane (TMS). The spectrometer is a Varian Inova 400-MHz high-power system that is equipped with Chemagnetics probes and accessories. Figure 1 depicts the modified CRAMPS sequence that yields a decay to zero mode for <sup>1</sup>H  $T_1$  measurements. <sup>1</sup>H  $T_{1\rho}$  was measured with a 40-kHz spin-lock pulse inserted between the initial 90° pulse and the BR24 pulse train.

## RESULTS AND DISCUSSION

### Differential scanning calorimetry

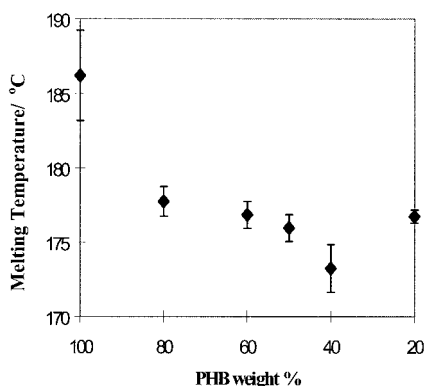
Two cycles of scanning were adopted in this experiment, so as to eliminate the effect of moisture presence in chitosan containing blends. The maximum temperature region in DSC scanning was set at 250°C, to prevent any thermal degradation of chitosan in the first heating scan.<sup>14</sup> The DSC melting curves of PHB/chitosan blends in Figure 2 show that PHB is a crystalline polymer with a melting point of about 186°C. All the blends containing PHB show two endotherms in the range of 25 to 250°C during the first heating scan, but not during the second scan. The broad low-temperature endotherm in the first scan is probably due to the evolution of bound water from chitosan.



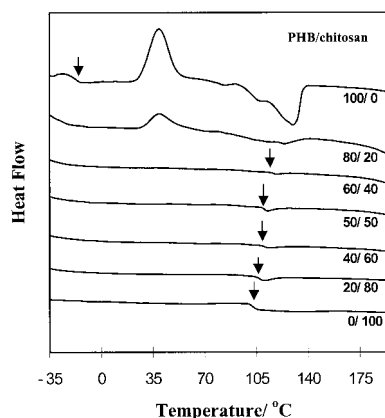
**Figure 2** DSC endotherms of PHB/chitosan blends during the first heating scan at a rate of  $20^{\circ}\text{C min}^{-1}$ .

Two endotherms are also observed in the blends of P(HB-co-HV)/chitosan during the first heating scan, but P(HB-co-HV) has a melting point at  $114^{\circ}\text{C}$ , which overlaps with the broad water evolution peak. For the PHB/chitosan blends, a general trend in the depression of  $T_m$  with respect to that of PHB is detected in the blends indicating strong intermolecular interactions between PHB and chitosan, which change the crystallizing behavior of PHB and result in thinner lamellar thickness of the crystals (Figure 3).<sup>12,13</sup>

The glass transition temperatures,  $T_g$ s, of PHB/chitosan and P(HB-co-HV)/chitosan blends were measured by DSC in the second heating scan which are shown in Figures 4 and 5. The  $T_g$ s for PHB and P(HB-co-HV) are found to be  $-9.6$  and  $-5.3^{\circ}\text{C}$ , respectively. Both are in reasonable agreement with the generally accepted values for these polymers. The  $T_g$  of chitosan is found to be  $103^{\circ}\text{C}$  in our case, which is lower than that ( $203^{\circ}\text{C}$ ) reported by Sakurai et al.<sup>14</sup> The  $T_g$  of chitosan ( $103^{\circ}\text{C}$ ) that is reported in this article is determined by averaging several DSC measurements. The  $T_g$  of blends in all weight compositions are averaged from three different batches of measurement carried out under identical conditions. The experimen-

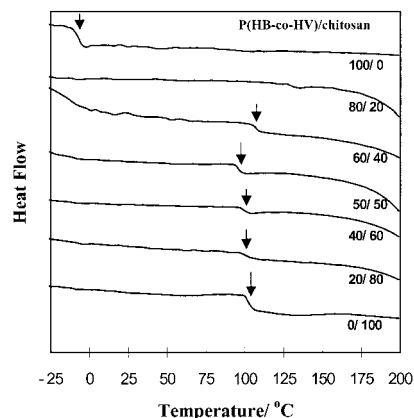


**Figure 3** Melting point depression of PHB as a function of PHB wt %. The error bars indicate  $\pm 1$  standard deviation from three measurements.

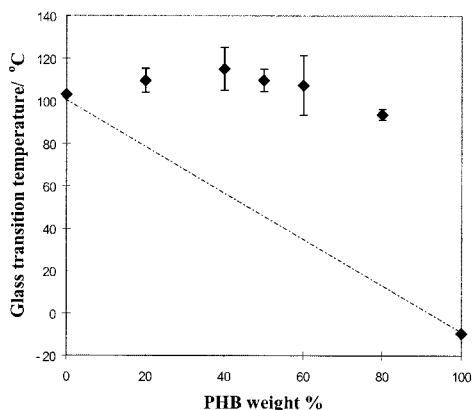


**Figure 4** DSC thermograms of PHB/chitosan blends in the second heating scan at a scanning rate of  $5^{\circ}\text{C min}^{-1}$ . The arrow indicates the glass transition temperature.

tal values of  $T_g$  are plotted against blend compositions in Figures 6 and 7. Based on the existence of a single glass transition temperature, both PHB and P(HB-co-HV) are likely to be miscible in all proportions with chitosan. For all different compositions, the  $T_g$ s are higher than those of the calculated weight-averaged values. This is attributed to the strong intermolecular hydrogen bonding between the PHB or P(HB-co-HV) carbonyls and the hydroxyl groups or amide groups of chitosan. However, DSC is not a good method to accurately measure  $T_g$ s of chitosan and its blends.<sup>12,13</sup> The molecular structure of chitosan consists of rigid  $\beta$ -1,4-linked D-glucosamine units, and so the change in heat capacity corresponding to the change in specific volume (or molecular mobility) at the glass transition temperature is equally small. This gives rise to a very small observed baseline step change on the DSC curves.<sup>14</sup> This will introduce a large error in the DSC measurement of chitosan's  $T_g$ . Nonetheless, the evidence gathered from the observation of both  $T_m$  depression and single effective  $T_g$  in the blends strongly suggest that PHB/chitosan and P(HB-co-HV)/chi-



**Figure 5** DSC thermograms of P(HB-co-HV)/chitosan blends in the second heating scan at a scanning rate of  $5^{\circ}\text{C min}^{-1}$ . The arrow indicates the glass transition temperature.



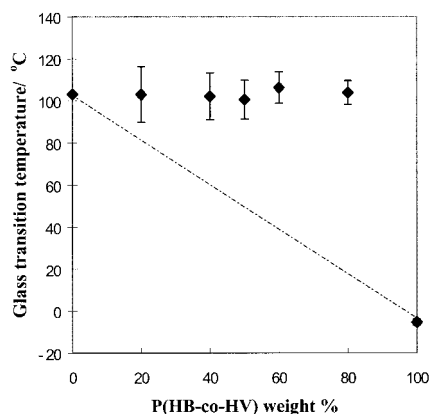
**Figure 6** Plot of glass transition temperatures for PHB/chitosan blends vs. wt % of PHB. The error bars indicate  $\pm 1$  standard deviation from three measurements.

tosan are miscible blends. We verify this conclusion with  $^1\text{H}$   $T_1$  and  $T_{1\rho}$  measurements via CRAMPS.

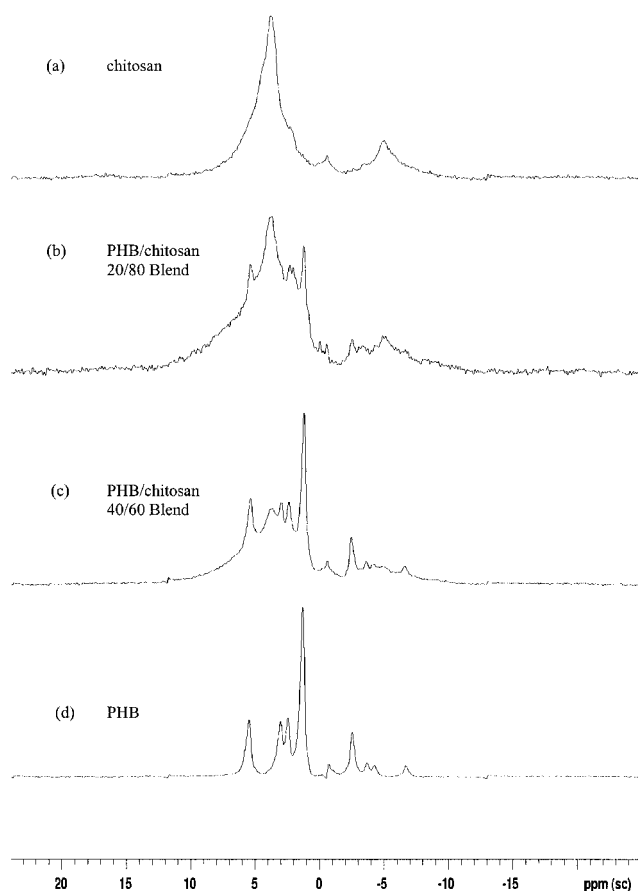
### CRAMPS

Figure 8 shows the typical  $^1\text{H}$  CRAMPS spectra observed in this work; represented here are those of (a) plain chitosan, (b) PHB/chitosan 20/80 blend, (c) PHB/chitosan 40/60 blend, and (d) plain PHB. The peaks at negative ppm values (relative to TMS) are experimental artifacts. Miscibility and phase behavior of PHB/chitosan and P(HB-co-HV)/chitosan blends are studied at 22°C by measuring  $^1\text{H}$   $T_1$  and  $T_{1\rho}$  at the  $\beta$ -hydrogen resonance (5.4 ppm) and at the chitosan resonance (3.7 ppm). The twin-peak at 3.0 and 2.4 ppm is of the nonequivalent  $\text{CH}_2$  hydrogens of chiral PHB. The methyl group's resonance is at 1.27 ppm.

Figures 9 and 10 show the  $^1\text{H}$   $T_1$  relaxation in the traditional inversion-recovery mode and decay-to-zero mode, respectively. The decay-to-zero mode is preferred because it allows quick inspection of whether we have single exponential or multiexponen-

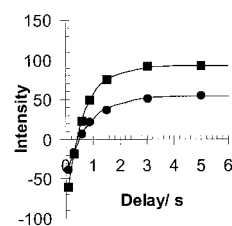


**Figure 7** Plot of glass transition temperatures for P(HB-co-HV)/chitosan blends vs. wt % of P(HB-co-HV). The error bars indicate  $\pm 1$  standard deviation from three measurements.



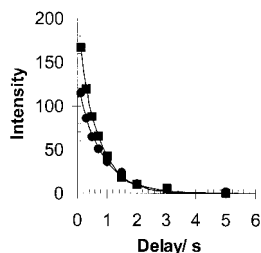
**Figure 8**  $^1\text{H}$  CRAMPS spectra of (a) plain chitosan, (b) PHB/chitosan 20/80 blend, (c) PHB/chitosan 40/60 blend, and (d) plain PHB. Peaks at negative ppm values (relative to TMS) are quadrature images. The twin-peak at 3.0 and 2.4 ppm is due to the nonequivalent protons in  $\text{CH}_2$  group of chiral PHB.

tial relaxations by simply changing the intensity axis to logarithmic scale. This cannot be done with inversion-recovery data unless we have the fully recovered intensity at long delay times. If there are not enough data points gathered at sufficiently long delay times, the inversion-recovery approach leads to systematic errors in the  $T_1$  measurements.<sup>15</sup> The same range of intensity change is realized with the decay-to-zero



**Figure 9**  $^1\text{H}$   $T_1$  inversion recovery of P(HB-co-HV)/chitosan 20/80 blend measured at 22°C. Solid squares (■) represent the intensity of chitosan vs delay time, and solid circles (●) the intensity of  $\beta$ -hydrogen of P(HB-co-HV).  $T_1$  for chitosan and  $\beta$ -hydrogen are fitted to be 0.63 and 0.78 s, respectively.



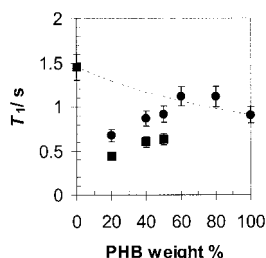


**Figure 10**  $^1\text{H}$   $T_1$  relaxation of P(HB-*co*-HV)/chitosan 20/80 blend measured at 22°C in the exponential decay to zero mode. The same range of intensity change is realized as with the inversion-recovery approach but with the added advantage that it requires only two fitted parameters for a single  $T_1$  instead of three for traditional inversion-recovery.  $T_1$  for chitosan (■) and  $\beta$ -hydrogen (●) are fitted to be 0.65 and 0.80 s, respectively.

approach as with the inversion-recovery approach, but it requires only two fitted parameters for a single  $T_1$  instead of three for inversion-recovery.

### $^1\text{H}$ $T_1$

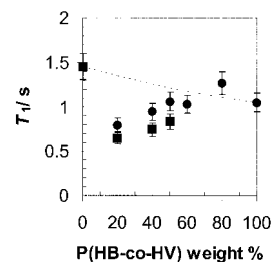
Figures 11 and 12 show the  $^1\text{H}$   $T_1$  values of PHB/chitosan and P(HB-*co*-HV)/chitosan blends, respectively.  $^1\text{H}$   $T_1$  relaxations of the blends are either faster than or intermediate to those of the plain polymers, which suggest that  $^1\text{H}$  spin diffusion is averaging out the intrinsic  $T_1$  relaxation of the different phases or domains within the blends. The spin diffusion coefficient within the rigid chitosan domain is mostly likely to be many times faster than that within either the more mobile PHB or P(HB-*co*-HV) domain. PHB and P(HB-*co*-HV) are semicrystalline, and so the spin diffusion coefficient within the crystalline phase and that within the amorphous phase are also different. We have not attempted to model our complicated mul-



**Figure 11**  $^1\text{H}$   $T_1$  for chitosan (■) at 3.7 ppm (relative to TMS) and  $\beta$ -hydrogen of PHB (●) at 5.4 ppm (relative to TMS) vs. wt % of PHB. The error bars indicate  $\pm 10\%$  uncertainty. Single exponential  $T_1$  values are observed, and the  $T_1$  values of chitosan and  $\beta$ -hydrogen follow each other closely. The dotted line represents the weight-averaged values based on the  $T_1$  of both plain chitosan and PHB according to the equation,

$$\frac{1}{T_1} = \frac{w_{\text{PHB}}}{T_{1,\text{PHB}}} + \frac{(1 - w_{\text{PHB}})}{T_{1,\text{chitosan}}},$$

where  $w_{\text{PHB}}$  is the weight fraction of PHB.

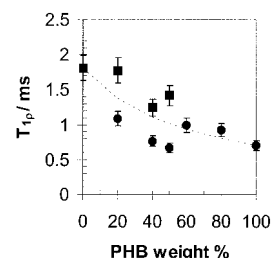


**Figure 12**  $^1\text{H}$   $T_1$  for chitosan (■) and  $\beta$ -hydrogen (●) vs. wt % of P(HB-*co*-HV). The error bars indicate  $\pm 10\%$  uncertainty. Single exponential  $T_1$  values are observed, and the  $T_1$  values of chitosan and  $\beta$ -hydrogen follow each other closely. The dotted line represents the weight-averaged values based on the  $T_1$  of both plain chitosan and P(HB-*co*-HV).

tiphase blends like other previously published works.<sup>16,17</sup> The single exponential  $T_1$  values of chitosan at 3.7 ppm, and  $\beta$ -hydrogen of PHB or P(HB-*co*-HV) at 5.4 ppm are not exactly the same but the differences are only 20–30%, which may be accounted for by the complex morphology in semicrystalline blends. The trends in the  $T_1$  values of chitosan, and  $\beta$ -hydrogen are clearly the same as shown in Figures 11 and 12. Therefore, together with the DSC results that show  $T_m$  depression and single effective  $T_g$  in the blends, the  $^1\text{H}$   $T_1$  results strongly suggest that chitosan is miscible with either PHB or P(HB-*co*-HV) on the length scale of less than 100 nm.<sup>18</sup>

### $^1\text{H}$ $T_{1\rho}$

Figures 13 and 14 show the  $^1\text{H}$   $T_{1\rho}$  values of PHB/chitosan and P(HB-*co*-HV)/chitosan blends, respec-



**Figure 13**  $^1\text{H}$   $T_{1\rho}$  for chitosan (■) and  $\beta$ -hydrogen (●) vs. wt % of PHB. The error bars indicate  $\pm 10\%$  uncertainty. Bi-exponential  $T_{1\rho}$  decay of  $\beta$ -hydrogen is observed. The single exponential  $T_{1\rho}$  of chitosan at 3.7 ppm and the fast  $T_{1\rho}$  decay component of  $\beta$ -hydrogen at 5.4 ppm in the blends follow the same trend as the weight-averaged values (dotted line) based on the  $T_{1\rho}$  of both plain chitosan and PHB according to the equation,

$$\frac{1}{T_{1\rho}} = \frac{w_{\text{PHB}}}{T_{1\rho,\text{fast,PHB}}} + \frac{(1 - w_{\text{PHB}})}{T_{1\rho,\text{chitosan}}},$$

where  $w_{\text{PHB}}$  is the weight fraction of PHB. The fast  $T_{1\rho}$  decay component of PHB is interpreted as the amorphous phase of PHB.

tively. A bi-exponential decay function is used to fit the  $T_{1\rho}$  relaxation data of the  $\beta$ -hydrogen at 5.4 ppm:

$$M_\tau = M_{0,\text{fast}} \exp\left(\frac{-\tau}{T_{1\rho,\text{fast}}}\right) + M_{0,\text{slow}} \exp\left(\frac{-\tau}{T_{1\rho,\text{slow}}}\right) \quad (1)$$

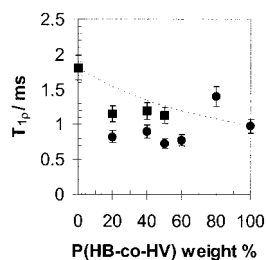
The fraction of the intensity of the slow decay component  $M_{0,\text{slow}}$  over the total intensity  $M_0$  is calculated, and is interpreted as the degree of crystallinity of either PHB or P(HB-*co*-HV). Figure 15 shows that  $(M_{0,\text{slow}}/M_0)$  has the same trend as the DSC data in Figure 2. The  $\beta$ -hydrogen  $T_{1\rho}$  values of the fast decay component and the chitosan  $T_{1\rho}$  values in the blends either follow the same trend as or faster than the weight-averaged values (dotted line in Figs. 13 and 14) according to the equation:

$$\frac{1}{T_{1\rho}} = \frac{w_{\text{PHA}}}{T_{1\rho,\text{fast, PHA}}} + \frac{(1 - w_{\text{PHA}})}{T_{1\rho,\text{chitosan}}} \quad (2)$$

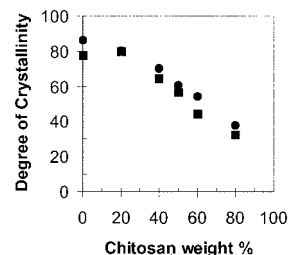
where  $w_{\text{PHA}}$  is the weight fraction of PHB or P(HB-*co*-HV). This strongly suggests that the amorphous phase of PHB or P(HB-*co*-HV) is miscible with chitosan on the length scale of less than 10 nm.<sup>18</sup>

## CONCLUSIONS

Based on the NMR and DSC results, we conclude that PHB/chitosan and P(HB-*co*-HV)/chitosan are intimately mixed at all compositions. The degree of crystallinity of PHB or P(HB-*co*-HV) in the blends measured with NMR decrease with increasing chitosan wt %, which agrees with the literature.<sup>12,13</sup> We have not attempted to measure the size of the crystalline PHB or P(HB-*co*-HV) domains with NMR but the depression of  $T_m$  with respect to that of plain PHB observed by DSC is indicative of strong intermolecular interactions between PHB and chitosan, and probably thinner lamellar thickness of the PHB crystals. The modi-



**Figure 14**  $^1\text{H}$   $T_{1\rho}$  for chitosan (■) and  $\beta$ -hydrogen (●) vs. wt % of P(HB-*co*-HV). The error bars indicate  $\pm 10\%$  uncertainty. Bi-exponential  $T_{1\rho}$  decay of  $\beta$ -hydrogen is observed. The single exponential  $T_{1\rho}$  of chitosan at 3.7 ppm and the fast  $T_{1\rho}$  decay component of  $\beta$ -hydrogen at 5.4 ppm in the blends are generally faster than the weight-averaged values (dotted line), which strongly suggests intimate mixing. The fast  $T_{1\rho}$  decay component of P(HB-*co*-HV) is interpreted as the amorphous component of P(HB-*co*-HV).



**Figure 15** The slow  $T_{1\rho}$  decay components of PHB and P(HB-*co*-HV) are interpreted as the crystalline component. The degree of crystallinity of PHB (●) and P(HB-*co*-HV) (■), which is calculated from the  $\beta$ -hydrogen slow  $T_{1\rho}$  decay component, vs. chitosan wt % agrees with the DSC data in Figure 2.

fied CRAMPS sequence for  $T_1$  decay-to-zero measurement mode suppresses background noise and yields a more desirable baseline. The method does not require the measurement of the fully recovered intensity at long delay times, and so it requires only two fitted parameters for a single  $T_1$  instead of three as in the traditional inversion-recovery method.

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