Miscibility and crystallization behavior of poly (3-hydroxybutyrate) and poly (ethylene glycol) blends studied by positron annihilation spectroscopy

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Abstract. Positron annihilation Lifetime (PAL) spectroscopy has been used to study the effect of PEG concentrations on the free volume properties of PHB. The data revealed that the ortho-positronium (o-Ps) lifetime τPs increases with 20% increase in concentration, decrease as the concentration increases to 40%, then rapid increase at 50% concentration of PEG. The o-Ps intensity, I3, shows a linear dependence as the concentration increases with a discontinuity at 20% concentration of PEG. Furthermore, the results presented and discussed in this work show that the PHB and PEG are miscible up to 40% of PEG but greater than 40%, the blend is immiscible. In addition, the mechanical properties of PHB are well improved by the addition of PEG with a low concentration up to 20%, while at higher concentration the blend becomes waxy.

1. Introduction

Positron annihilation lifetime (PAL) technique turned out to be a very useful method for the investigation of different aspects of polymer properties. It has been demonstrated that PAL technique is uniquely sensitive to free volume-based structural changes (glass transition, relaxation processes) in polymers. PHB is biotechnological polyester, highly crystalline, totally biodegradable with low versatility in mechanical properties and offers a high potential for application in drug-delivery systems. PHB has disadvantage: Thermally unstable during processing, stiff and brittle and low biodegradation rate. To overcome these problems, a reactive blend with a water soluble polymer is formed. Among the water soluble polymers, PEG is the most preferred candidate. The aim of this work is to improve the mechanical properties of PHB to be used in medical applications.

2. Experimental

2.1 Materials and Sample Preparation

PHB and PEG are white powders purchased from ALDERICH with a molecular weight of 230 kg/mol and 6000 g/mol, respectively. All PHB/PEG blend films were prepared by solution-cast technique using chloroform as the co-solvent. The PHB and PEG were dissolved separately in
chloroform before blending. Since PHB is insoluble in chloroform at room temperature, a magnetic stirrer was used to stir it for 150 min at 60 °C. The polymer concentration of each solution was 30 g/l. After the PHB and PEG solutions were well homogenized, they were mixed and stirred for 12 h. The mixed solution was poured on a poly Petri dish, then left at room temperature for 48 h and subsequently dried at 60 °C for further 120 h to eliminate the solvent completely [1].

2.2. PAL measurements
The PAL measurements were performed using a conventional fast-fast coincidence system. A positron source (22Na), sealed in a thin Kapton foil, and was sandwiched between sample (10 x10 mm² with a thickness of 1 mm) materials. The time resolution of the system was 240 ps (full width at half maximum, FWHM) with a time calibration of 54 ps/ch. PAL spectra containing 1.5x10⁶ counts were analyzed into three components (τ₁, τ₂, and τ₃) and their intensities (I₁, I₂ and I₃) determined using PALS Fit [2] and LT 9.0 programs [3] without source correction.

3. Results and discussion
The effect of concentration of PEG in PHB varying from 10% to 50% by weight on τ₃ & I₃ at room temperature is shown in (Figure 1). As shown in figure 1, the o-Ps lifetime, τ₃, increases with increasing PEG concentration up to 20% and then starts to decrease as the concentration increases up to 40% followed with a rapid increase at 50% concentration of PEG. The o-Ps intensity, I₃, shows a linear dependence as the concentration increased with a discontinuity at 20% concentration of PEG. The behavior of the lifetime parameters can be explained as follows: some PEG molecules must be retained in the PHB matrix and can also enter the free-volume holes of the PHB matrix during the transformation of blend solution into the dried blend membrane. However, the interaction between PHB and PEG can only occurs through the terminal hydroxyl groups of PEG via hydrogen bonds with the carbonyl groups of PHB. Increases in PEG increase the space between the chains of PHB, (forcing them a part) and therefore weakens the interactions between them. This effect is major at low concentrations, and hence the o-Ps lifetime, τ₃, increases as the PEG content rises till 20% [4].

![Figure 1. The effect of PEG concentration on (a)The o-Ps lifetime, τ₃, and the free volume hole size(b) The o-Ps lifetime intensity, I₃.](image-url)

At the range (0 - 20 %) of PEG concentration, the interaction between PEG segments and PHB chains is slightly increased and this lead to a partition effect to the free-volume holes of the PHB matrix. With further addition of PEG until 40%, the PEG molecules will fill the free volume inside the PHB matrix. Therefore, the o-Ps lifetime τ₁ and its intensity I₁ decrease .i.e. the PHB/PEG blend is fully miscible in the range (0 - 40 %) concentration [5]. At the concentration greater than 40%, the PEG molecules apt to crystallize and form a separate phase. Their poor interaction causes phase
separation, and the molecules in the interfacial zone of the PHB/PEG blend are less compact than within the PHB matrix. Therefore, the free-volume size in the interfacial zone was much larger than it is in the PHB matrix or the PEG phase. So, at higher concentration greater than 40%, the PHB/PEG blend is partially miscible [6]. The variation of the fractional free volumes with PEG concentrations shows two inflection points at 20% and 40% concentration of PEG (figure 2). It can be noticed that, the decrease in the fractional free volumes does not exceed 3.37% until 10% concentration of PEG. However, from 10 to 20% concentration of PEG, FFV increases then an appreciable decrease is observed in fractional free volume up to 40%. In addition, at 50% concentration of PEG, the FFV increases leading to the formation of much larger free volume holes which is due to the phase separation.

Figure 2. The Relative Fractional Free Volume hole, FFV, as a Function of PEG Concentration.

Figure 3 shows the effect of PEG concentration on the mechanical properties of PHB. As shown from the figure, the young’s modulus (E) slightly increases as the concentration of PEG increases, up to 40%, above which a rapid increase in E is observed. This is attributed to the interaction of PEG with PHB which hinders the chains from motion and reduces the force of secondary intermolecular bonds between PHB chains [7]. On the other hand, it is obvious that the tensile strength decreases with increasing the PEG concentration. It can be concluded that, the mechanical properties of PHB are approved with low concentration of PEG (20%), while at higher concentrations of PEG the flexibility decreases due to the increase in Young’s modulus.

Figure 3. The effect of PEG concentration on (a) Young’s Modulus (b) Tensile Strength

Using FT-IR, the frequency of the functional group, such as carbonyl, ether, or amide, is usually determined by the force constant (K) and mass of the bonded atoms [8]. If there is intermolecular hydrogen bonding between the hydroxyl group of PEG and the carbonyl group of PHB, the carbonyl bond energy of PHB may be reduced. Consequently, K of the carbonyl group will weaken and the peak may shift to a lower frequency [8]. Figures 4 & 5 show FT-IR spectra for the pure PHB and 50% concentrations of PEG, respectively. As can be seen from these figures the carbonyl peak of the
blends shifts to lower numbers gradually as the PEG contents are increased. This indicates that with increasing PEG content, the intermolecular hydrogen bonding in the PHB/PEG blends is gradually increased.

Figure 4. FT-IR spectrum for pure PHB.

From the wave number the force constant can be calculated [8]. It was found that the force constant decreases with increasing the PEG concentration then starts to increase at 50% of PEG concentration. This may be attributed to the fact that not all PEG molecules are included in the PHB matrix, i.e. PEG molecules agglomerate. Since the region between 880 cm\(^{-1}\) and nearly 1300 cm\(^{-1}\) is a crystalline-sensitive region [9]. One can confirm that the crystallinity of the PHB in the blend was suppressed by increasing PEG contents. The number of absorption peaks decreases with PEG content and disappear at the concentration greater than 20% of PEG concentration.

3. Conclusion
The differences in the miscibility of two blend systems in the solid state were demonstrated with PALS methods. PHB and PEG (6000) are miscible up to 40% of PEG but greater than 40% the blend is immiscible (PEG agglomeration). Mechanical properties of PHB are well improved by the addition of PEG up to 20%, while at higher concentration the blend becomes waxy. PHB interacts with PEG via the formation of a hydrogen bond but the hydrogen bond between PEG molecules is greater than that between PHB and PEG at high concentrations and consequently the phase separation (immiscibility) occurs at higher concentrations.

5. References
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