

Crystallization and Thermal Behaviour of Poly(3-hydroxybutyric acid)/Poly(vinyl acetate) Blend Films

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Blending of poly(3-hydroxybutyric acid) films with poly(vinyl acetate) was studied. The melting phase morphology and crystallization behaviour of the poly(3-hydroxybutyric acid) and poly(vinyl acetate) blends prepared by casting films have been studied by Fourier transform infrared (FT-IR), field emission scanning electron microscopy (FESEM) and differential scanning calorimetry (DSC). Likewise, there is no specific interaction between the two polymers was found by FTIR. In the blend the crystallization of poly(3-hydroxybutyric acid) was affected by the poly(vinyl acetate) component, particularly in their blends. The properties of poly(3-hydroxybutyric acid) were found to be improved by blending with poly(vinyl acetate) and the improvement is a function of the proportion of poly(vinyl acetate) in the blend. The thermal stability for the blends was more stable than the pure polymers. Thermogravmetric analysis (TGA) results showed three-step decomposition assigned to the thermal degradation of poly(3-hydroxybutyric acid) and poly(vinyl acetate). The melting temperatures of poly(3-hydroxybutyric acid) in the blends exhibited a slight shift. For the X-ray diffraction analysis, the crystallization rate was decreased by blending poly(3-hydroxybutyric acid) with poly(vinyl acetate).

Keywords: Poly(3-hydroxybutyric acid), Poly(vinyl acetate), Blending.

INTRODUCTION

Poly(3-hydroxybutyric acid) (PHB), was first observed in 1901. Poly(3-hydroxybutyric acid) described in detail only in 1920s, (by Lemogine who produced PHB using B. megaterium bacteria) [1]. Poly(3-hydroxybutyric acid) belongs to the polyhydroxyalkanoates (PHA) family. The research proceeded gradually on this material after its discovery [2,3]. Poly(3hydroxybutyric acid) has attracted a great deal of attention because of their thermoplastic properties and biodegradability. It is a thermoplastic polyester with a great potential owing to its biodegradability, biological synthesis and bioreabsorbation from a renewable source [4,5]. Poly(3-hydroxybutyric acid) has received considerable attention because of its renewability and biocompostability under both aerobic and anaerobic conditions. It has high crystallinity (more than 65 %), with a melting temperature of 170-180 °C. It has a glass transition temperature (T_g) between 4-8 °C, like those of polypropylene, but with very different mechanical properties.Usually PHB mixture with polymers that has good mechanical properties and degradability can be a solution to get additional environmental friendly biodegradable polymers [6-8]. Poly(3-hydroxybutyric acid) can be degraded to carbon dioxide and water under environmental conditions by various bacteria. It has much potential for applications of environmentally degradable plastics. But the physical properties of PHB are not suitable for some biomedical applications and biodegradable plastic because it displays some disadvantages properties, such as a lower biodegradation rate more than synthetic aliphatic polyesters and a limited process ability window [9]. Nevertheless, it is reported to be comparatively brittle and its melting behavior is unstable with a limited thermal processing [10,11]. The properties of poly(3-hydroxybutyric acid) are always compared to those of polypropylene since together compounds have similar melting degree (T_m), glass transition temperatures (T_g) and degrees of crystallinity. Nevertheless, PHB is more brittle and stiffer than polypropylene. Poly(3-hydroxybutyric acid) brittleness is mainly due to the existence of large crystallinities in the form of spherulites that are being formed upon cooling from the melt [12]. Polymer blending has been used to modify PHB and improve its properties and lower production costs. The growth of biodegradable polymer blends is of key importance to relieve environmental problems concerning the disposal of non-degradable plastic materials. Among these, PHB has been investigated and developed as one of the potential candidates for biodegradable plastics to decrease pollution caused by synthetic polymer waste [13].

The significance of PHB is included in twofold. Firstly, the uniqueness of its characteristics as both a thermoplastic and thus melt processable. Therefore, the biological origin of PHB gives it the potential to replace existing oil-based commodity polymers. Definitely, ICI Agricultural Division in association with Marlborough Biopolymers has explored this potential, setting a pilot scale fermentation plant to produce PHB in multikilogram batches. Secondly, PHB is an ideal model substance for fundamental studies for polymer nucleation, morphology and crystallization due to its exceptional purity and chemical regularity [9]. Poly(3-hydroxybutyric acid) has been well known that it has similar thermal and mechanical properties to polypropylene [14]. It is biodegradable in the environment by either hydrolytic degradation via variety of bacteria [15-18]. Poly(3-hydroxybutyric acid) has high crystallinity, brittle and stiff because it has been the matter of general studies as an environmentally friendly polymeric substance [18].

Biodegradable plastics are considered to bean attractive approach to environmental waste management and a suitable alternative of conventional polymers when recovery for recycling or incineration is not cost-effective or difficult. Numerous researches have focused on both the purely biodegradable, natural and synthetic polymers and on addition of biodegradable polymers to common thermoplastics [13]. Furthermore, blending of PHB has an effect in decreasing T_m, that implies the possibility of processing the materials within lesser temperature to limit degradation or avoid it [12]. Miscibility, biodegradation, blending and thermal stability between PHB and poly(vinyl alcohol) (PVA) [19,20], poly(hydroxybutyrate)/ poly(ethylene-co-vinyl acetate)/starch (PHB/EVA/starch) [21], poly(dl-lactide)-co-poly(ethylene glycol) [5], poly(ethyleneco-vinyl acetate) [22,23], poly(vinyl acetate-co-vinyl alcohol) [24], poly(vinylidene chloride-co-acrylonitrile) [25], chitosan [26], poly(*p*-vinylphenol) [27], cellulose acetate butyrate [28], poly(ethylene oxide) (PEO) [22,29,30], poly(epichlorohydrinco-ethylene oxide) (PECH-EO) [31], poly(epichlorohydrin) [32-36], dendrimers [6], poly([ɛ-caprolactone) [4,37], grafted with vinyl acetate [38]. Poly(3-hydroxybutyric acid) is grafting with PVAc (PHB-g-PVAc) and the surfaces of films were completely covered with graft chains. Also the enzyme PHB depolymerize could not attack the PHB substrate, lignin [39,40], poly(butylenesuccinate-co-[ɛ-caprolactone) [41], poly(butylene succinate) [42], hydroxyethyl cellulose acetate [10], starch acetate [43], poly(lactic acid) (PLA) [21,44], grafted poly-(ethylene glycol) (PEG) [45], organoclay nanocomposite [46], (glycidyl methacrylate) [47], poly(methyl methacrylate) (PMMA), (cyclohexyl methacrylate) (PCHMA) [48], grafted with acrylic acid [49], with flax fibers modified [50] have been investigated. In addition, PVAc is a thermoplastic which belong to the polyvinyl esters family. It is very useful polymers in everyday life. It has good adhesion to textiles, wood, paper, glass and leather [51,52].

There are many investigations being conducted on miscibility, crystallization behaviour, degradability of biodegradable polymers and thermal properties and their blends systems. However, there are few studies examine the rheological properties of PHB/PVAc blends or generic biodegradable polymeric system [13,53,54]. This result is improving the general physical properties of PHB and reducing the excess brittleness. Poly(3-hydroxybutyric acid) is well-known biodegradable thermoplastic polyester with a high degree of crystallinity. To improve these material properties, blending of PHB seems to decrease the melting temperature, thereby implying an improved possibility at a lower temperature to limit degradation. The aim of this research was modifications of PHB and to seek the possibility of improving the PHB thermal, mechanical properties and processability of PHB *via* the addition of PVAc.

EXPERIMENTAL

Poly(vinyl acetate) was bought from Sigma Aldrich (m.w. average = 100,000 by GPC), beads and used as receive without further purification. Poly(3-hydroxybutyric acid) was bought from Sigma Aldrich (m.w. average = 150,000) powder, natural source. Poly(3-hydroxybutyric acid) was melted in chloroform. Then, it poured into (1:1 v/v %) mixed solvent of methanol and *n*-hexane.

Procedure: Poly(3-hydroxybutyric acid) was dissolved in chloroform and poured into a mixed solvent of (1:1 v/v %)methanol and *n*-hexane. Poly(vinyl acetate) and PHB were weighted and dissolved in chloroform and followed by moderate stirring and heating around 55 °C for 48 h. Poly(3hydroxybutyric acid)/poly(vinyl acetate) blended solutions were prepared by adding the PVAc gradually drop by drop to the PHB. After that, they continued on the homogenizer under magnetic stirrer, around 55 °C. Then the PHB/PVAc mixtures were stirred at the thin speed for 1 h (Table-1).

TABLE-1 PREPARATION OF PHB AND PVAc BLENDS				
Solution blends	V _{PHB} (v/v %)	V _{PVAc} (v/v %)		
PHB/PVAc (100/0)	100	0		
PHB/PVAc (0/100)	0	100		
PHB/PVAc (95/05)	95	5		
PHB/PVAc (85/15)	85	15		
PHB/PVAc (75/25)	75	25		
PHB/PVAc (65/35)	65	35		

Preparation of blends: Thin films of PHB/PVAc blends with weight ratios of 0/100, 95/5, 85/15, 75/25, 65/35 and 100/0 were prepared by casting in glass dishes in chloroform as solvent. And on that point were allowed to evaporate the solvent at room temperature about 48 h, then keeping around 60 °C under vacuum for 48 h.

The range of the added PVAc to PHB was with various ratios and stirring for 1 h after blending. Blending films of solutions were obtained by casting onto glass dishes followed by drying around 60 °C for 48 h. Similar films from pure polymers were prepared using the same casting processes [55]. Structure details of pure PHB and pure PVAc are shown in Fig. 1.

Fourier transforms infrared spectroscopy (FTIR): The FTIR spectrum (Perkin Elmer, 2000) of polymer thin film was recorded on a spectrometer in the range of 4000- 400 cm⁻¹ at room temperature with a resolution of 4 cm⁻¹.

X-ray diffraction analysis (XRD): The XRD analysis is a convenient tool to determine the crystallization and structuren



Vol. 28, No. 3 (2016)

Fig. 1. Structure of pure PHB and pure PVAc

of the polymer [64]. XRD measurements of polyester sample were made on a PANalytical diffractometer system (High Score Plus) using CuK_{α} radiation (40 mA; $\lambda = 0.154$ nm; 40 kV) and the XRD patterns of polyesters were recorded at room temperatures in the range of $2\theta = 5^{\circ}$ to 80° atscan speed of 98 Sec. The percentage of crystallinity was calculated from diffracted intensity data [6,56,57].

Thermogravmetric analysis (TGA): Thermogravmetric analysis was done on a Perkin Elmer Pyris Diamond thermal instrument (TGA 4000) in the temperature range 50-700 °C. It is under N₂ at a flow rate of 10 cm³ min⁻¹ and scan rate of 20 °C min⁻¹ for temperature well above the degradation temperature of the polymers. Approximately 4-15 mg of samples was weighed into pan, then put it in TGA instrument and analyzed by the TGA. Both the onset degradation and maximum temperature are reported. The weight loss of curves *versus* temperature was constructed from the data found by the TGA instrument. The conversion rate curve was produced to indicate the mass loss conversion (%) during the time.

Field emission scanning electron microscopy (FESEM): The FESEM measurement was carried out to study the surface morphology of the blend and to study the compatibility of the blended films. The film surface image was observed at a voltage of 10 KV.

Differential scanning calorimetry (DSC): The DSC analysis was performed to study the thermal behaviour of the blends on DSC (Mettler-Toledo, model DSCC822e). It was used to measure T_m and T_g . Approximately 3-10 mg of samples was weighed. The samples were scanned under a nitrogen atmosphere at a constant rate of 10 °C per min.

RESULTS AND DISCUSSION

Fourier transform infrared spectroscopy analysis (FTIR): Fig. 2 shows the spectra of pure PVAc, pure PHB thin films and their blends. They show a broad peak at 3434 cm⁻¹ which is due to the O-H stretching. The PVAc shows a strong and sharp absorption peak at 1738 cm⁻¹ assign to C=O and in the pure PHB at 1734 cm⁻¹, but in their blends shown broad peak and decrease the value [46,58]. As shown in Table-2. The peaks in 2900-2800 cm⁻¹ region in all sample spectra are combining CH₂, CH₃ asymmetric and symmetric stretching modes.

Thermogravimetric analysis (TGA): Thermal degradations of PHB and PVAc have been studied by many researchers. The results of the degradation of PHB/PVAc blends by TGA have previously been reported by many researches. They showed that the addition of PVAc lowers the onset of PHB degradation temperature, although the addition of PVAc reduces



Wavelength (cm⁻¹)

Fig. 2. Typically FTIR spectra of pure PHB, PVAc and their blends 85/15, 75/25 and 65/35

TABLE-2 FTIR CHARACTERISTIC BANDS OF PHB/PVAc BLENDED THIN FILMS WITH DIFFERENT RATIOS AND THEIR PURE COMPONENTS

Perpetration		$v (cm^{-1})$		
reipenation	O-H	C-H	C=O	CH ₃
PHB/PVAc (100/0)	3436	2976, 2934	1734	1379
PHB/PVAc (0/100)	3457	2960, 2926	1738	1378
PHB/PVAc (95/5)	3437	2976, 2934	1735	1379
PHB/PVAc (85/15)	3436	2929, 2876	1715	1380
PHB/PVAc (75/25)	3435	2976, 2934, 2874	1730	1378
PHB/PVAc (65/35)	3436	2975-2874	1730	1378

the amount of material lost over the wide range of temperatures. The TGA results of PHB, PVAc and their blends shown in Fig. 3. It showed TGA curve was obtained in the range of temperature between 50 to 700 °C for the PHB, PVAc and their blends. The real percentages of weight were determined from these curves. The TG data analysis thermal degradation of the compounds is provided in Table-3. It was evident that intended compositions had been achieved for the composites. Poly(3-hydroxybutyric acid) thin film degrades thermally in one step with weight loss around 97.57 % at 276 °C [7,46,47,59]. The pure PVAc, whose thermal degradation takes place as two stages with weight loss around 67.4 % at 315°C [60]. The first stage is due to acetic acid at 280 °C, known as deacetylation while the second stage is due to the structural degradation of the polyene backbone occurs, leading to the



Fig. 3. TGA curves for (a) pure PHB; (b) PVAc, (c) 95/5, (d) 85/15, (e) 75/ 25 and (f) 65/35

TABLE-3 THERMAL PROPERTIES OF PHB/PVAc BLENDED THIN FILMS WITH VARIOUS PROPORTION				
	$T_{(decom.)}$ (°C)	T ₁ (%)	T ₂ (5)	T ₃ (%)
Pure PHB	276	97.57 % 238-311 °C	-	_
Pure PVAc	315	67.4 % 280- 404 °C	10.8 % 423-535 °C	-
PHB/PVAc (95/5)	282	95.623 % 237-308 °C	-	-
PHB/PVAc (85/15)	279	85.432 % 246-313 °C	8.753 % 313-396 °C	2.169 % 425-502 °C
PHB/PVAc (75/25)	274	80.6 % 248.8-312 °C	12.155 % 315-386 °C	2.804 % 432-496 °C
PHB/PVAc (65/35)	278.9	73.12 % 254.2-310.3 °C	16.88 % 310-387 °С	6.17 % 432-556 °C

evolution of toluene, aliphatic hydrocarbon and benzene at 423 °C [37,45,61,62]. The first peak due to decomposition of PHB while the second peak is corresponds to deacetylation of PVAc. The third stage corresponds to structural breaking of polyolefinic backbone of the polymers.

X-ray diffraction analysis (XRD): Fig. 4 shows typical X-ray diffraction patterns of pure PHB, PVAc and their blends. The XRD pattern of pure PVAc is shown to have low crystallinity or amorphous nature [18,51,63]. The XRD of the pure PHB showed that it has a semi crystalline nature, which is in good agreement with the results reported earlier [46]. The crystallinities decrease from 73.6 to 50 % as the PVAc fraction was increased from 5 to 35 % [56]. The diffraction patterns of physical mixtures showed varied peaks which is similar to pure form. It indicates that the crystallinity of PVAc and PHB was not changed [6,56,57,64]. While by adding PVAc, the curves present a better resolution for peaks than that of PHB. Moreover, the intensities of the crystalline peaks of the blending obviously increased, thereby appear small peaks [46].

Field emission scanning electron microscopy (FESEM): In this work, the morphology of the blends was examined using



Fig. 4. XRD pattern for (a) pure PHB, PVAc and (b) their blends

a field emission scanning electron microscope to study the compatibility of the blended films (FESEM). The film surface was observed at a voltage of 10 KV to examine the phase morphology. It was observed on the surface of pure polymers and their blends are shown in Fig. 5. Poly(vinyl acetate) was amorphous while PHB was semi-crystalline. It presents the micrographs of the pure polymer and their blends and an increase in the porosity of the samples can be seen when the proportion of PVAc is increased. The pure PVAc surface was strap surface and also their blends shown pores and smooth surface [65]. The pure PHB surface was homogenous. It has pores even though itis quite brittle [1,66,67] while pure PVAc was strap surface.



Fig. 5. Field emission scanning electron micrographs of pure polymers and their blends

Differential scanning calorimetry (DSC): Fig. 6 showed the DSC of pure polymer and their blends. Poly(3-hydroxybutyric acid) exhibited two endothermic peaks at 158 and 176 °C. The higher temperature peak at 176 °C is assigned to the melting of the crystalline film, which means the existence of main crystallite regions with more perfect structure. The Δ H and T_m were taken as the peak values of the endothermic processes in the curves. As shown in Table-4, PHB/PVAc (75/25) and PHB/PVAc (65/35) have a higher thermal stability than others compositions, where melting temperatures are higher. The melting point of PHB/PVAc blends in the heating cycle was a bit increased when PVAc increased. With increasing PVAc contents, it's easy to understand as stated that blending of the PHB with high melting point cause the increase of PHB melting point. Both

TABLE-4						
THERMAL PROPERTIES OF PURE POLYMER THIN FILMS TOGETHER WITH THEIR BLENDED FILMS						
Blend composition PHB/PVAc	100/0	95/5	85/15	75/25	65/35	0/100
T _m °C first run	176	172.91	174.03	175.21	175.07	150
ΔH (J/g)	106.6	101.27	90.61	79.95	69.29	127



melting temperatures were decreased, as the PVAc content in the blend was increased (Table-4). The size of each endotherm was gradually decreased with the PVAc content [1,68].

Conclusion

The properties of PHB were modified by blending with various proportions of PVAc. The results of TGA showed that the addition of the PVAc causes improved the thermal stability of PHB component. Thermal stability of the pure polymers was less stable than their blends. The thermal stability of pure PHB was improving with blending with PVAc. Evidence of miscibility has been investigated by means of DSC. The thermal degra-dation and mechanical properties of pure polymers and their blends were investigated. With increasing PVAc content in the PHB/PVAc blends, the C=O for the blends decreased from 95 to 65 mL for the pure polymers. When PVAc to PHB add does not affect the crystal structure. The decrease in crystallinity is an indication of miscibility. For the XRD, the crystallization rate was decreased by blending PHB with PVAc.

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