Miscibility and Thermal Degradation Kinetics of Poly-β-Alanine/Poly(3-hydroxypropionate) Blends

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Abstract: Poly-β-alanine (PBA) and poly(3-hydroxypropionate) (PHP) were synthesized via base-catalyzed hydrogen transfer polymerization (HTP) of acrylamide and acrylic acid, respectively. Blends of PBA/PHP with different composition (PHP content, 5% to 75%) were studied using FTIR, DSC, TGA, XRD and polarized optical microscope to reveal both miscibility and thermal degradation kinetics of PBA/PHP blends. Optical images of blends were transparent and entirely uniform. Characteristic FTIR bands of both components shifted in higher frequencies with increasing fraction of another component. Melting temperature (T_m), thermal decomposition temperatures (T_d), and enthalpy of fusion (ΔH_f) of PHP decreased with increasing PBA fraction in blends. Thermal degradation kinetics of both components were studied by Freeman-Carroll method. Activation energies of thermal degradations of blend components were determined with good regression coefficients (at least 0.994). Activation energies of decomposition decreased from 224.14 to 86.125 kJmol^{-1} with increasing PHP content. XRD spectra of blends exhibited lower peak intensities than those of neat polymers. The spectroscopic, thermal, and optical methods revealed that PBA and PHP were miscible with a good compatibility in amorphous phase.

INTRODUCTION

Poly(3-hydroxypropionate) (PHP) or poly(β-propiolactone) is a well-known biodegradable [1] thermoplastic polyester with high tensile strength, elongation at breaking, and high moisture permeability. There are some reports on its potential utilization as scaffold material in tissue engineering [2] and polymeric matrix for drug delivery [3]. Although PHP has attracted much attention as an environmentally degradable polymer to be used for medical applications, it has limitations due to its brittleness (high crystallinity), narrow processability, and high hydrophobicity. Some studies were reported on blends [4-7] of PHP to eliminate these limitations. Similarly, various [8-11] copolymers of PHP have been prepared in order to combine its favorable properties with those of other components.

Comparing to aliphatic polyesters, aliphatic polyamides possess higher thermal stability, higher moduli, and higher tensile strength. Poly-β-alanine (PBA), sometimes described as nylon-3 or polyamide-3, is a crystalline poly(amino acid) with a high thermal (melts above 350 °C with decomposition [12]) and mechanical resistance [13].

Polymer blends are becoming more important in specific sectors of polymer industry, as they can frequently meet performance requirements that cannot be satisfied by the currently available commodity polymers. It is possible to obtain polymer blends of more desirable properties by mixing miscible polymers, and thus it is very important to examine the factors affecting the miscibility of polymer mixtures. Therefore, it is reasonable to combine the favorable properties of these two classes of polymers to produce a new polymeric material possessing good material properties and processability.

Thermal degradation of polymers and polymer blends is generally investigated by using thermogravimetry (TGA), differantial thermal analysis (DTA) and differantial scanning calorimetry (DSC). Mass losses and heat transfers due to the physical and chemical phenomena are examined by TGA and DSC or DTA, respectively.

The consideration of favorable properties of PHP and PBA motivated us to investigate their blends in the aspect of miscibility and thermal degradation behavior. Moreover, thermal stabilities of PHP, PBA and some of their blends were compared in the study.

MATERIALS AND METHODS

Acrylic acid (99%, Aldrich), acrylamide (99%, Aldrich), sodium tertiary butoxide (97%, Aldrich), phenyl-β-naphthylamine (97%, Aldrich), potassium chloride (99%, Sigma-

Aldrich), formic acid (99%, Sigma), o-dichlorobenzene (99%, Aldrich) were obtained commercially and used without purification.

Hydrogen transfer polymerization (HTP)

Acrylic acid ([M] = 0.07 mol) was placed into a three-necked flask. tBuONa ([I]=[M]/70) as initiator and catalyst, phenyl-β-naphthylamine (5 mg) as radicalic polymerization inhibitor and well-dried KCl ([KCl]=[M]/3) were added into the reaction flask. Reaction mixture was stirred under nitrogen flux at 90 °C in the dark for 48 h. The reaction mixture was poured into excess amount of diethyl ether to precipitate the PHP crystals out. The product was filtered and dried at room temperature and stored at 40 °C in a vacuum oven. PBA was prepared as described in Masamoto's report [14].

Blending and characterizations

Gel permeation chromatography (GPC) was performed using a Tosoh EcoSEC system equipped with a refractive index detector. Chloroform and hexafluoroisopropanol (HFIP) were used as solvents for PHP and PBA, respectively. The flow rate was 0.35 mL/min, and the column temperature was 35 °C. Monodispersed poly(methyl methacrylate) standards were used to calibrate the column. Number average molecular weights of PHP and PHP were determined as 3200 and 40000 gmol^{-1}, respectively. Polymer blends (10% w/v) were prepared using formic acid. PHP contents of the blends were in ratios of 5%, 10%, 25%, 50% and 75% by weight. The blend solutions were stirred vigorously overnight at room temperature. The solutions were cast into Petri dishes, dried at room temperature, and stored in vacuum oven overnight before analysis. DSC curves of neat polymers and blends were recorded using TA instrument 2920 Modulated DSC with 10 °C min^{-1} heating rate under nitrogen flux. Thermogram of neat polymers and blends were obtained using TA instrument Hi-Res TGA 2950 with 10 °C min^{-1} heating rate under nitrogen flux. XRD spectra of the film samples were recorded using a Bruker AXS Dimension D8 X-Ray System in a range of 7 to 35° (2-theta) using 20 kV with 5 mA current. FTIR spectra of neat polymers and blend films were recorded at room temperature using a Nicolet 380 FTIR spectrometer. The spectra were collected over the range 3400 to 1200 cm^{-1} with a resolution of 4 cm^{-1} using 32 scans.

RESULTS AND DISCUSSION

Optical Microscopy

Optical microscopic images of the blend films were recorded to obtain the first information about the compatibility of polymers. Although both PHP and PBA are white powders before

blending due to the high crystallinity of the polymers, solution-cast films of 10% and 25% PHP blends were completely transparent and uniform. This is a simple indication of miscibility of PHP and PBA. Optical microscopic images of blends were shown in Figure 1.
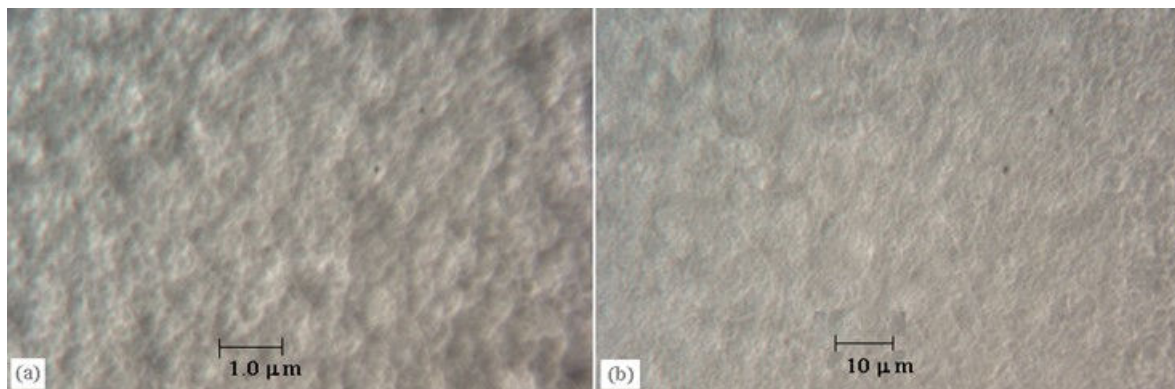

Figure 1. Polarized optical microscopic images of (a) 10% PHP and (b) 25% PHP blends.

FTIR Spectroscopy

FTIR spectroscopy provides crucial evidences on both crystallization and miscibility of polymer blends. Both PBA and PHP are highly crystalline due to the strong segmental interactions (dipole-dipole interactions in PHP and hydrogen bondings in PBA). The strong segmental interactions lead to decrements in the bond orders of corresponding functional groups ($C=O_{amide}$, NH_{amide} and $C=O_{ester}$) in the neat polymers. Consequently, FTIR spectra of the neat polymers give corresponding FTIR bands at lower frequencies than those in case of the strong interactions eliminated. Blending the polymers may destroy the strong interactions between the neat polymer chains resulting in increment in distance between the chains, decrement in crystallinity and hence increment in chain mobility. FTIR spectra of blends were expected to show corresponding bands at higher frequencies [15-18] than those in neat forms since chain mobility enhanced. Consequently, FTIR spectra of PBA/PHP blends were obtained to assess any structural changes that may have occurred upon blending as they affect the crystallinity and miscibility of the blend films. FTIR spectra of PBA/PHP blends with various compositions are shown in Figure 2.
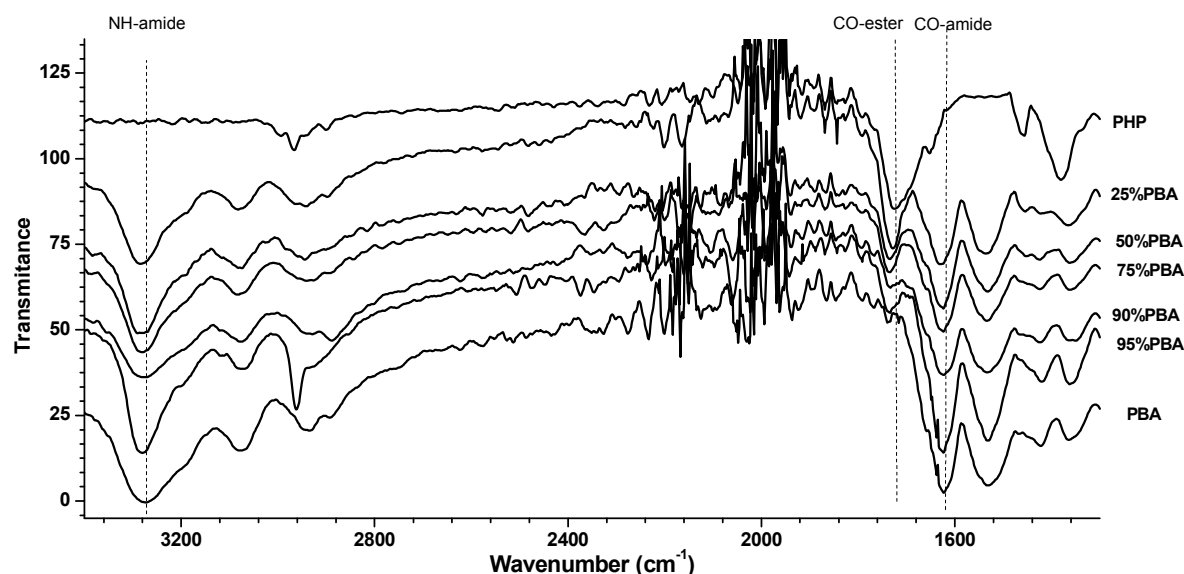
Figure 2. FTIR spectra of neat polymers and blends a) NH stretching b) CO_{ester} and CO_{amide} stretching.

Wavenumber shifts originating from blending for characteristic amide (N-H stretching and CO carbonyl stretching) and ester (CO carbonyl stretching) bands are summarized in Table 1. Examination of data listed in Table 1 reveals that, upon blending, wavenumber, $v_{C=O}$ $_{(ester)}$ value of 1725.0 cm^{-1} in neat PHP shifted up to 1737.2 cm^{-1} with increasing PBA content. These shifts to higher wavenumbers mean improvement of bond order for the corresponding group (ester CO) due to extinction of the previous segmental interactions (here, dipole-dipole interactions).

Similarly, $v_{NH(amide)}$ values in neat PBA (3272.5 cm^{-1}) also shifted to higher wavenumbers (3289.1 cm^{-1} for 75% PHP) with increasing PHP content, revealing increment in bond order for NH, and hence, the extinction of hydrogen bonding between amide CO and amide NH.

We also have observed shifts in v_{CO} amide band (1622.8 cm^{-1}) to higher wavenumbers (1629.8 cm^{-1} for 75% PHP) by increasing the ratio of PHP in the blends. This result indicates enhancement in bond order for the corresponding amide CO group due to the extinction of self-associated hydrogen bonding, and it provides a clear evidence for penetration of PHP chains through the nylon crystal lattice.

Table 1. FTIR data of neat components and their blends.

	PBA	5% PHP	10% PHP	25% PHP	50% PHP	75% PHP	PHP
CO_{amide}	1622.8	1623.1	1623.7	1623.7	1624.3	1629.8	-
CO_{ester}	-	1737.2	1733.6	1735.4	1735.4	1729.3	1725.0
NH_{amide}	3272.5	3280.4	3280.6	3280.6	3284.9	3289.1	-

Differential Scanning Calorimetry

DSC curves for pure PHP and PBA/PHP blends are shown in Figure 3. Thermal behavior of PBA was not examined since PBA melted at around 350 °C and decomposition accompanied immediately after melting process began. The data derived from the first heating scans of DSC for PHP powder and PBA/PHP blends are listed in Table 2. The DSC curves show endothermic melting peak centered at 69.0 °C for pure PHP. The melting temperature of PHP in the blends decrease consistently with increasing PBA content. Even blends with minor PHP content (5% and 10% PHP) did not exhibit any melting peak. These decrements indicate that PHP chains acquire enhanced mobility after blending leading to lower T_m values. In general, a decrease in the melting point in a polymeric blend can be due to both morphological effects (decrease in lamellar thickness) and to thermodynamic factors [15] (polymer-polymer interactions).
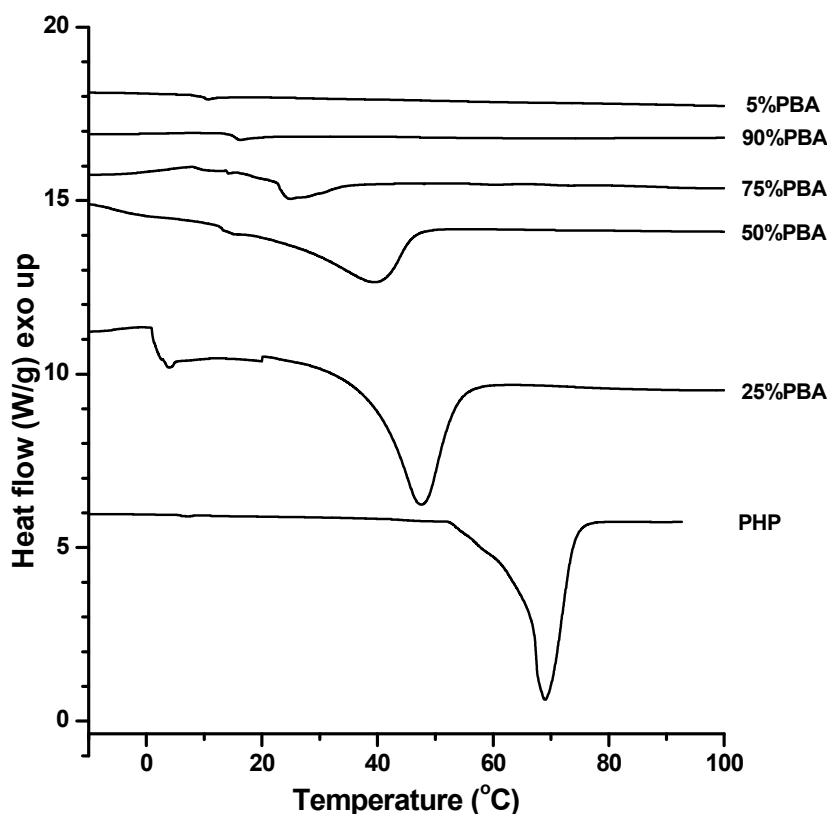

Figure 3. DSC curve of PHP and its blends with PBA.

Apparent enthalpy of fusion for PHP decreased in the blend samples. Percent crystallinities of PHP in the blend films were estimated by dividing the apparent fusion enthalpies of PHP in blends to fusion enthalpy of neat PHP [19], 140.9 J/g. Based on the data listed in Table 2, relative crystallinities of PHP in all blend samples were lower than that in neat PHP. Although both PHP and blend films were prepared using the same route (solvent, drying time, drying temperature), suppression of percent crystallinity of PHP in the blends may

be attributed to penetration of PBA to the crystal lattice of PHP. Another factor that lowers the degree of crystallinity for PHP is the difference in the molecular mobility between PHP and PBA. The difference in the glass-transition temperature between PBA and PHP (110-120 °C) influences the degree of crystallinity of their blends. Such a result is probably due to the trapped fraction of PBA in the interlamellar amorphous regions of PHP spherulitic behavior which is not allowed to crystallize. Therefore, the influence of PBA on the crystallinity of PHP can be considered to be the proof of miscibility (compatibility) of the two polymers. The DSC results in this work revealed that blending PBA with PHP suppressed the crystallinity of PHP in the blend films. In all, the DSC results supported our earlier finding in FTIR analysis that the crystallinities of PBA/PHP blends were suppressed compared with pure components.

Table 2. DSC data of neat PHP and blends.

	PHP	25 % PHP	50% PHP	75% PHP	10% PHP	5% PHP
T_m (°C)	69.0	28.4	39.5	48.4	-	-
ΔH_f (J g^{-1})	104.3	9.1	27.9	34,3	-	-
X_c	74.0	6.5	19.8	24.3	-	-

X-ray Diffraction Spectroscopy

XRD spectra patterns of crystalline polymers may be used to extract qualitative information on the degree of crystallinity of polymers and blends [17, 20]. In this study, XRD spectra of neat PHP /PBA and their blend films shown in Figure 4 were obtained to understand the effect of blending on the degree of crystallinity of each component. The XRD spectra reveal that diffraction intensities of blend films are lower than those of the individual components. The sharp peaks observed in the neat PHP film spectrum diminish in intensity with increasing PBA content in the spectra. Since the areas under these peaks can be used as measure of the degree of crystallinity, reduction in these areas may be attributed to suppression in the degree of crystallinity for both components (PHP and PBA) upon blending. Each blend component seems to trap the segments of the other in the amorphous phase hindering the mobility required for crystallization. This results in a lower degree of crystallinity.
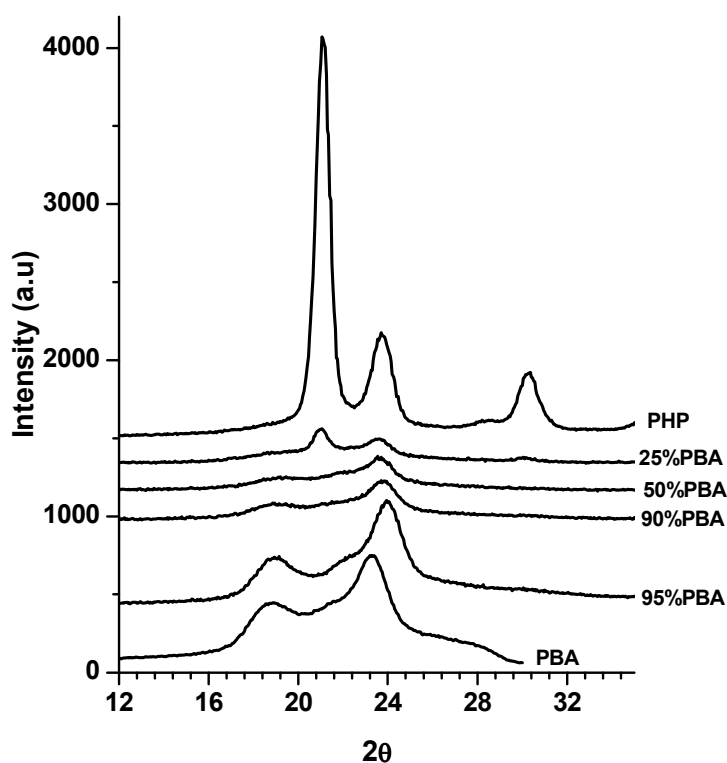
Figure 4. XRD spectra of the neat polymers and their blends.

Thermogravimetric Analysis

Thermogravimetric analyses of neat components and blend films were performed to see the effect of each component on the decomposition behavior over the others. The TGA and DTG decomposition curves of neat polymers and blends are shown in Figures 5 and 6. The TGA and DTG curves were used not only to compare thermal stabilities of neat polymers and their blends but also to investigate the kinetics of thermal degradation reactions [21]. It is obvious that both neat polymer decomposes through a fast reaction at single-step in different temperature domains.

Onset temperature of degradation (T_i), half-life temperature (T_h), maximum rate temperature (T_{max}), final temperature at degradation (T_f) and maximum mass loss rate (R_{max}) were listed in Table 3 to compare thermal stabilities of neat polymers and their blends. As easily shown in Figure 5 and 6, thermal stability of PBA is much higher than PHP. Moreover, PHP decomposes completely before PBA begins to decompose. It may be estimated that blending with PHP and PBA will result in elevation of thermal stability of PHP. Thus, the changes in T_i (488 to 492K), T_f (523 to 531K) and T_{max} (514 to 519) for 25% blend confirm this estimation. However, the values of T_i, T_f and T_{max} for the 50%, 75% and 90% blends (PBA dominant blends) are lower than those of neat PHP, that is an

indication of negative impact of PBA on the thermal stability of PHP. The values of T_i, T_f and T_{max} given in brackets, corresponding to the thermal degradation of PBA in the blends, increase with increasing PBA content in the blends. Similarly, the half-life temperatures (T_h), represent both degradation reactions, increase with increasing PBA content. Besides, addition of PBA causes depression in the rate of first degradation reaction, R_{max} and elevation in the rate of second degradation, R_{max} (in brackets).
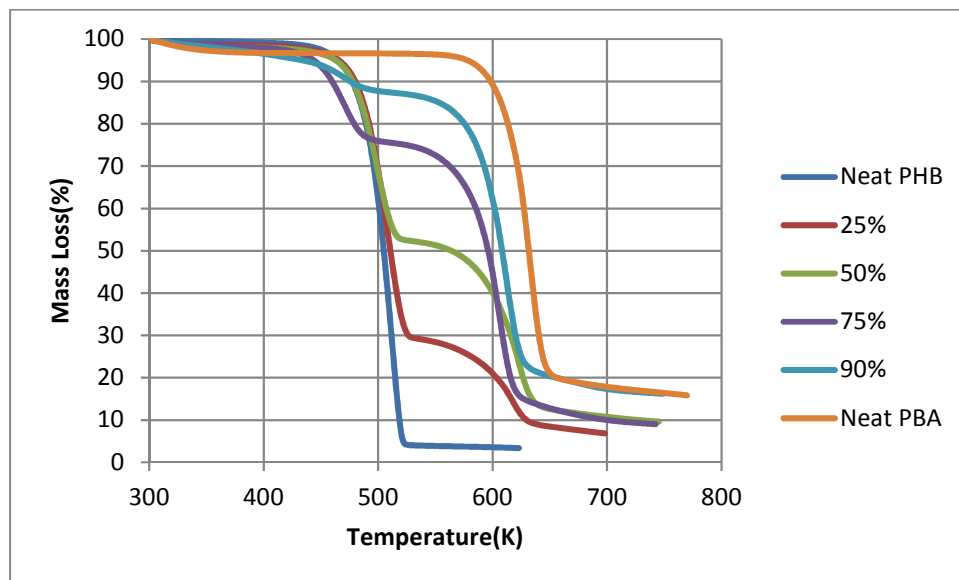

Figure 5. TGA curves of the neat polymers and their blends.
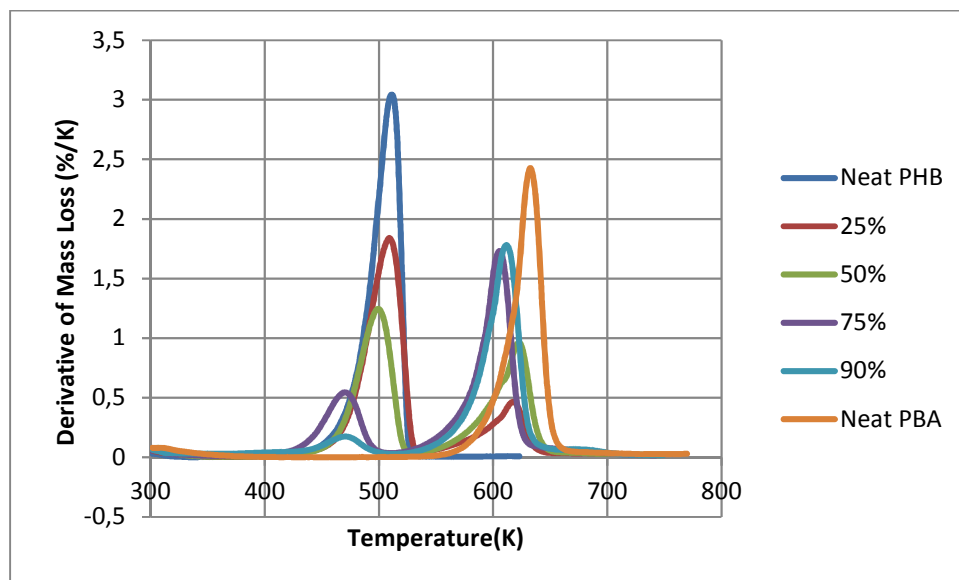

Figure 6. DTG curves of the neat polymers and their blends.

Table 3. Differential TGA curve data of the neat polymer and their blends. *The values given in brackets belong to the second thermal degradation.

PBA%	T_i(K)	T_f(K)	T_h(K)	T_{max}(K)	R_{max}(%/K)
0	488	523	507	514	3,04
25	492(592)	531(639)	520	519(627)	1.839(0.465)
50	484(602)	518(641)	571	505(630)	1.246(0.962)
75	475(612)	512(644)	623	497(633)	0.5446(1.73)
90	470(611)	507(646)	629	492(632)	0.175(1.780)
100	(610)	(644)	631	(633)	(2.427)

Freeman-Carroll method [22,23] is widely used in the kinetic analysis of thermal degradation of polymers and blends since it gives not only total reaction order but also activation energy of degradation. Since the activation energy of thermal degradation reaction obtained from the method belongs to overall of the thermal degradation, it is more useful than the parameters (T_i, T_{max}, T_h and T_f), which represents specific points of the reaction, for comparison of thermal stability of polymers.

Freeman-Carroll equation (Eq.1) has been used to determine the total reaction orders and activation energies of thermal degradation reactions. Graphs of $\Delta \ln(dC/dT)/\Delta \ln(1-C)$ versus $\Delta(1/T)/\Delta \ln(1-C)$ for each neat polymer and their blends have been plotted.

$$\frac{\Delta \ln(dC/dT)}{\Delta \ln(1-C)} = n - \frac{E_A}{R} \frac{\Delta(1/T)}{\Delta \ln(1-C)}$$

(Eq. 1)

Figure 7 shows the Freeman-Carroll graph of 90% PBA blend. Intercept and slope of the straight line give total reaction order and activation energy of the thermal degradation, respectively. Activation energies of thermal degradations of blends were determined with good regression coefficient (at least 0.994). Activation energies of decomposition increased from 86.125 to 224.14 kJmol^{-1} with increasing PBA content. The results obtained for the all sample were listed in Table 4.
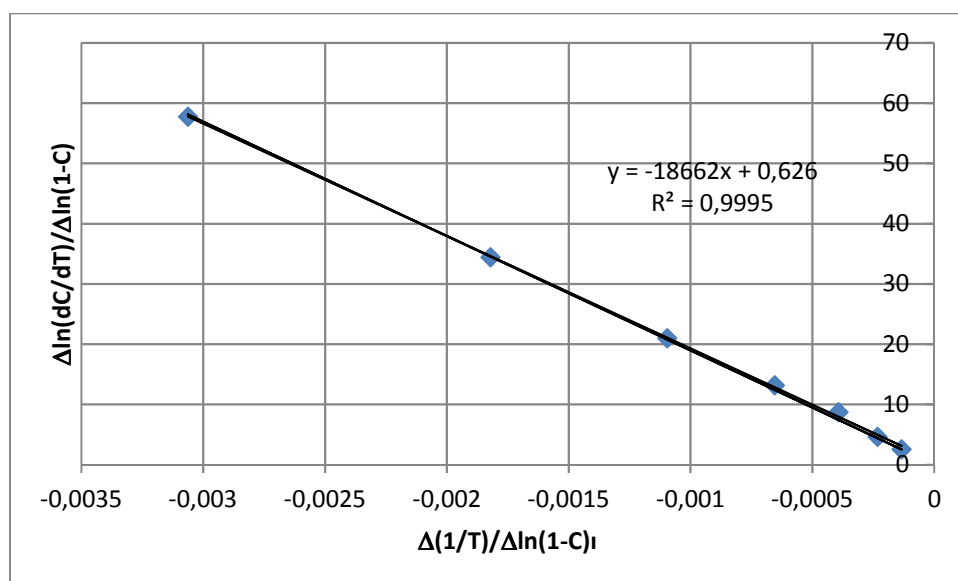
Figure 7. Freeman-Carroll graph of 90% PBA blend.

Table.4 Data obtained from Freeman-Carroll method for thermal degradations of neat PBA and PHP, and their blends.

PBA (%)	n	Slope	E_A(kJ/mol)	R^2
0	0.311	-10359	86	0.994
25	0.475	-10109	84	0.9961
50	-0.370	-13476	112	0.9985
75	0.198	-13702	113	0.9954
90	0.626	-18662	155	0.9995
100	-0.329	-26963	224	0.9996

CONCLUSION

In a thermodynamic sense, the formation of miscible PHP /PBA blends were favorable as attributed to the formation of strong hydrogen bonds between the components (enthalpic decrement), and suppression of high crystallinity in both the PHP and PBA components (entropic enhancement). Based on this point of view, the purpose of this work was to study the miscibility of PBA and PHP blends by using Differential Scanning Calorimetry (DSC), Fourier Transform Infrared Spectroscopy (FTIR), Thermogravimetric Analysis (TGA), X-Ray Diffraction Spectrometry (XRD), and Polarized Optical Microscopy (PEM).

These thermal, spectroscopic, and optical techniques revealed that the blends of PBA/ PHP are miscible in amorphous phase. The miscibility has been shown to be based mainly on suppression of crystallinity of both components in the blends. Such a decrease in the total crystallinity should be considered a very important factor for decreasing its brittleness and improving its other relevant material properties by tuning the amount of PBA to be blended.

PBA and PHP decompose thermally via fast and single step degradation. Thermal stability of PBA is higher than that of PHP. Moreover, PHP decomposes completely before PBA begins to decompose. Hence, blends of the polymers give TGA curves with two steps. Basically, PHP in the blends decomposes at the first step and then PBA decomposes at the second step. Increase in the PBA content (excluding 25%) in the blends depresses T_i, T_f and T_{max} values of first step and elevates T_i, T_f and T_{max} values of second step. Conversely, values of T_h and E_A, represent overall reaction, show that addition of PBA elevates the thermal stability of PHP. This behavior may be explained through wrapping of PHP chains by PBA chains, which is a result of miscibility. Blend with 25% PBA supports this approach. However, when PBA is dominant in blends (50%, 75% and 90%) it may behave as a barrier, hinder to remove of primary degradation product of PHP (acrylic acid), and then cause an autocatalytic effect on the thermal degradation of main polymer [24].

REFERENCES

1.   Furuhashi Y, Iwata T, Kimura Y, Doi Y. Structural characterization and enzymatic degradation of α-, β-, and γ-crystalline forms for poly(β-propiolactone). Macromol. Biosci. 2003; 3:462–470. DOI: 10.1002/mabi.200350020.

2.   Cortizo M S, Molinuevo M S, Cortizo A M. Biocompatibility and biodegradation of polyester and polyfumarate based-scaffolds for bone tissue engineering. J. Tissue. Eng. Regen. Med. 2008; 2:33–42. DOI: 10.1002/term.62.

3.   Cortizo M S, Alessandrini J L, Etcheverr S B, Cortizo A M. A vanadium/aspirin complex controlled release using a poly(beta-propiolactone) film. Effects on osteosarcoma cells. J. Biomater. Sci. Polym. Ed. 2001;12: 945-959. DOI: 10.1163/156856201753252499.

4.   Cao A, Asakawa N, Yoshie N, Inoue Y. Phase structure and biodegradation of the Bacterial poly(3-hydroxybutyric acid)/chemosynthetic poly(3-hydroxypropionic acid) blend. Polym. J. 1998; 30:743-752. DOI: 10.1295/polymj.30.743.

5.   He Y, Asakawa N, Inoue Y. Biodegradable blends of high molecular weight poly(ethylene oxide) with poly(3-hydroxypropionic acid) and poly(3-hydroxybutyric acid) a miscibility study by DSC, DMTA and NMR spectroscopy. Polym. Int. 2000; 49:609–617. DOI: 10.1002/1097-0126(200006)49:6<609:AID-PI426>3.0.CO;2-6.

6.   Kumagai Y, Doi Y. Enzymatic degradation of binary blends of microbial poly(3-hydroxybutyrate) with enzymatically active polymers. Polym. Degrad. Stabil. 1992;37: 253-256. DOI: 10.1016/0141-3910(92)90167-4.

7.   Autran J P M. US Patent 7,265,188 B2 Sept 4 2007 assigned to The Procter&Gamble Company. URL: https://www.google.com/patents/US7265188.

8.   Ichikawa M, Nakamura K, Yoshie N, Asakawa N, Inoue Y. Morphological study of bacterial poly(3-hydroxybutyrate-co-3-hydroxypropionate). Macromol. Chem. Phys. 1996; 197: 2467–2480. DOI: 10.1002/macp.1996.021970811.

9.   Cerrai P, Tricoli M, Andruzzi F. Synthesis and characterization of polymers from β-propiolactone and poly(ethylene glycol)s. Polymer 1987; 28:831-836. DOI: 10.1016/0032-3861(87)90236-9.

10.   Zhou Q, Shi Z Y, Meng D C, Wu Q, Chen J C, Chen G Q.   Production of 3-hydroxypropionate homopolymer and poly(3-hydroxypropionate-co-4-hydroxybutyrate) copolymer by recombinant Escherichia coli. Metab. Eng. 2011; 13:777–785. DOI: 10.1016/j.ymben.2011.10.002.

11.   Andreeßen B, Steinbüchel A. Biosynthesis and Biodegradationof 3-Hydroxypropionate-Containing   Polyesters. Appl. Environ. Microbiol. 2010; 76:4919-4925. DOI: 10.1128/AEM.01015-10.

12.   Camino G, Guaita M. A DTA Study of Crystallization on Heating of Branched Poly(imino(1-oxotrimethylene)), Nylon3. Euro. Polym. J. 1977; 13:903-905. DOI: 10.1016/0014-3057(77)90063-5.

13.   Masamoto J. Nylon-3. Rep. Prog. Polym. Phys. Jpn. 2000; 43:867-876.

14.   Yamamoto F, Misumi T. US Pat. 5,015,707, (1991) assigned to Asahi Chemical. URL: http://www.google.com/patents/US5015707

15.   He Y, Zhu B, Inoue Y. Hydrogen-Bonds in Polymer Blends. Prog. Polym. Sci. 2004; 29:1021-1051. DOI: 10.1016/j.progpolymsci.2004.07.002.

16.   Zakaria Z, Izzah Z, Jawaid M, Hassan A. Effect of degree of deacetylation of Chitosan on thermal stability and compatibility of Chitosan-polyamide blends. Bioresources.2012;7:5568-5580. URL: https://www.ncsu.edu/bioresources/BioRes_07/BioRes_07_4_5568_Zainoha_THJ_Deacetylation_Chitosan_Thermal_Stab_Amide_3078.pdf

17.   Liu Y, Shao Z, Zhou P, Chen X. Thermal and crystalline behavior of silk fibroin/nylon 66 blend films. Polymer. 2004; 45:7705- 7710. DOI: 10.1016/j.polymer.2004.09.005.

18.   Mousavioun P, Doherty W O S, George G. Thermal stability and miscibility of poly(hydroxybutyrate) and soda lignin blends. Ind. Crop. Prod. 2010; 32:656-661. DOI: 10.1016/j.indcrop.2010.08.001.

19.   Watanabe M, Togo M, Sanui K, Ogata N, Kobayashi T, Ohtaki Z. Ionic conductivity of polymer complexes formed by poly(β-propiolactone) and lithium perchlorate. Macromolecules. 1984; 17:2908-2912. DOI: 10.1021/ma00142a079.

20.   Guirguis O W, Moselhey M T H. Thermal and structural studies of poly(vinyl alcohol) and hydroxypropyl cellulose blends. Nat. Sci. 2012; 4:57-67. DOI: 10.4236/ns.2012.41009.

21.   Shamshad Ahmed A A, Basfar M M. Comparison of thermal stability of sulfur, peroxide and radiation cured NBR and SBR vulcanizates, Polym. Degrad.Stab.2000;67:319-323. URL: http://www.iaea.org/inis/collection/NCLCollectionStore/_Public/31/016/31016367.pdf

22.   Freeman E S, Carroll B. The Application of Thermoanalytical Techniques to Reaction Kinetics: The Thermogravimetric Evaluation of the Kinetics of the Decomposition of Calcium Oxalate Monohydrate J. Phys. Chem. 1958; 62:394-397. DOI: 10.1021/j150562a003.

23.   Jerez A A. Modification to the Freeman and Carroll Method for the analysis of the kinetics of non-isothermel processes, J. Therm. Analysis. 1983; 26:315-318. DOI: 10.1007/BF01913218 S.

24.   Aouachria K, Quintard G, Nageotte V M, Bensemra N B. The Effect of Di-(-2-ethyl hexyl) phthalate (DEHP) as Plasticizer on the Thermal and Mechanical Properties of PVC/PMMA Blends, Polímeros, 2014; 24:428-433, 2014. DOI: 10.1590/0104-1428.1588.

Türkçe Öz ve Anahtar Kelimeler
Poli-β-Alanin / Poli(3-hidroksipropiyonat) Karışımlarının Birbiri İçinde Çözünürlüğü ve Isıl Bozunma Kinetikleri

Efkan ÇATIKER, Satılmış BASAN

Öz: Poli-β-alanin (PBA) ve poli(3-hidroksipropiyonat) (PHP) sırasıyla akrilamid ve akrilik asidin baz katalizli hidrojen iletim polimerizasyonu (HTP) ile sentez edilmiştir. Farklı bileşimdeki (PHP içeriği %5 ile 75 arası) PBA/PHP karışımları FTIR, DSC, TGA, XRD ve polarize optik mikroskop çalışmalarıyla PBA/PHP karışımlarının birbiri içinde çözünebilirlik ve ısıl bozunma kinetiğini ortaya çıkarmıştır. Karışımların optik görüntüleri şeffaf ve tamamen tek biçimlidir. Her iki bileşenin karakteristik FTIR bantları, diğer bileşenin artan kısmı ile daha yüksek frekanslara kaymıştır. PHP'nin erime sıcaklığı (T_m), ısıl bozunma sıcaklığı (T_d) ve kaynaşma entalpisi (ΔH_f), karışımlardaki PBA kısmının artması ile azalma göstermiştir. Her bir bileşenin ısıl bozunma kinetiği Freeman-Carroll yöntemiyle çalışılmıştır. Karışımı oluşturan bileşenlerin ısıl bozunmalarının aktivasyon enerjileri iyi regresyon katsayıları ile (en az 0,994) belirlenmiştir. Bozunma aktifleşme enerjileri artan PHP içeriği ile 224,14'den 86,125 kJmol^{-1}'e azalmıştır. Karışımların XRD spektrumları, saf polimerlere oranla daha düşük pik şiddeti vermiştir. Spektroskopik, termal ve optik yöntemlere göre PBA ve PHP, amorf fazda iyi bir uyuma sahip olacak şekilde birbiri içinde çözünmektedir.