

Oxygen-Barrier Properties of Poly(lactic acid)/Poly(vinyl acetate-co-vinyl alcohol) Blends as Biodegradable Films

S. M. Razavi,¹ Susan Dadbin,² Masoud Frounchi¹

¹Department of Chemical and Petroleum Engineering, Sharif University of Technology, Tehran, Iran

²Radiation Applications Research School, Nuclear Science and Technology Research Institute, Tehran, Iran

Received 22 August 2011; accepted 13 October 2011

DOI 10.1002/app.36376

Published online in Wiley Online Library (wileyonlinelibrary.com).

ABSTRACT: The oxygen-barrier properties of poly(lactic acid) (PLA)/poly(vinyl acetate-co-vinyl alcohol) [P(VAc-co-VA)] were investigated. P(VAc-co-VA)s with vinyl alcohol (VA) contents of 5, 10, and 15 mol % were prepared with the acid-catalyzed hydrolysis of poly(vinyl acetate). The obtained copolymers with various contents of VA were blended with PLA at 5/95, 10/90, and 15/85 compositions. Films of the blends were prepared by a solution-casting method with chloroform as the cosolvent. Although the blend with 5% VA in the copolymer appeared to be miscible, the blends with 10 and 15% VA content in the copoly-

mer were immiscible, as verified by dynamic mechanical analysis. The oxygen-barrier properties of the PLA films were enhanced when they were blended with P(VAc-co-VA). There was a reduction of about 40% in permeability with the addition of only 5% P(VAc-co-VA). The reduction in the permeability was more noticeable at higher VA contents. Also, the incorporation of P(VAc-co-VA) into PLA improved the elongation at break of the films significantly. © 2012 Wiley Periodicals, Inc. *J Appl Polym Sci* 000: 000–000, 2012

Key words: biodegradable; blends; films; gas permeation

INTRODUCTION

As a packaging material, thermoplastic polymers have many advantages, including light weight, lower process temperatures than metal and glass, appropriate printability, and variable barrier properties for diverse uses. Currently, most polymeric materials are based on nonrenewable fossil resources. Approximately 140 million tons per year of petroleum-based synthetic polymers are produced in the world, and a significant amount of these polymers is disposed of in the natural environment. Because petroleum-based plastics cannot be degraded over a short time in nature, the development of biodegradable polymers is vital.^{1,2}

Poly(lactic acid) (PLA) is a biodegradable, renewably derived thermoplastic polyester and is produced either by the polycondensation of lactic acid or by the ring-opening polymerization of lactide.^{3,4} As a packaging material, this aliphatic polyester has many advantages, including biodegradability, good processibility, and clarity. However, it also has drawbacks, including low ductility (<10% elongation) and low gas-barrier properties, which limit its use in certain applications.⁵ Plasticizers are widely used to improve the flexibility and ductility of PLA.

Lactide monomer, dibutyl sebacate, tributyl citrate, and poly(ethylene glycol) are efficient plasticizers for PLA.^{6–8} Also, for some other applications, the tensile strength and elastic modulus of PLA can be improved by the addition of organic or inorganic fillers, such as microclays and nanoclays, metallic oxides, carbon fibers, and natural fibers, to the PLA matrix.^{9–15}

Many studies have been done to overcome low barrier properties of PLA and, thereby, expand the potential applications of this polymer in packaging applications. The focus of these studies has mainly been on development of nanocomposites based on PLA and on the use of this polymer as part of a multilayer structure.¹⁶

Another way to improve the barrier and mechanical properties of PLA is through its blending with other polymers. PLA can be blended with other polymers obtained from renewable resources, such as chitosan, starch, and PHB, or with petroleum-based polymers, such as poly(vinyl acetate) (PVAc), polycaprolactone (PCL), and poly(ethylene glycol) to improve its properties.¹⁷

PVAc and poly(vinyl alcohol) (PVA) are two polymers that have been studied in blends with PLA. PVAc is miscible with PLA in all compositions. The addition of a small amount of PVAc (5 wt %) increased the tensile strength at yield and the elongation at break of extruded blend films compared to a neat PLA film. However, the addition of PVAc to PLA led to a dramatic decrease in the degradation

Correspondence to: M. Frounchi (frounchi@sharif.edu).

rate for enzymatic degradation.^{18,19} On the contrary, PLA/PVA blends have been reported in which the nonenzymatic and enzymatic hydrolysis of PLA was accelerated by the presence of the hydrophilic PVA, but these blends were immiscible in inducing a phase-separated system.²⁰

To overcome the drawbacks of PLA/PVA blends (a phase-separated system) and PLA/PVAc blends (a decreased enzymatic degradation of PLA), blends of PLA and poly(vinyl acetate-co-vinyl alcohol) [P(VAc-co-VA)] were examined. It was demonstrated that only the blend composed of 10 wt % P(VAc-co-VA) containing 10 mol % vinyl alcohol (VA) were miscible and blends containing more copolymer or more VA were immiscible.¹⁸ To the best of our knowledge, there has been no effort made to examine the barrier and mechanical properties of the mentioned blend.

This study was undertaken to determine the effect of the addition of P(VAc-co-VA) on the mechanical and barrier properties of PLA. Our aim was to make a blend that could produce a barrier film appropriate for use as a packaging layer. Moreover, we examined the miscibility range of the two polymers and the effects of the miscibility on the properties of the blends.

EXPERIMENTAL

Materials

Film-grade PLA was supplied by a Chinese company with a weight-average molecular weight of 238,000 g/mol and a number-average molecular weight of 100,000 g/mol. PVAc was obtained from Sigma-Aldrich with a weight-average molecular weight of 140,000 g/mol. Chloroform, methanol, and hydrochloric acid were from Merck Co.

Sample preparation

P(VAc-co-VA) was synthesized by the hydrolysis of PVAc. First, 50 g/L PVAc was dissolved in a 9/1 (v/v) solution of methanol-water, and then, hydrochloric acid was added to an approximate concentration of 0.2M in the solution. The hydrolysis reaction took place at 50°C, and the degree of hydrolysis was controlled by reaction times of 70, 140, and 210 min to obtain 5, 10, and 15 mol % hydrolyzed products, respectively. The products were precipitated in water, followed by dissolution in methanol, and reprecipitation in water. The precipitates were dried *in vacuo* at 45°C for 48 h.

The blends of PLA and P(VAc-co-VA) containing 5, 10, and 15 wt % copolymers were prepared by dissolution in chloroform. The blend films were cast from a 4 wt % solution onto a glass plate and dried

subsequently at room temperature for 1 day and then in a vacuum oven at 40°C for 2 days. The films were about 100 μm thick. The notation shown for the blend [e.g., PLA/P(VAc-co-VA)10 85/15] indicates that the blend composition was 85% PLA and 15% P(VAc-co-VA) and the copolymer P(VAc-co-VA) contained 10% VA.

Methods

NMR spectroscopy

To determine the degree of hydrolysis, ¹H-NMR measurements were carried out. Spectra were obtained with a Bruker (Switzerland) DRX-Avance spectrometer at 500 MHz. As the solvent and internal standard reagent, CDCl₃ was used.

Dynamic mechanical thermal analysis (DMTA)

DMTA was performed on a TRITEC-2000-DMA analyzer (DMTA-Triton, England) operated in the tension mode at a constant frequency of 1 Hz. The experiments were carried out in a temperature range from -60 to 140°C at a heating rate of 3°C/min, and $\tan \delta$ was recorded as a function of the temperature.

Tensile testing

The elastic modulus, tensile strength, and elongation at break of each film were determined with a HIWA (Tehran) 212S testing machine. Specimens were rectangular and 4.1 \times 60 mm². The initial grip separation was set at 35 mm, and the crosshead speed was set at 10 mm/min. For each film sample, measurements were made on five specimens taken from the same film, and the average of their results was reported.

Permeability

The apparatus used for oxygen permeability measurements was GPD-C (Brugger, München, Germany). The sample was put between the top and bottom parts of the permeation cell. Before each test, the bottom part of the permeation cell was evacuated. During testing, the top part was filled with the test gas. The gas permeating the material caused a pressure increase at the bottom part of the permeation cell. Gas permeability was detected by an evaluation of this increase in pressure in relation to time and the device-specific volume. The increase in pressure during the test period was evaluated and displayed by an external computer.

Polarized optical microscopy

The blends morphology was observed with an Olympus (Japan) BX51 polarized light microscope.

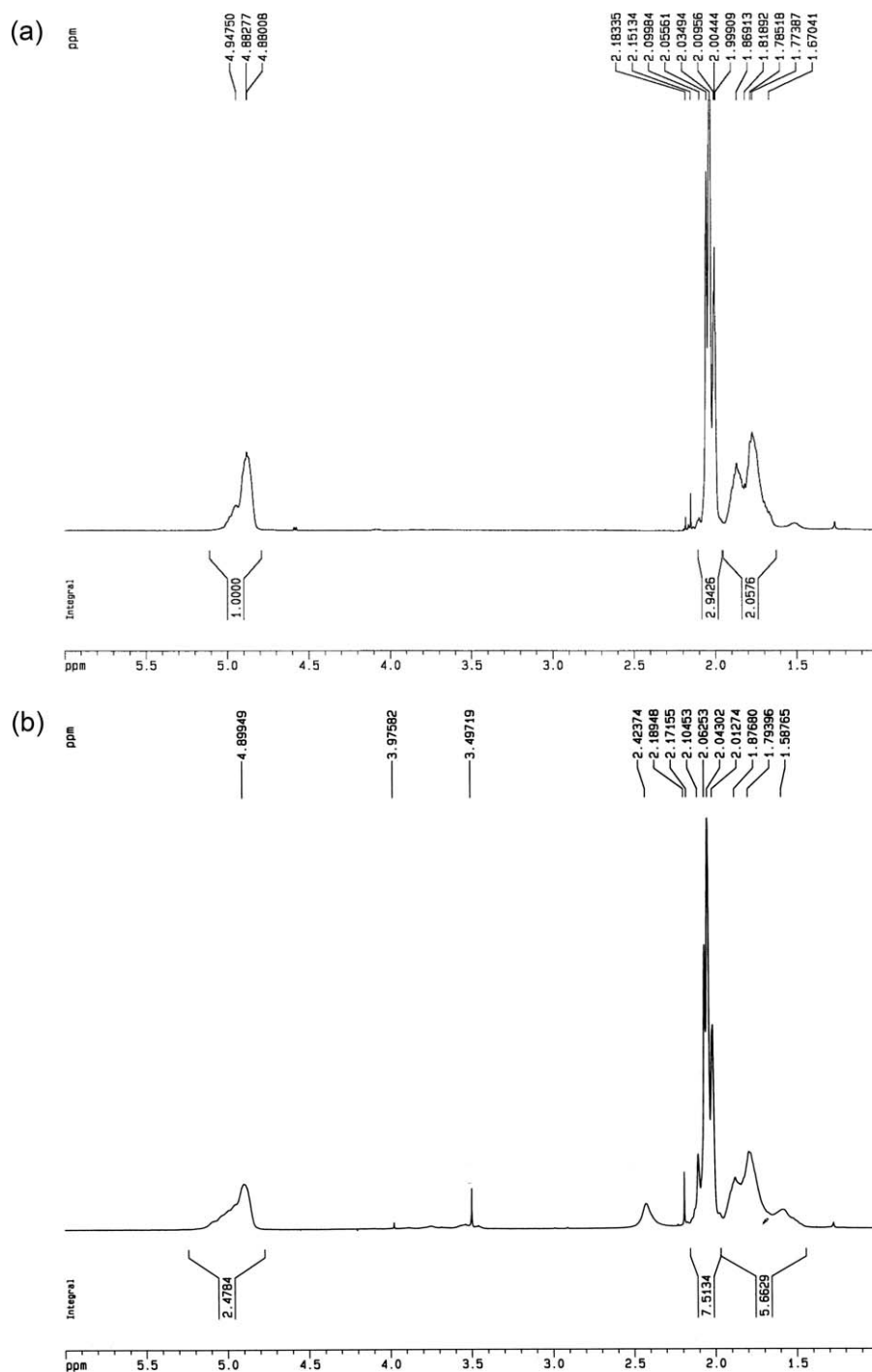


Figure 1 $^1\text{H-NMR}$ spectra of (a) PVAc and (b) partially hydrolyzed PVAc after the hydrolysis reaction for 200 min.

RESULTS AND DISCUSSION

Degree of hydrolysis determination

The $^1\text{H-NMR}$ spectra of PVAc and partially hydrolyzed PVAc after 200 min of the hydrolysis reaction are compared in Figure 1. On the spectrum of PVAc, the methylene (CH_2) peak (1.1–1.9 ppm), the methyl (CH_3) peak (1.9–2.4 ppm), and the CH group of vinyl acetate (VAc) (4.7–5.2 ppm) could be seen. In

addition to those peaks, new peaks representing the hydroxyl (OH) peak (4.2–4.7 ppm) and the CH group of VA (3.4–3.9 ppm) appeared after the hydrolysis. However, the peak areas of the hydroxyl peaks at the high VAc molar fractions used in this study were too small to be detected.

The molar fraction of VAc during the hydrolysis reaction (X_{VAc}) was obtained from the following equations:

TABLE I
Molar Fractions of VAc after Various Hydrolysis Times as Determined by NMR

Reaction time (min)	X_{VAc} from eq. (1)	X_{VAc} from eq. (2)	Average
0	0.975	0.990	0.983
50	0.952	0.966	0.959
130	0.934	0.919	0.927
200	0.851	0.884	0.868
300	0.805	0.815	0.810
420	0.710	0.658	0.684

$$X_{VAc} = \frac{2I_{CH_3}}{2I_{CH_2}} \quad (1)$$

$$X_{VAc} = \frac{2I_{CH,VAc}}{2I_{CH_2}} \quad (2)$$

where I_{CH_3} , I_{CH_2} , and $I_{CH,VAc}$ represent the peak areas of methyl, methylene, and methin groups of VAc, respectively.²¹ The molar fractions of VAc after different hydrolysis reaction times, which were calculated from eqs. (1) and (2), are collected in Table I. The VAc molar fractions calculated from the two equations were not equal. We suspected that this was because the methyl and methylene peaks were not completely resolved in the NMR spectra of P(VAc-co-VA). There was also a possibility of overlap between the methin and hydroxyl peaks. So we took the average of the two values obtained via eqs. (1) and (2), instead of using the values obtained from one of them exclusively.

From the data in Table I, the change of the VAc molar fraction with respect to the reaction time can be approximately shown by eq. (3):

$$X_{VAc} = -7 \times 10^{-4}t + 0.9998 \quad (3)$$

where t is the reaction time (min). Also, $X_{VAc} + X_{VA} = 1$, so changes in VA mole fraction (X_{VA}) by time could be shown by eq. (4):

$$X_{VA} = 7 \times 10^{-4}t \quad (4)$$

Because our aim was to prepare P(VAc-co-VA) copolymers with 5, 10, and 15% VA, reaction times of 70, 140, and 210 min were needed, respectively.

DMTA

Blends of PLA and P(VAc-co-VA) are miscible at low copolymer contents. DMTA was used to examine the miscibility of the blends that we prepared. The glass-transition temperatures were determined from the maxima of the $\tan \delta$ peaks. DMTA curves of the PLA blends with the P(VAc-co-VA) copolymers are shown in Figures 2 and 3.

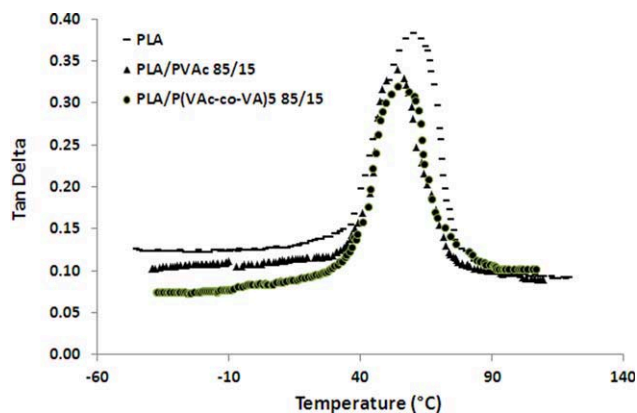


Figure 2 DMTA curves of the PLA blend with PVAc and P(VAc-co-VA). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

In Figure 2, the $\tan \delta$ curve of PLA/PVAc 85/15 showed one peak at 54.2°C that was lower than the temperature in which the peak of pure PLA was located (60.6°C). The curve related to PLA/P(VAc-co-VA)5 85/15 also had a peak at a lower point (54.3°C). Because only one peak was observed for both of mentioned blends, PLA/PVAc and PLA/P(VAc-co-VA)5 85/15 were miscible blends. The miscibility of PLA with P(VAc-co-VA) increased with decreasing copolymer content,¹⁸ so we inferred that PLA was miscible with PVAc and PLA/P(VAc-co-VA)5 in 5 and 10% copolymer as well.

For the blend of PLA with P(VAc-co-VA)15, the miscibility of the blend was dependent on the copolymer content. The glass-transition temperature (maximum of the $\tan \delta$ curve) of the PLA/P(VAc-co-VA)15 blend with 5% copolymer was 52°C (Fig. 3), and only that peak was observed on the $\tan \delta$ curve. So PLA/P(VAc-co-VA)15 95/5 was a miscible blend. On the contrary, there were two peaks at 27 and 58.3°C for the $\tan \delta$ curve of the PLA/P(VAc-co-VA)15 90/10 blend. The temperatures at which those peaks were located were slightly different from the glass-transition temperatures of the pure polymers

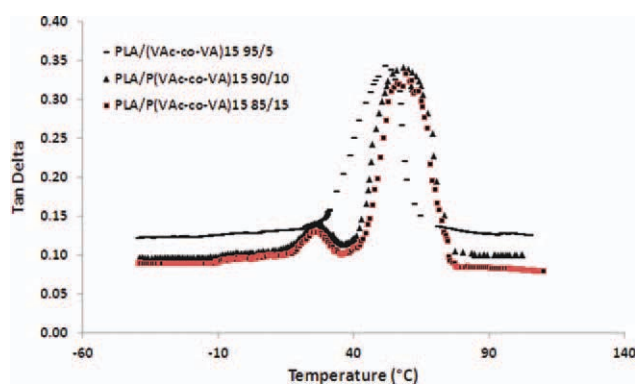


Figure 3 DMTA curves of the PLA blend with P(VAc-co-VA) at different compositions. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

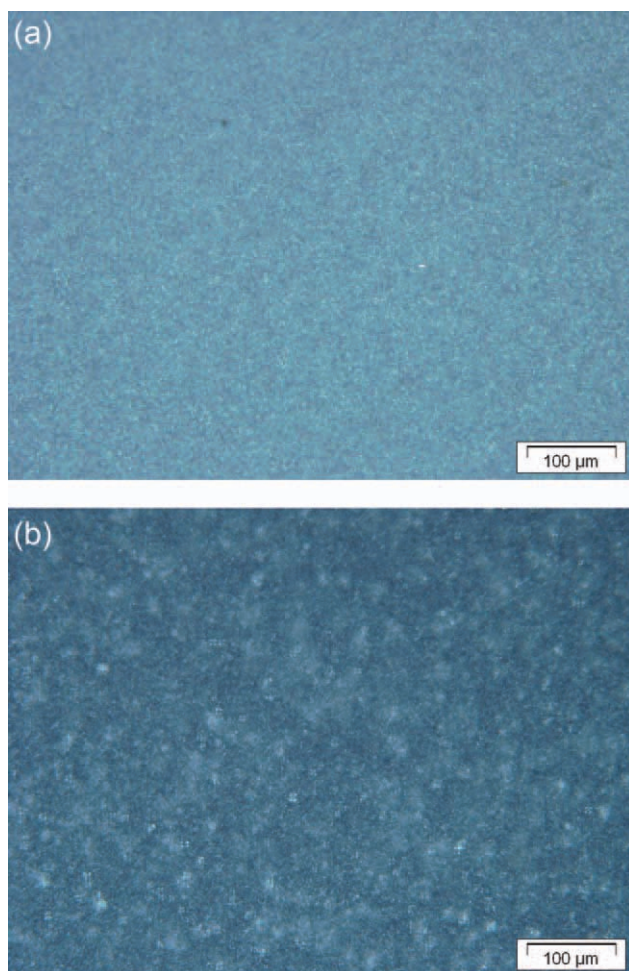


Figure 4 Polarized optical micrographs of the samples: (a) PLA/P(VAc-co-VA) 15/90 and (b) PLA/P(VAc-co-VA) 15/85. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

(60.6°C for PLA), so PLA/P(VAc-co-VA)15/90 could be known as a partially miscible blend with a low miscibility. The $\tan \delta$ curve of the PLA/P(VAc-co-VA)15/85 blend also had two peaks with maxima on 26 and 59.6°C that were close to the glass-transition temperature of the pure polymers. Therefore, the latter blend was an immiscible blend.

Morphology

The films of the blends of PLA and P(VAc-co-VA) were transparent.

Figure 4(a,b) shows polarized optical micrographs of the samples. The small domains of P(VAc-co-VA) appeared uniformly dispersed at the whole surface of the blends. The observed phase separation was consistent with the DMTA results.

Tensile testing

The tensile properties of PLA blended with pure PVAc and the 10% hydrolyzed PVAc co-

TABLE II
Tensile Properties of the PLA/PVAc Blends

PVAc content (%)	Tensile strength (MPa)	Modulus (MPa)	Elongation at break (%)
0	26	1051	16.1
5	27.6	967	21.2
10	28.8	918	25.9
15	29.1	798	29

polymer, P(VAc-co-VA)10, are presented in Tables II and III.

For the PLA/PVAc blends (Table II), the tensile strength and elongation at break of the samples was increased and the modulus was decreased with increasing PVAc content. With regard to the changes in the modulus and elongation at break of PLA after it was blended with PVAc, we inferred that PVAc improved the ductility and tensile strength of PLA. The same results were reported by Gajria et al.¹⁹ for PLA/PVAc blends at low PVAc contents. Additionally, an increase in the tensile strength is a great advantage for packaging applications.

When PVAc was replaced with the P(VAc-co-VA)10 copolymer, a different trend in the tensile properties was observed (Table III). For compositions in which P(VAc-co-VA)10 was immiscible with PLA (10 and 15% copolymer), the tensile strength decreased slightly. This should have been due to the immiscibility and low interaction between the polymer chains in the blend. Another effect of the increase in the concentration of the copolymer in the blends was a decrease in the modulus. This decrease was observed under both miscible and immiscible conditions. The addition of 5% of P(VAc-co-VA)10 to PLA increased the elongation at break of the polymer by about 50%. However, when the composition of copolymer increased to 10 and 15%, no notable change in elongation at break was detected. This could be explained by the effect of two opposite factors. On one hand, the immiscibility of the polymers in higher copolymer contents led to a decrease in the elongation at break; on the other hand, the addition of a more ductile copolymer increased the elongation at break by increasing the ductility of PLA. So, we could infer that at higher copolymer contents,

TABLE III
Tensile Properties of the PLA/P(VAc-co-VA)10 Blends

P(VAc-co-VA) 10 content (%)	Tensile strength (MPa)	Modulus (MPa)	Elongation at break (%)
0	26	1051	16.1
5	26.9	914	24
10	25.7	860	24.4
15	23.3	821	24.1

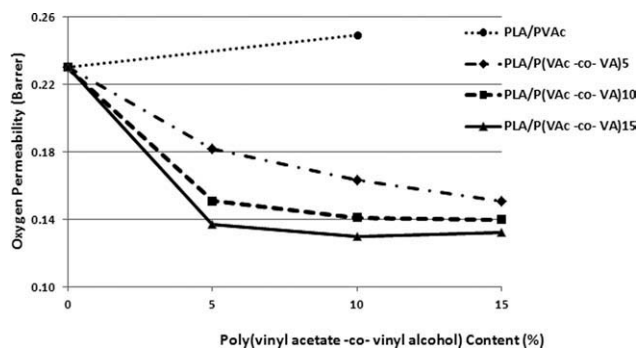


Figure 5 Oxygen permeability of various blends as a function of the blend composition.

those opposite factors counterbalanced each other and caused no significant change in the elongation at break of the blends.

Oxygen permeability

The oxygen permeability of various blends as a function of the blend composition is shown in Figure 5. The oxygen-barrier properties of PLA were slightly increased after its blending with PVAc homopolymer. However, P(VAc-co-VA) copolymers significantly decreased the oxygen permeability of PLA; this reduction was proportional to the amount of copolymer added and also to the VA content of the copolymer.

The oxygen permeability of the blends decreased abruptly at a P(VAc-co-VA) content of 5%. For the blends containing 5% copolymer, compared to pure PLA, the permeability decreased by 22, 35, and 39% for copolymers containing 5, 10, and 15% VA, respectively. The permeability reduction of the blends continued with increases in the copolymer content to 10 and 15%. In summary, the oxygen-barrier properties of the blends improved with increasing VA units of copolymer in the blend. The VA units contained hydroxyl groups that were polar pendant groups; this led to strong energetic interactions between the polymer chains by hydrogen bonds, efficient polymer chain packing, low free volume, and in turn, low permeability in the blends. As a result, PLA became a better barrier against oxygen when it was blended with P(VAc-co-VA).

An inconsistency in the permeability reduction trend of the blends by copolymer content was observed for the PLA/P(VAc-co-VA)15 85/15 blend. The permeability of the mentioned blend was a bit greater than that of the PLA/P(VAc-co-VA)15 90/10 blend. This may have been due to the immiscibility of the PLA/P(VAc-co-VA)15 85/15 blend. When immiscible polymers are blended, as when inorganic filler is added to a polymer matrix, it results in the formation of a dispersion of one component in a

continuous matrix of the other. The barrier properties of those systems depend on the permeabilities of the individual components, their volume fractions, the phase continuity, and the aspect ratio of the dispersed (or discontinuous) phase. So, an increase in the dimensions or probable changes in the shape and dispersion of the dispersed phase might have caused the discrepancy in the observed trend.

CONCLUSIONS

Blends of PLA and P(VAc-co-VA) were prepared, and the miscibility, tensile properties, and oxygen permeability of the blends were investigated. P(VAc-co-VA) copolymers were obtained by the hydrolysis reaction of PVAc, and the degree of hydrolysis was specified by $^1\text{H-NMR}$ characterization, which revealed a linear relation between the degree of hydrolysis and the reaction time.

The miscibility of the blends was examined by DMTA. Blends of PLA and PVAc were miscible in all of the investigated compositions. Also, PLA formed a miscible blend with the P(VAc-co-VA) copolymer, which contained only 5% VA. The blends of PLA and P(VAc-co-VA) containing 10 and 15% VA were immiscible at 90/10 and 85/15 blend compositions, respectively. The results of tensile testing showed that P(VAc-co-VA) improved the ductility of PLA, and this was more remarkable when two polymers were miscible. The oxygen permeability of PLA decreased when it was blended with P(VAc-co-VA). The decrease in permeability was proportional to the content of polar VA units in the blend, and miscible blends had better barrier properties than immiscible ones. So, P(VAc-co-VA) significantly improved the barrier properties and the mechanical properties of PLA for possible use as a packaging material.

References

- Lima, L.-T.; Auras, R.; Rubino, M. *Prog Polym Sci* 2008, 33, 820.
- Shah, A. A.; Hasan, F.; Hameed, A.; Ahmed, S. *Biotechnol Adv* 2008, 26, 246.
- Rasal, R. M.; Janorkar, A. V.; Hirt, D. E. *Prog Polym Sci* 2010, 35, 338.
- Tsuji, H. In *Biopolymers for Medical and Pharmaceutical Applications*; Steinbuchel, A.; Machessault, R. H., Eds.; Wiley-VCH: Weinheim, 2005; p 183.
- Hiljanen-Vainio, M.; Varpomaa, P.; Seppala, J.; Tormala, P. *Macromol Chem Phys* 1996, 197, 1503.
- Pillin, I.; Montrelay, N.; Grohens, Y. *Polymer* 2006, 47, 4676.
- Martin, O.; Avérous, L. *Polymer* 2001, 42, 6209.
- Lemmouchi, Y.; Murariu, M.; Dos Santos, A. M.; Amass, A. J.; Schacht, E.; Dubois, P. *Eur Polym J* 2009, 45, 2839.
- Auras, R.; Harte, B.; Selke, S. *Macromol Biosci* 2004, 4, 835.
- Ogata, N.; Jimenez, G.; Kawai, H.; Ogihara, T. *J Polym Sci Part B: Polym Phys* 1997, 35, 389.
- Rhim, J.-W.; Hong, S.-I.; Ha, C.-S. *LWT-Food Sci Technol* 2009, 42, 612.

12. McManus, A. J.; Doremus, R.; Siegel, R.; Bizios, R. J. *Biomed Mater Res* 2005, 72, 98.
13. Wan, Y. Z.; Wang, Y. L.; Li, Q. Y.; Dong, X. H. *J Appl Polym Sci* 2001, 80, 367.
14. Hu, R.-H.; Sun, M.-Y.; Lim, J.-K. *Mater Des* 2010, 31, 3167.
15. Bledzki, A.-K.; Jaszkwicz, A.; Scherzer, D. *Compos A* 2009, 40, 404.
16. Almenar, E.; Auras, R. In *Poly(lactic acid): Synthesis, Structures, Properties, Processing, and Applications*; Auras, R., Lim, L.-T., Selke, S. E. M., Tsuji, H., Eds.; Wiley: Hoboken, NJ, 2010; p 155.
17. Paul, D. R.; Newman, S. *Polymer Blends*; Academic: New York, 1980.
18. Park, J. W.; Im, S. S. *Polymer* 2003, 44, 4341.
19. Gajria, A. M.; Davé, V.; Gross, R. A.; McCarthy, S. P. *Polymer* 1996, 37, 437.
20. Tsuji, H.; Muramatsu, H. *J Appl Polym Sci* 2001, 81, 2151.
21. Park, S.; Yoon, H. *Polymer (Korea)* 2005, 29, 304.