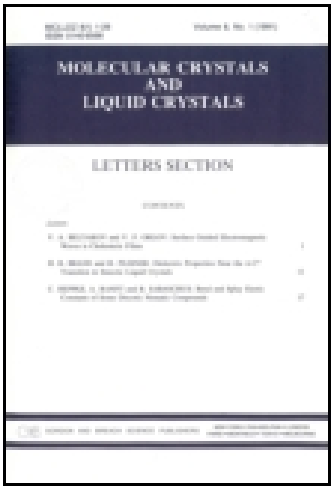

Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

Solvent-Induced Surface Structure of Poly(vinylidene fluoride)/Biodegradable Polyester Blend Films

Ildoo Jung[a], Chang-Sik Ha[a], Yongkwang Cho[b], Seongil Yoo[b] & Won-Ki Lee[b]

[a] Department of Polymer Science & Engineering, Pusan National University, Busan, Korea

[b] Division of Chemical Engineering, Pukyong National University, Busan, Korea

Published online: 17 Nov 2014.

To cite this article: Ildoo Jung, Chang-Sik Ha, Yongkwang Cho, Seongil Yoo & Won-Ki Lee (2014) Solvent-Induced Surface Structure of Poly(vinylidene fluoride)/Biodegradable Polyester Blend Films, Molecular Crystals and Liquid Crystals, 598:1, 23-27, DOI: 10.1080/15421406.2014.932676

To link to this article: http://dx.doi.org/10.1080/15421406.2014.932676

Mol. Cryst. Liq. Cryst., Vol. 598: pp. 23–27, 2014

ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421406.2014.932676

Taylor & Francis
Taylor & Francis Group

Solvent-Induced Surface Structure of Poly(vinylidene fluoride)/Biodegradable Polyester Blend Films

ILDOO JUNG,[1] CHANG-SIK HA,[1] YONGKWANG CHO,[2] SEONGIL YOO,[2] AND WON-KI LEE[2,*]

[1]Department of Polymer Science & Engineering, Pusan National University, Busan, Korea
[2]Division of Chemical Engineering, Pukyong National University, Busan, Korea

To commercialize a degradable material, it is necessary to control the initial stability which is strongly depended on their life time. One approach to modify physical properties of degradable polyesters is a blend with a non-degradable polymer because a non-degradable polymer with low surface energy is enriched at surface. Biodegradable polyesters, such as poly(dl-lactide) (dl-PLA), semi-crystalline poly(l-lactide) (l-PLA) and poly(ε-caprolactone) (PCL) were blended with poly(vinylidene fluoride) (PVDF) as a non-degradable polymer because PVDF has a low surface energy. Their surface structure and morphology were measured by X-ray photoelectron spectrometer and atomic force microscopy, respectively. (dl-PLA/PVDF) and (PCL/PVDF) blend films showed the enrichment of PVDF at surface whereas the surface of (l-PLA/PVDF) blend film was similar with its bulk one due to different solubilities to solvent and miscibility. These results will be useful to control of the initial stability of degradable polymers.

Keywords Initial stability; surface composition; surface energies

Introduction

The surface property of the polymeric materials has become an important subject because industrial applications are deeply related to their surface properties such as adhesion, friction, wetting, painting etc. The surface structure of the solid films composed of multicomponent polymers has attracted much interest due to the difference between the properties of the surface and the bulk. It has been revealed that the glass transition temperature (Tg) of glassy polystyrene (PS) at the surface is much lower than its bulk one [1]. The molecular weight of PS which is smaller than 23000 mol/g (bulk Tg: 90°C) showed high friction force due to active molecular motion of surface-enriched chain end groups. This leaded to significant depression of Tg at the surface. Also, the surface structure of multicomponent polymeric systems is quite different from its bulk one, mainly depending on the surface free energy of polymer components [2]. Since the degradation of most degradable polymers proceeds via surface erosion process, a degradability could be controlled by the change of surface

*Address correspondence to Won-Ki Lee, Dept. of Polymer Engineering, Pukyong National University, Busan 608-739, Korea. Tel.: (+82)51-629-6451. Fax: (+82)51-629-6429. E-mail: wonki@pknu.ac.kr

Table 1. Characteristics of polymers used in blend films

Polymer	Mw	PDI	Tm (°C)	γ_{SV} (mNm^{-1})
l-PLA	108k	1.6	181	40.2*
dl-PLA	130k	1.7	–	40.2*
PCL	80k	1.4	44	41.7
PVDF	320k	2.1	170	26.0

*Calculated by group contribution method

property [3–5]. A short fluorocarbon modified polymer showed the improved thermal and hydrolytic stability [3].

Also, the biodegradation of poly(3-hydroxy butyrate) was significantly retarded by blending with a small amount of non-degradable polymer segregated at surface [4].

One approach to modify surface properties of commercial biodegradable polymers is a blend method. In this work, we prepared the blend films of poly(lactide) (PLA) or poly(ε-caprolactone) (PCL) as a degradable polymer with small amounts of a non-degradable and low-surface energy polymer, poly(vinylidene fluoride) (PVDF) by a solution casting technique. The surface structure was measured by X-ray photoelectron spectroscopy (XPS) and ATR-FTIR.

Experimental

PVDF used in this study was obtained from Showa Chemical Co. l-PLA, dl-PLA, and PCL were synthesized by the ring polymerization. The characteristics of polymers in this study are listed in Table 1. Blend solutions were prepared by dissolving polymers in dimethylacetoamide (DMAc) at 65°C, followed by a casting method. All blend solutions were transparent. The solvent was evaporated on hot plate at 65 °C and the films were kept in vacuum oven.

The Tm behaviors of PVDF homopolymer and blends including PVDF, such as (l-PLA/PVDF), (dl-PLA/PVDF), and (PCL/PVDF), were measured by differential scanning calorimeter (DSC) (Perkin Elmer DSC 7) calibrated with pure indium as a standard. The homopolymer and blend samples were melted at 200°C for 1 min under dried helium purge, cooled quickly to room temperature and then heated to 200°C at a heating rate of 20°C min^{-1} for measuring Tm of PVDF. Surface chemical composition of the blend films were evaluated on the basis of Physical Electronics 5100 ESCA by using MgKα radiation. Typical operating conditions were 15 kV, 20 mA x-ray source and under pressure in the analytical chamber-10^{-8} Pa. ATR-FTIR spectra (Perkin-Elmer FTIR 5500 spectrometer) were obtained using 30° KRS-5 prism.

Results and Discussion

In general, the miscibility of a blend including semi-crystalline component is achieved by the interaction between amorphous parts of each component. The melting temperature (Tm) depression of a crystalline component means that the re-growth of a crystal is interrupted by the interaction between components in blend.

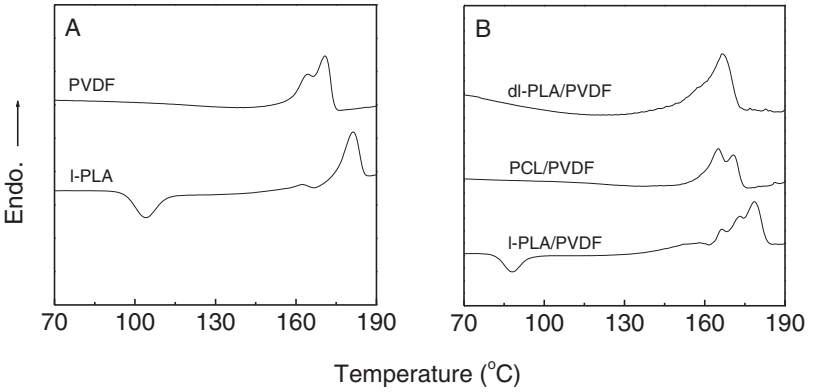

Figure 1. DSC thermograms of homopolymers (A) and (PVDF/polyester 50/50 by wt.) blends (B).

Figure 1 shows Tm behaviors of homopolymers and their blends. PVDF gives two endothermic peaks: lower melting peak is due to α phase crystal and higher one is from β phase crystal [6]. The Tm behavior of (l-PLA/PVDF) blend is very similar to that of each homopolymer. It indicates that this blend system is immiscible. Although the Tms of (PCL/PVDF) blend are the same of each homopolymer, The heat of fusion(ΔH) of β phase crystal is decreased. (dl-PLA/PVDF) blend showed the depression of Tm of PVDF. Thus both blends, (PCL/PVDF) and (dl-PLA/PVDF), are partially miscible.

To determine the surface composition, XPS was used and the analytical depth at a take -off angle of 45° is 5 nm. According to their architectures, the C1s region of PCL and l-PLA (or dl-PLA) can be deconvoluted with three peaks at 285, 287.5, and 289.5 eV assigned to that correspond to the neutral carbon (-C-***C***-C-), ether carbon(-***C***O-), and carbonyl carbon(-***C***OO-), respectively. The C1s region of PVDF can be resolved into two components 285.9 and 290.3 eV, corresponding to -***C***H_2- and -***C***F_2-, respectively.

It has been known that a component with lower surface energy in multicomponent polymeric systems is enriched at the surface in comparison to its partner component of higher surface energy [2–5]. The C1s spectra of blends are shown in Figure 2. The C1s spectrum of partially miscible blend, (PCL/PVDF 95/5 by wt), is very similar to that of

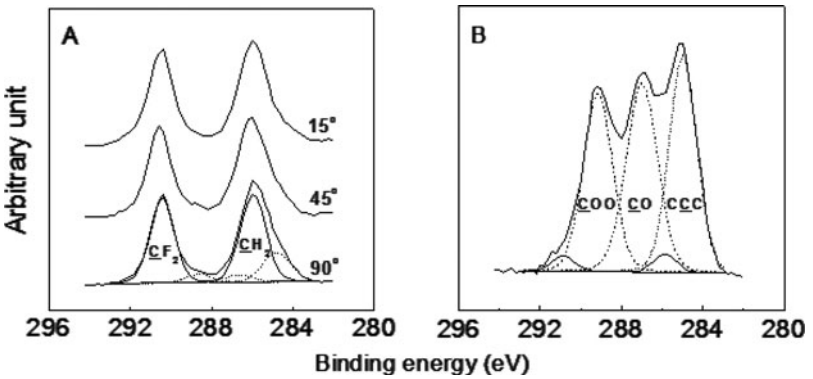

Figure 2. AFM images of l-PLA/PVDF blend (1/1 by wt) before (A) and after (B) enzymatic degradation.

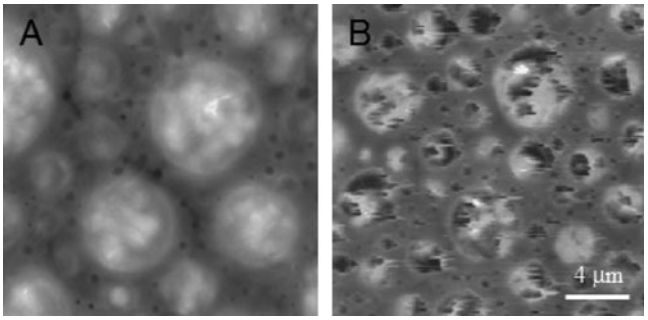

Figure 3. High resolution C 1s spectra of (PCL/PVDF 95/5 by wt) and (l-PLA/PVDF 95/5 by wt) blend films. The dotted lines are from polyester in the blend.

PVDF even though PVDF in the blend is 5 wt%. A similar result was obtained in the (dl-PLA/PVDF 95/5 by wt). These results suggest that the composition of PVDF at surface is much higher than that at the deeper regions due to the surface segregation of PVDF which has lower surface energy than that of PCL or dl-PLA.

Figure 2B shows the C1s spectrum of (l-PLA/PVDF 80/20 by wt) which is similar to that of l-PLA. It indicates that the surface of (l-PLA/PVDF) is covered by l-PLA. This could not be acceptable if we consider that the component with lower surface energy in multicomponent polymeric systems is usually enriched in the surface region in order to minimize the air/material interfacial energy. Figure 3 shows AFM images of (l-PLA/PVDF 50/50 by wt) blends before and after enzymatic degradation by Proteinase K for 2 hr. The phase-separated morphology was observed and the enzymatic degradation partially occurred in the l-PLA domain while the (PCL/PVDF 50/50 by wt) blend was almost unchanged after the degradation (not shown here).

Usually, a curve fitting method for XPS analysis is effective to evaluate the surface composition if each peak has enough intensity. However, the curve fitting method gives analysis much error when the intensity of a minor component is too weak. To reduce this effect, an elemental analysis method was applied. Figure 4A showed the atomic ratio (F 1s/C 1s) of blends by XPS and the dotted line indicates atomic ratio calculated from bulk

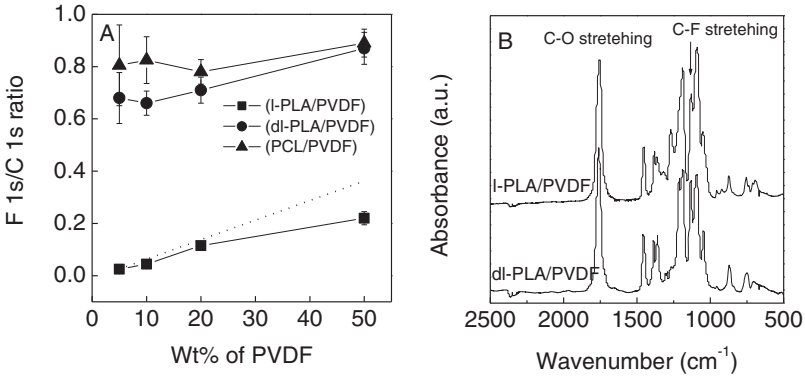

Figure 4. Surface atomic ratio profiles at a takeoff angle of 45° (A) and ATR-FTIR spectra (B) of on-drying blend films.

compositions. The atomic ratios of both partially miscible blends are much higher than the bulk one (dotted line), which was calculated on the basis of its chemical composition. This means the PVDF is enriched at the surface. In the immiscible (l-PLA/PVDF) blend, however, the atomic ratio is a little lower than the bulk one. An immiscible blend usually shows a phase separation during mixing or drying.

To understand the phase separation during drying, ATR-FTIR was measured when almost 90% solvent in the blend solution was evaporated. Carefully, surface of on-drying sample was contacted to KRS-5 prism and the coated prism was dried. Figure 4B shows ATR-FTIR spectra of on-drying (l-PLA/PVDF) and (dl-PLA/PVDF) blend samples. ATR-FTIR gives surface information within a few μm surface region. The bands at 1250 cm^{-1} and 1760 cm^{-1} are attributed to the C-F stretching and C-O stretching, respectively. The relative intensity of C-F stretching to C-O stretching of the (dl-PLA/PVDF) blend is higher than that of (l-PLA/PVDF) blend. The results indicate that during the drying the l-PLA in the immiscible (l-PLA/PVDF) blend is moved on the surface due to the immiscibility and low solubility of semicrystalline l-PLA to DMAc.

Conclusions

The purpose of this study is to investigate solvent-induced surface structure of biodegradable polymer blends with a small amount of PVDF which is a low surface energy. Since the surface structure of biodegradable polymers is strongly related to their initial degradation rate which is important for the commercial applications, partially miscible blends, (PCL/PVDF) and (dl-PLA/PVDF), showed the surface enrichment of PVDF which will be act as a retardant to initial degradation. However, immiscible (l-PLA/PVDF) blend did not show surface enrichment of PVDF due to the crystallizable property of l-PLA, no interaction with PVDF, and poor solubility to PVDF.

Acknowledgments

This work was supported by National Research Foundation of Korea (2011-0010106).

References

[1] Mayes, A. M. (1994). *Macromolecules*, *27*, 3114.
[2] Lee, W. K., Wells, D. D., Goacher, R. E., & Gardella, J. A. (2011). *Surf. Interface Anal.*, *43*, 385.
[3] Lee, W. K., Losito, I., Gardella, J. A., & Hicks, W. L. (2001). *Macromolecules*, *34*, 3000.
[4] Lee, W. K., Ryou, J. H., & Ha, C. S. (2003). *Surf. Sci.*, *542*, 235.
[5] Ha, C. S., & Gardella, J. A. (2005). *Chem. Rev.*, *105*, 4205.
[6] Lu, F. J., & Hsu, S. L. (1986). *Macromolecules*, *19*, 326.