The 2014 World Congress on
Advances in Civil, Environmental, and Materials Research (ACEM14)
Busan, Korea, August 24-28, 2014

Influence of Melt-draw Ratio on the Structure and Properties of Polylactic Acid Cast Film

*Caihong Lei[1)],Ruijie Xu[2)], Qi Cai[2)], Haibin Mo[2)] and Changbin Chen[2)]

[1), 2)] *School of Materials and Energy, Guangdong University of Technology, Guangzhou 510006,China*
[1)]*Guangdong Provincial Key Laboratory of Functional Soft Condensed Matter, Guangzhou 510006, China*
[1)] *Lch528@gdut.edu.cn*

ABSTRACT

The polylactic acid cast film was prepared with different melt-draw ratio by extrusion casting process. The structure and properties of the prepared films were characterized. The results showed that with increasing the melt-draw ratio (MDR), the crystallinity was increased and the cold crystallization temperature decreased, indicating improved crystallization property. With the increase of MDR, the orientation induced the formation of crystal nucleus. Further increase of the MDR value induced the appearance of some imperfect primary crystals. The polarized FTIR results also indicated the increase of crystalline orientation degree for the samples with different melt-draw ratios.

1. INTRODUCTION

Polylactic acid (PLA) is a well-known biodegradable semi-crystalline polyester which has a wide range of applications in biomedical, packaging and agriculture fields (Reddy 2013, Saeidlou 2012). In recent years, many studies have been focused on structural changes of PLA, such as crystal transformation (Kalish 2011, Lv 2013, Oh 2013), mesophase formation (Stoclet 2011), and an endotherm peak formed just above glass transition temperature(Lee 2009). However, the relatively slow crystallization rate of pure PLA makes it easily quenched into the amorphous state during a fast cooling process such as injection molding or extrusion (Gui 2013). It can be crystallized upon annealing and/or orientation. Oriented crystallization significantly increases the nucleation density and improves the crystallinity (De Oca 2007).

During the melt extrusion casting process, the polymer molecular orients along the flow direction in the flow field. High molecular weight chains form stable oriented row nuclei (Shish) and the other chains create the chain folded lamellae over these nuclei sites. With the increase of melt-draw ratio, the crystallinity and orientation are enhanced. Blundell (2000) showed that the poly(ethylene terephthalate) (PET) crystallinity was improved with the increase of orientation order parameter. Hu et al. (2013) reported that

---

[1)] Professor

[2)] Graduate Student

with increasing melt-draw ratio from 0 to 77, the polyvinylidene fluoride crystalline orientation increased from 0.02 to 0.55 by polarized FTIR testing and the crystalline morphology transformed from spherulites to parallel lamellae perpendicular to the extrusion direction. Persson (2013) proposed that after melt-draw and solid-state draw, the crystallinity and mechanical properties of melt-spun PLA fiber was improved obviously.

Many works have been carried out to investigate the crystallization behavior of PLA during stretching or annealing. Normally, firstly amorphous PLA samples are obtained and then they are annealed or stretched. This experimental condition is different from that during the fiber fabrication process, where the elongation stress field is applied after the materials leave the extruder die. Up to now, there are no works showing the PLA crystallization behavior in the melt-draw flow field. In this article, the PLA cast film was prepared under different melt-draw ratios between the cast roll and extruder. The influence of melt-draw ratio on the structure and properties of PLA cast film was studied.

2. Experimental

2.1 Material

A polylactic acid with melt flow index of 5.1g/10min (190ºC, 2.16Kg) from Ningbo Institute of Material Technology and Engineering, China, was used.

2.2 Preparation of PLA cast films

The cast film was prepared by extrusion cast through a T-slot die. During extrusion, the uniaxial (machine direction, MD) stretching was applied to PLA melt. The die temperature was set at 200ºC and the melt-draw ratio (MDR) was set at 40, 54, 80, 107, 134, 152, 177 and 211. The MDR was calculated based on the difference between the line speed of chill roll and the extrudate velocity at the exit of the die. The films were produced at chill roll temperature of 50 ºC.

2.3 Characterization

A DSC-Q2000 (TA, USA) was used to measure the melting curves at a heating rate of 10ºC/min. The crystallinity was calculated as:

$$Crystallinity(\%) = \frac{\Delta H_m + \Delta H_{cc}}{\Delta H_m^0} \times 100\%$$

where ΔH_m was the endothermic heat of melting, ΔH_{cc} was exothermic heat of cold-crystallization, and ΔH^0_m was the heat of melting of perfectly crystalline PLA (93J/g) (Gogolewski 1983).

The wide-angle X-ray diffraction (WAXD) measurements were carried out using a Bruker AXS X-ray goniometer (Germany). The generator was set up at 40 kV and 40mA and the copper Cu K_α radiation was selected using a graphite crystal monochromator. The sample to detector distance was fixed at 8 cm with the scan direction parallel to the extrusion direction. The crystallinity was determined as:

$$Crystallinity(\%) = \frac{I_{cryst}}{I_{total}} \times 100\%$$

where I_{cryst} was the intensity of crystalline phase and I_{total} was the total intensity of all phases.

For Fourier transform infrared (FTIR) spectroscopy, spectra were recorded on a Nicolet Magna 860 FTIR instrument from Thermo Electron Corp. (DTGS detector, resolution 4/cm, accumulation of 128 scans). The beam was polarized by means of a Spectra-Tech zinc selenide wire grid polarizer from Thermo Electron Corp.

3 Results and discussion

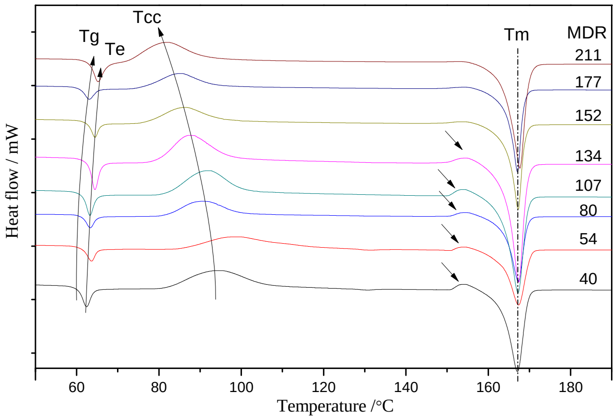


Fig. 1 DSC curves of PLA films at different melt-draw ratios

Fig.1 shows the DSC curves of PLA films with different melt-draw ratios. All the curves have a glass transition temperature (Tg), an endotherm peak just above glass transition (Te), a broad cold-crystallization exotherm (Tcc), and a melting peak (Tm). Also a weak endotherm peak before the melting peak is observed when the melt-draw ratio is below 134. It can be seen that the Tg and Te move to higher temperature with increasing the melt-draw ratios. This is similar to that observed in uniaxially drawn poly(lactic acid) films (Lee 2013), which is due to the decrease of molecular mobility induced by deformation in the rubbery state. And the cold-crystallization exotherm shifts to lower temperature and becomes sharper with increasing the melt-draw ratios, because the melt drawing process enhances the molecular orientation and crystals nuclei formation. The weak endotherm peak around 150ºC is associated with the transformation of retarded onset of ordering states formed by molecular orientation during melt-draw process to some more perfect crystals. When the molecular orientation is high enough at the higher melt-draw ratio, the endotherm peak disappears.

Fig. 2 shows the WAXD curves of PLA cast films with different melt-draw ratios. The crystalline peaks are observed at 2θ values around 21.4º and 23.8º for all samples. They are attributed to the diffraction from (210) and (015) lattice planes, respectively. The (210) lattice plane is one of the characteristic of α crystal reported by Zhang et al.(2008). Cho (2006) mentioned that when the annealing temperature was higher than 155 ºC, the 015-reflection appeared and it was attributed to the transformation of disorder part to crystals during heating. The main reflection peak from α form or α' form crystal at 16.8º for both (200) and (110) reflections appears only when the melt-draw ratio is up to 177 and this peak is very weak. During the melt-draw process, the molecular orientation induces the formation of crystal nucleus and some imperfect primary crystals appear at high melt-draw ratio.

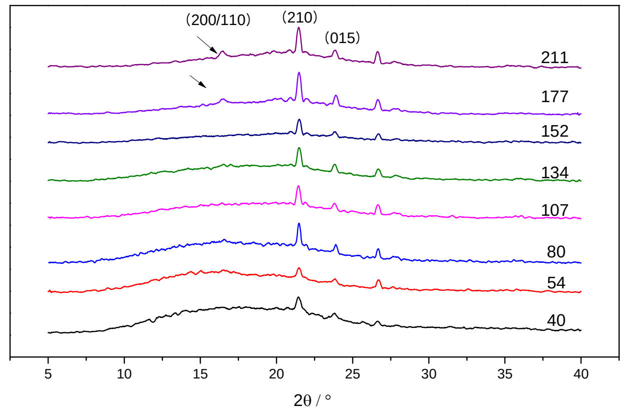


Fig. 2 WAXD curves of PLA cast films with different melt-draw ratios

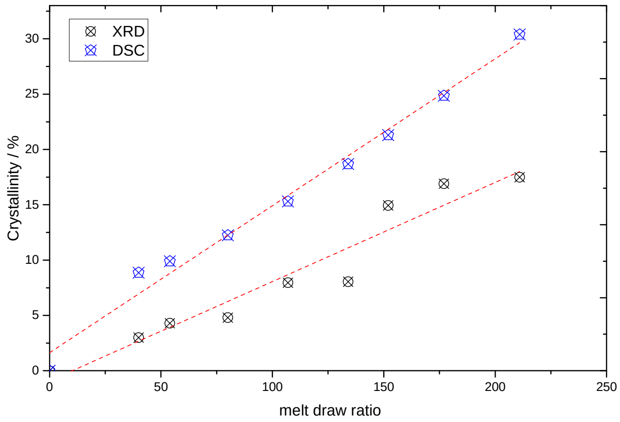
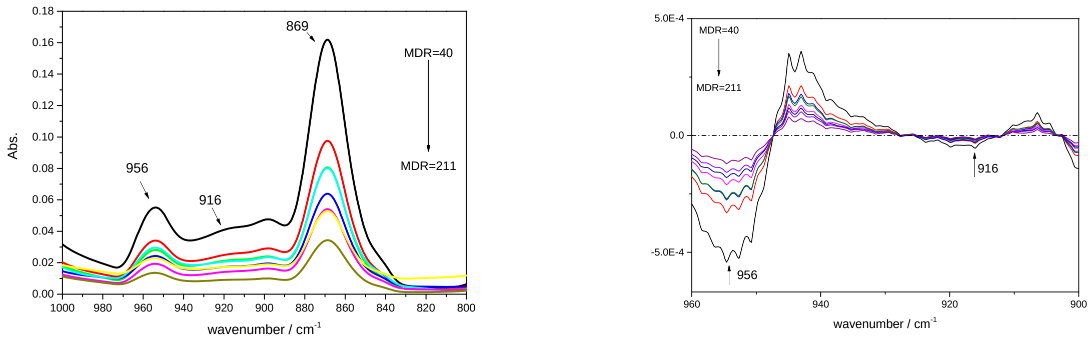


Fig. 3 The crystallinity of PLA films with different melt-draw ratios

The crystallinity of PLA cast film is showed in Fig. 3. The crystallinity increases with increasing the melt-draw ratio. Fig. 3 shows that the crystallinity calculated by DSC is larger than that from WAXD result. The two different techniques detect different aspects of crystalline phase. The DSC is sensitive to the thermal energy change of crystalline structures. During the extrusion cast process, the molecular orientation along the machine direction limits the molecular deformation. A part of thermal energy is used to melt the crystals and the others make the molecular disorientation. But the X-ray diffraction is only sensitive to the crystal parts. The oriented structure cannot form diffraction peaks on the WAXD profiles.

Fig.4 shows the IR spectra of PLA films with different melt draw ratios. Apparent absorption bands locate at 956 and 869cm^{-1}. To show the existence of band at 916cm^{-1}, the second derivatives spectra was calculated. Weak band exists at 916cm^{-1}.The band at 956cm^{-1} is ascribed to the amorphous phase in the PLA. The band at 869cm^{-1} is assigned to the C-C backbone stretching. In the crystal lattice, due to the dipole-dipole interaction, this band shifts to 871cm^{-1} (Na 2010). Here, the oriented crystalline structure is imperfect, so this band still locates at 869cm^{-1}. The band at 916cm^{-1} is also from the contribution of the oriented primary crystal phase.



(a) (b)

Fig. 4 IR spectra (a) and the second derivatives in the 960~900 cm^{-1} (b) of PLA cast films with different melt-draw ratios

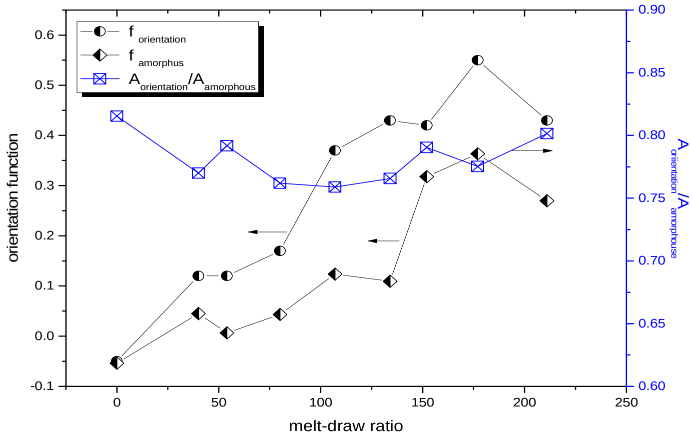


Fig. 5 Molecular orientation and relative orientation content of PLA cast films with different melt-draw ratios

The melt-draw ratios have remarkable influence on the molecular orientation. For quantitative comparison, dichroic ratio R and structural absorbance A were determined using relations (Lv 2013):

$$R = A_{\parallel} / A_{\perp}$$

$$A = (A_{\parallel} + 2A_{\perp})/3$$

where $A_{//}$ and $A_{\perp}$ are the parallel and perpendicular absorbance of a desired absorption band, respectively. Fig. 5 compares the dichroic ratio R of 916 and 956cm^{-1} band. With increasing melt-draw ratio, the orientation degree is improved both in the oriented primary crystal phase and amorphous phase. However, molecular orientation in the amorphous phase is lower than that in oriented crystal phases. The main difference in the oriented primary crystal and amorphous phases is the degree of molecular chain entanglement. The entanglement limits segmental extensibility. In addition, beyond the segmental extensibility limit, higher intermolecular cohesion exists in the oriented primary crystal phase, which can alleviate relative slippage among stretched segments and thus benefits the increase of molecular orientation. The relative orientation content between the oriented crystal and amorphous phases shown in Fig. 5 almost keeps constant. This may be due to the synchronized stretching in the oriented primary crystal and amorphous phase.

4 Conclusions

The structure and properties of PLA extrusion cast film with different melt-draw ratios were studied based on DSC, WAXD and polarized FTIR data. With increasing melt-draw ratio, the glass transition temperature and the endotherm peak move to higher temperature, the cold-crystallization temperature shifts to lower temperature and the crystallinity increases. The melt-draw process induces the PLA crystallization. But the crystal structure is imperfect and only primary ordered crystal structure is formed. The polarized FTIR confirms that the molecular orientation in the amorphous phase is much lower than that in the oriented crystal phases.

REFERENCES

Reddy, M. M., Vivekanandhan, S., Misra, M., Bhatia, S. K., and Mohanty, A. K. (2013). “Biobased plastics and bionanocomposites: current status and future opportunities.” Prog. Polym. Sci., Vol. **38**(10), 1653-1689.

Saeidlou, S., Huneault, M. A., Li, H., and Park, C. B. (2012). “Poly (lactic acid) crystallization.” Prog. Polym. Sci., Vol. **37**(12), 1657-1677.

Kalish, J. P., Aou, K., Yang, X., and Hsu, S. L. (2011). “Spectroscopic and thermal analyses of α′ and α crystalline forms of poly (L-lactic acid).” Polymer, Vol. **52**(3), 814-821.

Lv, R., Zou, S., Na, B., Deng, H., and Yu, Z. (2013). “Influence of mesophase-crystal transition on thermal and mechanical properties of stretched poly (L-lactide).” Polym. Eng. & Sci., Vol. **53**(12), 2568-2572.

Oh, M. O., and Kim, S. H. (2013). “Conformational development of polylactide films induced by uniaxial drawing”. Polym. Int. doi: 10.1002/pi.4630.

Stoclet, G., Seguela, R., Lefebvre, J. M., Li, S., and Vert, M. (2011). “Thermal and strain-induced chain ordering in lactic acid stereocopolymers: influence of the composition in stereomers.” Macromolecules, Vol. **44**(12), 4961-4969.

Lee, S. C., Han, J. I., Jeong, Y”.. G., and Kwon, M. (2009). “Strain-induced enthalpy relaxation in poly (lactic acid).” Macromolecules, Vol. **43**(1), 25-28.

Gui, Z., Lu, C., & Cheng, S. (2013). “Comparison of the effects of commercial nucleation agents on the crystallization and melting behaviour of polylactide.” Polym. Test., Vol **32**(1), 15-21.

De Oca, H. M., and Ward, I. M. (2007). “Structure and mechanical properties of poly / OODFWLF DFLG FU\VWDOV DQG ILEHUV´ - Polym. Sci. Polym. Phys., Vol. **45**(8), 892-902.

Blundell, D. J., Mahendrasingam, A., Martin, C., Fuller, W., MacKerron, D. H., Harvie, J. L., ... and Riekel, C. (2000). “Orientation prior to crystallization during drawing of poly (ethylene terephthalate).” Polymer, Vol. **41**(21), 7793-7802.

Hu, B., Lei, C., Xu, R., Shi, W., Cai, Q., Mo, H., and Chen, C. (2013). “Influence of melt-draw ratio on the structure and properties of poly (vinylidiene fluoride) cast film.” J. Plast. Film. Sheet., 8756087913508122.

Persson, M., Cho, S. W., & Skrifvars, M. (2013). “The effect of process variables on the

properties of melt-spun poly (lactic acid) fibers for potential use as scaffold matrix materials." J. Mater. Sci., Vol. **48**(8), 3055-3066.
Gogolewski, S., and Pennings, A. J. (1983). "Resorbable materials of poly (L-lactide). II. fibers spun from solutions of poly (L-lactide) in good solvents." J. App. Polym. Sci.,Vol. **28**(3), 1045-1061.
Lee, S. C., Han, J. I., and Heo, J. W. (2013). "Endotherm just above glass transition in uniaxially drawn poly (lactic acid) s films with various d-isomer contents." Polymer, Vol. **54**(14), 3624-3632.
Zhang, J., Tashiro, K., Tsuji, H., and Domb, A. J. (2008). "Disorder-to-order phase transition and multiple melting behavior of poly (l-lactide) investigated by simultaneous measurements of WAXD and DSC." Macromolecules, Vol. **41**(4), 1352-1357.
Cho, T. Y., and Strobl, G. (2006). "Temperature dependent variations in the lamellar structure of poly (l-lactide)." Polymer, Vol. **47**(4), 1036-1043.
Na, B., Tian, N., Lv, R., Li, Z., Xu, W., & Fu, Q. (2010). "Evidence of sequential ordering during cold crystallization of poly (l-lactide)". Polymer, Vol. **51**(2), 563-567.