

Three-Dimensional Simulation of the Shrinkage Behavior of Injection-Molded Poly Lactic Acid (PLA): Effects of Temperature, Shear Rate and Part Thickness

Wenhe Guo¹, Bin Yang^{1,*}, Ru Xia¹, Lifan Su¹, Jibin Miao¹, Jiasheng Qian¹, Peng Chen¹, Xuekang Yu¹, Qianlei Zhang^{1,2} and Shuangquan Deng³

¹College of Chemistry & Chemical Engineering, Anhui Provincial Laboratory of High-Performance Rubber & Products, and Key Laboratory of Environment-Friendly Polymeric Materials of Anhui Province, Anhui University, Hefei 230601, China

²School of Chemistry & Materials Science, University of Science & Technology of China, Hefei 230026, Anhui, China

³School of Polymer Science & Engineering, and State Key Laboratory of Polymer Materials Engineering, Sichuan University, Chengdu 610065, Sichuan, China

Abstract: The effects of injection temperature, shear and part thickness on the linear shrinkage of injection-molded poly (lactic acid) (PLA) were intensively analyzed using the Autodesk *Moldflow* software. The obtained results showed that both melt temperature and shear rate had obvious effects on the linear shrinkage of PLA, i.e., the linear shrinkage of PLA increases significantly with the increase of melt temperature and shear rate. In addition, the shrinkage of high-crystallinity PLA was remarkably larger than that of low-crystallinity PLA, and thin-walled parts was larger than thick-walled ones in shrinkage.

Keywords: 3D simulation, poly (lactic acid), temperature, shear rate, thickness, shrinkage.

INTRODUCTION

Injection molding (IM) technology is one of the main fabricating methods for mass production of high precision plastic parts with complex shapes, and IM products are widely used in daily life for the present time [1]. As is known, the shrinkage of IM products is an important factor that affects the accuracy of IM products. Otherwise, for sintering molding material, such as kaolin [2, 3], the shrinkage change may cause performance degradation. Generally speaking, the major factors influence the shrinkage of IM products included temperature, shear rate, mold shape, etc. Autodesk *Moldflow* is a well-known tool to analyze polymer flows in mold cavity during IM process. Through simulation set-up and illustration, the researchers can estimate the impact of the IM process of temperature, shear, thickness, etc. on shrinkage [4].

Recently, advance in synthetic polymers based on petroleum has brought in considerable convenience to our daily life, which meanwhile leads to severe problems, e.g., overexploitation of fossil resources, environmental pollution and so forth [5]. Therefore, it is

of practical significance to develop alternative and biodegradable polymers that are non-petroleum-based feedstock [6, 7]. Poly (lactic acid) (PLA), which is a biodegradable polymer with high strength and modulus. PLA has currently found wide applications in packaging, construction, medical and many other areas [7-10]. In addition to the relatively high cost, its poor dimensional stability, brittleness and poor impact strength considerably limit its further application.

Much attention has been paid to the effect of IM conditions on the shrinkage of IM polymers since 1990s [11-15]. Jansen *et al.* [16] reported that the main factor affected processing parameters were the melt temperature and the filling pressure. Higher filling pressure led to the lower shrinkage, and high temperature was better for pressure transmission, that means, the higher injection temperature generally resulted in lower shrinkage [17-20]. Kumazawa *et al.* [21] believed that higher mold temperatures would result in an increase of shrinkage. Kitti *et al.* [22] discovered that stronger shear led to lower linear shrinkage of polymers.

Up to now, the researches on PLA shrinkage were basically concentrated on the film industries [23-26]. Only scarce work has been carried out on the IM products of PLA materials. In this article, we studied the effects of temperature, shear rate and part

*Address correspondence to this author at the College of Chemistry & Chemical Engineering, Anhui Provincial Laboratory of High-Performance Rubber & Products, and Key Laboratory of Environment-Friendly Polymeric Materials of Anhui Province, Anhui University, Hefei 230601, China; Tel/Fax: +86-551-63861480; E-mail: yangbin@ahu.edu.cn

Table 1: Material Parameters of Nature Works PLA 7032D (PLA1) and Nature Works PLA 7000D (PLA2), as Provided by the Manufacturer

P-V-T parameters (unit)	Nature Works PLA 7032D	Nature Works PLA 7000D
b_5 (K)	348.15	542.15
b_6 (K/Pa)	9.55×10^{-8}	1.0×10^{-7}
b_{1m} (m ³ /kg)	8.259×10^{-4}	8.460×10^{-4}
b_{2m} (m ³ /kg·K)	8.503×10^{-7}	5.649×10^{-7}
b_{3m} (Pa)	1.628×10^8	1.35097×10^8
b_{4m} (1/K)	6.22×10^{-3}	4.67×10^{-3}
b_{1s} (m ³ /kg)	8.214×10^{-4}	7.327×10^{-4}
b_{2s} (m ³ /kg·K)	4.469×10^{-7}	8.609×10^8
b_{3s} (Pa)	2.142×10^8	4.322×10^8
b_{4s} (1/K)	6.079×10^{-3}	5.058×10^{-3}
b_7 (m ³ /kg)	0	1.132×10^{-4}
b_8 (1/K)	0	0.0332
b_9 (1/Pa)	0	6.121×10^{-9}

thickness on the shrinkage of PLA IM products based on the Computer Aided Engineering (CAE) method. The objective of the present study is to disclose the effect of various influencing factors on the shrinkage behavior of PLA IM products, which will be of great help to further optimize the operational variables of PLA during IM process.

EXPERIMENTS AND SIMULATION

Material Specifications

The polymer resins used in this study were Nature Works PLA 7032D (labeled as PLA 1) supplied by *Cargill Dow LLC*, with melt flow rate (MFR) of 8.0 g/10min under 210 °C/2kg, and Nature Works PLA 7000D (labeled as PLA 2) supplied by *Cargill Dow LLC*, with MFR of 7.0 g/10min under 210 °C/2kg. Table 1 lists the P-V-T parameters provided by the

manufacturer, Figure 1 shows the P-V-T curves of both PLA resins, with the material parameters listed in Table 1.

Part Geometry

The IM operations were carried out in two mold cavities with the dimensions of 1mm×10mm×150mm and 4mm×10mm×150mm, respectively, using the Pro/Engineer (PROE) package.

Processing Condition Set-Up

The specimens used for measurement of the shrinkage of the PLA were injected under different conditions by varying melt temperature, mold temperature, injection pressure, injection velocity, cooling and holding time, as demonstrated in Table 2. In various tests, only one of these parameters changed, with other parameter values kept constant for

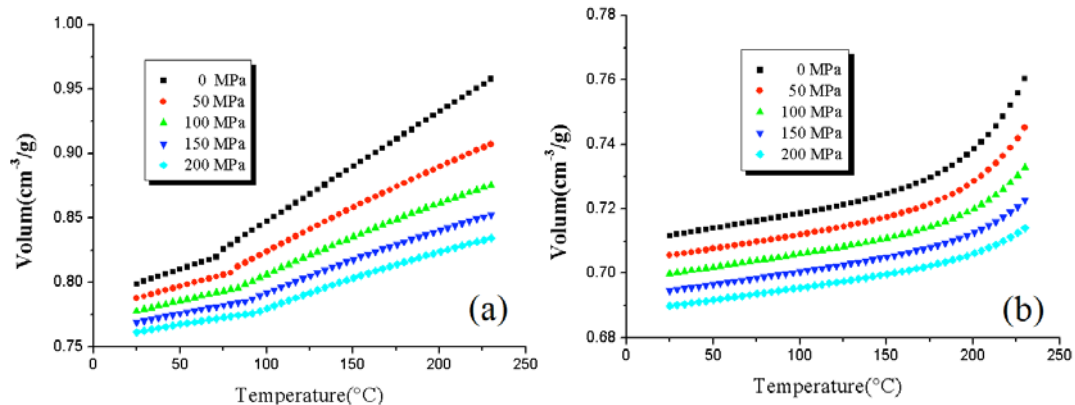
**Figure 1: P-V-T curves of Nature Works PLA 7032D and PLA 7000D.**

Table 2: Processing Parameters Selected in the Injection Moldings of PLA

Processing condition	Parameters values				
Melt temperature (°C)	180	190	200	210	220
Mold temperature (°C)	20	25	30	35	40
Injection pressure (MPa)	40	50	60	70	80
Injection velocity (g/s)	40	50	60	70	80
Holding time (s)	2	4	6	8	10
Cooling time (s)	10	15	20	25	30

better comparison. To be specific, the injection temperature is 200 °C, molding temperature 25 °C, injection pressure 60 MPa, injection velocity 60 g/s, holding time 6 s, and the cooling time 20 s.

RESULTS AND DISCUSSION

The variations of shear rate, temperature and linear shrinkage with temperature, at different thicknesses of

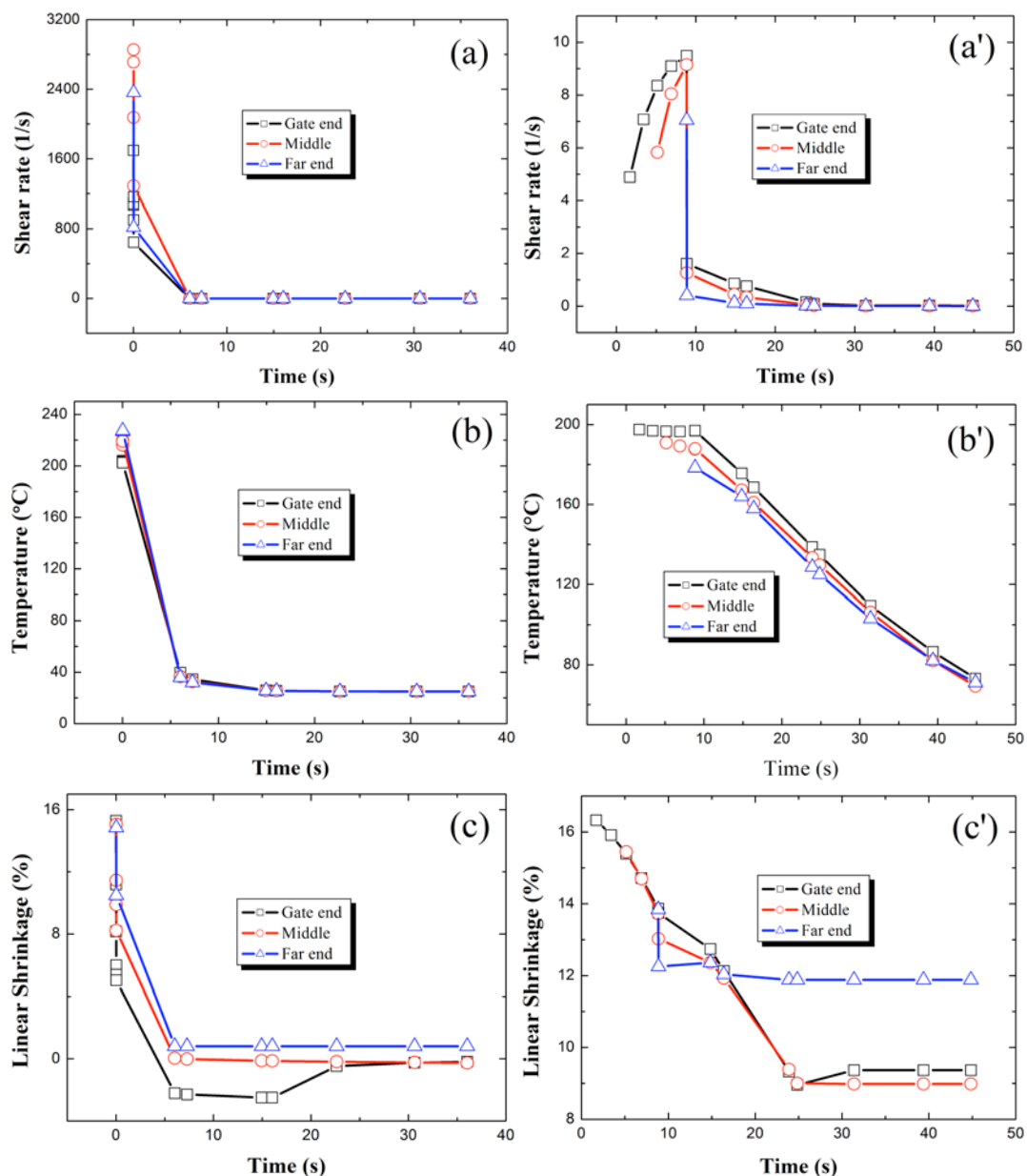


Figure 2: Effects of temperature and shear on shrinkage of PLA1. (a-c) cavity thickness = 1 mm, (a'-c') cavity thickness = 4 mm.

PLA1 at the gate end, middle and far end of the cavity were shown in Figure 2. From Figure 2a, it can be seen that there existed strong shear rate in flow direction during 0-6 s in the 1 mm cavity, indicating that the molecular chains had strongly been oriented. Figure 2b showed that the temperature of 1 mm cavity dropped to the mold temperature within an initial 6 s. In the range of 0-6 s, the PLA molecular chains were oriented along the flow direction, and during the same period the PLA melt dropped to mold temperature so fast that the orientation could be preserved, and the linear shrinkage was thus low [16].

From Figures 2a'-2c', it can be seen that the shear rate of 4 mm cavity in flow direction was relatively

small, and there was almost non-existent molecular chain orientation in flow direction. In the 4 mm cavity, melt temperature decreased slowly, as clearly shown in Figure 2b'. As can be seen from the comparison between Figures 2a-2c and Figures 2a'-2c', we can see that the effect of part thickness on the linear shrinkage for PLA1. The linear shrinkage of 4 mm cavity was larger than that of 1mm one, which is because the flow resistance of melt in the 4 mm cavity was lower than that of the 1 mm one. Considering the stronger shear rate and larger temperature drop, there was an obvious final crystallization phenomenon, and the relaxation of the molecular chains was larger as well, leading to higher linear shrinkage.

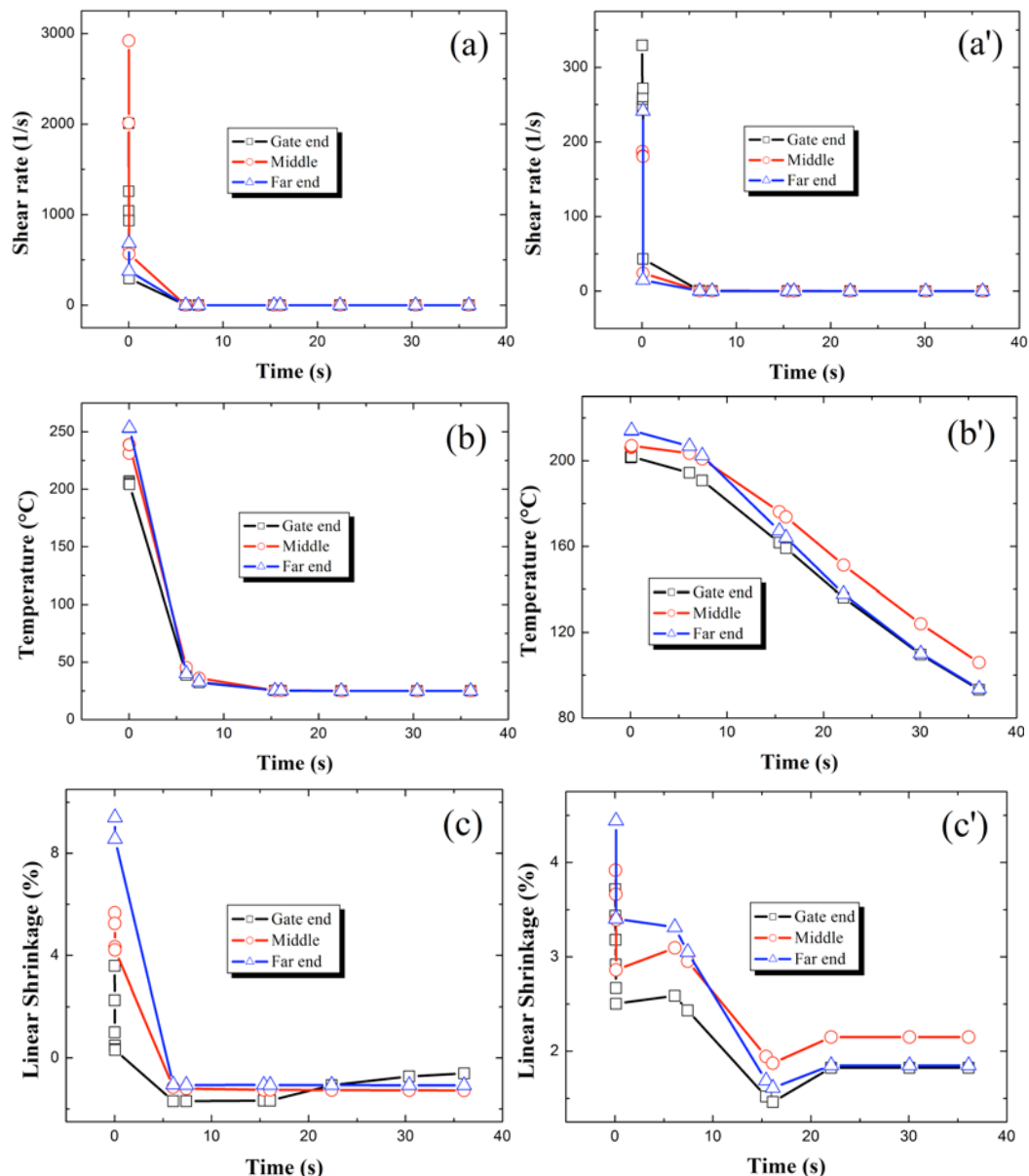


Figure 3: Effects of temperature and shear on shrinkage of PLA2. (a-c) cavity thickness = 1 mm, (a'-c') cavity thickness = 4 mm.

The variations of shear rate, temperature and linear shrinkage with time of PLA2 material at the gate end, middle and far end were shown in Figure 3. As shown in Figure 3a, in flow direction, there existed strong shearing effect in the 1 mm cavity during 0-6 s, which caused strong oriented molecular chains. As can be seen in Figure 3b, the temperature of 1 mm cavity dropped to the mold temperature in an initial 6 s. In the range of 0-6 s, the linear shrinkage of the 1 mm cavity decreased rapidly (*cf.* Figure 3c), mainly because the PLA molecular chains were oriented along the flow direction during this period, and the molecular orientation can be preserved due to a large temperature drop.

Comparison between Figures 3a-3c and Figures 3a'-3c' showed that the effect of part thickness on the linear shrinkage for PLA2. The linear shrinkage at the far end was greater than that at the gate end; while the linear shrinkage at the gate end was larger than that at the middle. Comparing Figures 2 and 3, it was obvious that the shrinkage of PLA2 was lower than PLA1, mainly due to the lower crystallinity of PLA2 (i.e., the larger crystallinity, the larger shrinkage).

CONCLUSIONS

In this work, we intensively investigated the effects of temperature, shear rate and part thickness on the shrinkage of two injection-molded PLAs using the MPI/3D flow simulation. The obtained results indicated that the melt temperature and shear rate had an obvious effect on the linear shrinkage of PLA, namely, the higher melt temperature or stronger shear rate, the larger linear shrinkage of PLA. Moreover, the shrinkage of high-crystallinity PLA was significantly larger than that of low-crystallinity PLA, and the shrinkage of thin-walled products was larger than that of thick-wall ones.

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REFERENCES

- [1] Zhou YY, Li S. Experimental study on injection molding of wheat-straw/high-density polyethylene composites. *Asian J Chem* 2013; 25: 2767-70.
- [2] Zibouche F, Kerdjoudj H, Mohamed TA. Thermal behavior of Kaolin of Tamazert (Algeria) deposit. *Asian J Chem* 2012; 24: 1111-17.
- [3] Kilic AM, Kilic O, Aritan AE, Duvertepe kaolin deposits in Balikesir (north-west Turkey) and ceramic properties. *Asian J Chem* 2006; 18: 1532-60.
- [4] Marcilla A, Odjo-Omoniyi A, Ruiz-Femenia R, *et al.* Simulation of the gas-assisted injection molding process using a mid-plane model of a contained-channel part. *J Mater Process Tech* 2006; 178: 350-57. <http://dx.doi.org/10.1016/j.jmatprotec.2006.04.095>
- [5] Wang YL, Qi RR, Xiong C, *et al.* Effects of coupling agent and interfacial modifiers on mechanical properties of poly(lactic acid) and wood flour biocomposites. *Iran Polym J* 2011; 20: 281-94.
- [6] Pilla S, Gong SQ, O'Neill E, *et al.* Poly(lactide)-pine wood flour composites. *Polym Eng Sci* 2008; 48: 578-87. <http://dx.doi.org/10.1002/pen.20971>
- [7] Tawakkal ISMA, Talib RA, Khalina A, *et al.* Optimisation of processing variables of Kenaf derived cellulose reinforced poly lactic acid. *Asian J Chem* 2010; 22: 6652-62.
- [8] Liu HZ, Zhang JW. Research progress in toughening modification of poly (lactic acid). *J Polym Sci Pol Phys* 2011; 49: 1051-83. <http://dx.doi.org/10.1002/polb.22283>
- [9] Sahin NO, Arslan H. Physicochemical characterization of poly(L-lactic acid) microspheres bearing bromhexine hydrochloride. *Asian J Chem* 2008; 20: 2754-62.
- [10] Mathew AP, Oksman K, Sain M. Mechanical properties of biodegradable composites from poly(lactic acid) (PLA) and microcrystalline cellulose (MCC). *J Appl Polym Sci* 2005; 97: 2014-25. <http://dx.doi.org/10.1002/app.21779>
- [11] Chang TC. Shrinkage behavior and optimization of injection molded parts studied by the Taguchi method. *Polym Eng Sci* 2001; 41: 703-10. <http://dx.doi.org/10.1002/pen.10766>
- [12] Liao SJ, Chang DY, Chen HJ, *et al.* Optimal process conditions of shrinkage and warpage of thin-wall parts. *Polym Eng Sci* 2004; 44: 917-28. <http://dx.doi.org/10.1002/pen.20083>
- [13] Fujiyama M, Kitajima Y, Inata H. Structure and properties of injection-molded polypropylenes with different molecular weight distribution and tacticity characteristics. *J Appl Polym Sci* 2002; 84: 2142-56. <http://dx.doi.org/10.1002/app.10372>
- [14] Fujiyama M, Wakino T. Molecular orientation in injection-molded polypropylene copolymers with ethylene. *Intern Polym Proc* 1992; 7: 97-105.
- [15] Kwon K, Isayev AI, Kim KH, *et al.* Theoretical and experimental studies of anisotropic shrinkage in injection moldings of semicrystalline polymers. *Polym Eng Sci* 2006; 46: 712-28. <http://dx.doi.org/10.1002/pen.20546>
- [16] Jansen KMB, Van Dijk DJ, Husselman MH. Effect of processing condition on shrinkage in injection molding. *Polym Eng Sci* 1998; 38: 838-46. <http://dx.doi.org/10.1002/pen.10249>
- [17] Mamat A, Trochu F, Sanschagrin B. Analysis of shrinkage by dual kriging for filled and unfilled polypropylene molded parts. *Polym Eng Sci* 1995; 35: 1511-20. <http://dx.doi.org/10.1002/pen.760351904>

- [18] Delbarre P, Pabiot J, Rietsch F, *et al.* Experimental study of processing conditions on shrinkage and on warpage of injected parts. SPE ANTEC Tech Pap 1991; 37: 301-304.
- [19] Bain MF, Janicki SL, Ulmer AS, Thomas SL. Mold shrinkage: Not a single data point. SPE ANTEC Tech Pap 1992; 1: 977-80.
- [20] Isayev AI, Hariharan T. Volumetric effects in the injection molding of polymers. Polym Eng Sci 1985; 25: 271-78. <http://dx.doi.org/10.1002/pen.760250504>
- [21] Kumazawa H. Prediction of anisotropic shrinkage of an injection molded part. SPE ANTEC Tech Pap 1994; 40: 817-21.
- [22] Kitti SS, Schultz M. The microstructure of injection-molded semicrystalline polymers: A review. Polym Eng Sci 1982; 22: 1001-17. <http://dx.doi.org/10.1002/pen.760221602>
- [23] Wu JH, Yen MS, Wu CP, *et al.* Effect of biaxial stretching on thermal properties, shrinkage and mechanical properties of poly (lactic acid) films. J Polym Environ 2013; 21: 303-11. <http://dx.doi.org/10.1007/s10924-012-0523-5>
- [24] Lee DY, Kim KY, Cho M, *et al.* Fabrication and characterization of environmentally friendly PLA/PPC/PLA multilayer film. Polym-Korea 2013; 37: 249-53. <http://dx.doi.org/10.7317/pk.2013.37.2.249>
- [25] Aou K, Kang S, Hsu SL. Morphological study on thermal shrinkage and dimensional stability associated with oriented poly (lactic acid). Macromolecules 2005; 38: 7730-35. <http://dx.doi.org/10.1021/ma051022e>
- [26] Tsai CC, Wu RJ, Cheng HY, *et al.* Crystallinity and dimensional stability of biaxial oriented poly (lactic acid) films. Polym Degrad Stabil 2010; 95: 1292-98. <http://dx.doi.org/10.1016/j.polymdegradstab.2010.02.032>

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