Crystallization, Rheology and Foam Morphology of Branched PLA Prepared by Novel Type of Chain Extender

Mi Zhou*,[1], Ping Zhou[1], Ping Xiong[1], Xin Qian[1], and Haha Zheng[2]

[1]College of Materials Science and Engineering, Zhejiang University of Technology, Hangzhou 310014, P. R. China
[2]College of Chemical Engineering, Zhejiang University of Technology, Hangzhou 310014, P. R. China

Abstract: Improving the melt strength of polylactide (PLA) is of continuing strategic research highlight, since this property affects the foaming processability. Using a novel type chain extender, namely polystyrene/poly(glycidyl methacrylate) random copolymer, PLA is branched through melt compounding. Comparing to the neat PLA, the new branched products characterize significantly improved complex viscosity as well as elongational viscosity shown from rheological experiments. Furthermore, differential scanning calorimetry analysis (DSC) indicates the branched structure could also hinder cold crystallization. Owing to the improved viscous and elastic properties, the foams of branched PLA exhibits smaller cell size and higher density, when we use supercritical carbon dioxide (Sc-CO$_2$) as the physical foaming agent.

Keywords: chain extender, branched polylactide (PLA), crystallization, rheology, foam morphology.

Introduction

Biodegradable polymers are now considered as promising alternatives to traditional (petro) polymers as they fulfill current environmental concerns in terms of environmental pollution, greenhouse gas emissions and the depletion of fossil resources. Polylactide (PLA) is the typical one derived from renewable resource (mainly corn and sugar beets),[1,2] which has been used in biomedical applications, including sutures, tissue engineering scaffolds, and drug delivery devices.[3] The need for biodegradable polymers in the context of designing materials for the environment is also opening up new markets of opportunities for PLA. For example, developing PLA foams could be used to replace polystyrene (PS) foams.[4,5]

Recently, a large volume of research has been devoted to produce PLA foam. The authors[6-9] concluded that melt strength is the most important properties to obtain desired foams. The use of chain extender (CE) has been reported to efficiently increase the melt strength. Dean *et al.*[10] prepared branched PLA by both small scale and large scale reactive extrusion with lauroyl peroxide. Lauroyl peroxide was used as an alkyl free radical source, abstracting hydrogen atoms from the PLA backbone leading to branching and chain extension reactions. The modified PLA shows increased melt strength and decreased crystallinity. Di *et al.*[11] prepared branched PLA using 1,4-butanediol and 1.4-butane diisocyanate. Foams showed two-fold density reduction and six-fold cell size deduction compared to plain

PLA. The studies by Pilla *et al.*[12,13] show that low contents of chain extender (CE) (1-2 wt%) were sufficient for branching the PLA and enabling its foaming by extrusion and injection-molding. Various chain extenders have been investigated.[14-20]

In this paper, we investigated batch foaming of branched PLA. The branching was done by polystyrene/poly(glycidyl methacrylate) random copolymer.[21] Foams were carried out using supercritical carbon dioxide (Sc-CO$_2$) as blowing agent. The aim of this investigation was to establish a relationship between the foaming behavior, crystallization, and the rheological behavior of branched PLA. The effect of chain-extender content on crystallinity and foam morphology and microstructure are discussed.

Experimental

Materials. A commercially available PLA (grade 2003D) was purchased from NatureWorks. The novel type of chain extender (CE), TMP6000, is from Seemore New Material Technology Co., Ltd, Hangzhou. Carbon dioxide (CO$_2$) was supplied by Huaxin Gas Company. PLA and CE were both dried at 70 °C for a minimum of 4 h before processing.

Chain Extension Through Melt Blending. Mixing of CE with PLA took place in a Haake Rheomix with a rotation speed of 80 rpm for 5 min at 170 °C. Four CE contents were studied (*i.e.*, 0.5, 1, 1.5, and 2 wt%) and the resultant materials were respectively denoted as PLA1, PLA2, PLA3, PLA4. Meanwhile, the neat PLA was also treated by the same ways without CE, named PLA0. After blending, all the samples

*Corresponding Author. E-mail: zhoumi@zjut.edu.cn

were molded into specimens by using compression molding (170 °C, 5 min) to measure their properties and prepare for foams.

Foam Processing. The foaming procedure was conducted in a high pressure system using Sc-CO$_2$ as the blowing agent. The samples were placed in the vessel and saturated at 12 MPa and 140 °C. After 2 h, the system was cooled to 100 °C and then reduced the pressure rapidly. The foamed samples was fixed using ice-water bath.

Characterization. The molecular weight and polydispersity index of the neat and branched PLAs were determined by gel permeation chromatography (GPC) using a Postnova 1021 solvent delivery pump, Viscotek 270 dual detector, Viscotek VE 3580 RI detector, and American Polymer Standards Corporation 10 μm AM Gel GPC columns with linear polystyrene (PS) standards. THF was used as elution at a flow rate of 1 mL/min at 25 °C. Differential Scanning Calorimetry (DSC) analysis was carried out on unfoamed and foamed samples using DSC (Mettler Toledo). The samples were first heated from 25 to 180 °C at a rate of 5 °C/min, kept isothermal for 3 min, followed by cooling to 25 °C, and finally reheated to 180 °C at 5 °C/min. All the experiments were performed under nitrogen atmosphere. Melt rheology under dynamical shear was investigated with a Physica MCR302 rheometer (Anton paar). A parallel plate (Ø=25 mm, gap= 1 mm) geometry (PP 25/pr) was selected for the dynamic frequency sweeps with controlled strain of 5%. This strain value was first verified to be in the linear viscoelastic region (LVE) for all evaluated samples. The angular frequencies were swept from 100 to 0.1 rad s^{-1} at 170 °C. A counter rotating cylinders module (SER) was used to determine the elongational properties of the PLA samples. Rectangular plates (15 mm× 10 mm×1 mm) were clamped on the cylinders and heated at given temperature before starting the test. The experiments were then performed at 170 °C with a strain rate of 0.1 s^{-1}. The cell morphologies of fractured foam specimens were observed *via* scanning electron microscopy (SEM) (Hitachi S-4700, Japan) operated at 15 kV. The specimens were frozen fractured in liquid nitrogen for around 10 min and then all specimens were sputtered with gold. The resulting micrographs were analyzed by Scion image software to determine the cell size and the cell density.[22]

Results and Discussion

Molecular Characterization of the Chain Extender and the Chain-Extended PLAs. As shown in Figure 1(a), the chain extender, TMP6000, is a kind of polystyrene/poly(glycidyl methacrylate) random copolymer. The chemical structure is characterized by ^{1}H NMR and GPC. According to the data of ^{1}H NMR (Figure S1), it is considered that the chain extender contains 20.6 wt% multi-functional epoxy group. Further, its weight averaged molecular weight (M_w) is around 8,200 g/mol, and the polydispersity index is closed to 1.72 from GPC curve (shown in Figure S2). The epoxy groups are believed to react preferentially with the end groups of PLA chains to form a branched structure, as shown in Figure 1(b). The PLA samples derived from reaction blending were first characterized by GPC. The results are tabulated in Table I. It is clearly shown that the weight average molecular weights (M_w) for branched were increased compared to the neat PLA because of the chain extension. The number average molecular weight (M_n) of PLA1 was slightly decreased in contrast to PLA0, which could be attributed to the degradation. For CE contents from 1.0 to 2.0%, the polydispersity index (PDI), M_w and M_n come to a steady state. This implies that a threshold of CE content was reached.
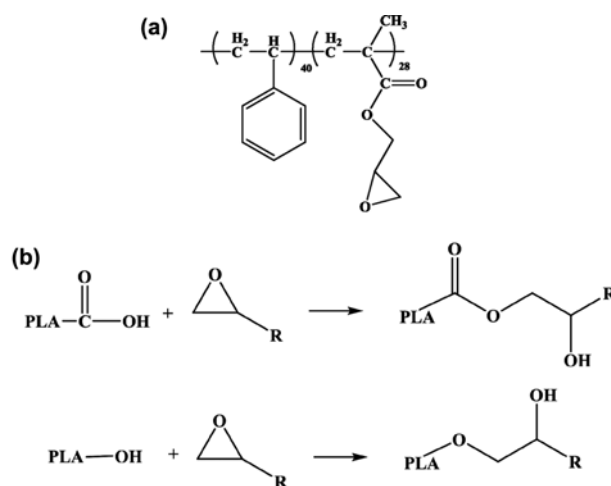

Figure 1. (a) Structure of the epoxy-base chain extenders and (b) reactional mechanism possible between epoxy groups and carboxyl or hydroxyl end groups of PLA chains.

Table I. Molar Mass Characteristics of Neat and Branched PLAs

Samples	Chain Extender Content (wt%)	M_n^a (gmol^{-1})	M_w (gmol^{-1})	PDI
PLA0	0	7.02×10^4	2.12×10^5	3.0
PLA1	0.5	6.24×10^4	3.45×10^5	5.5
PLA2	1	1.43×10^5	3.85×10^5	2.7
PLA3	1.5	1.44×10^5	3.80×10^5	2.6
PLA4	2	1.51×10^5	3.78×10^5	2.5

^{a}Determined by GPC calibrated with polystyrene standards, solvent: Tetrahydrofuran (THF).
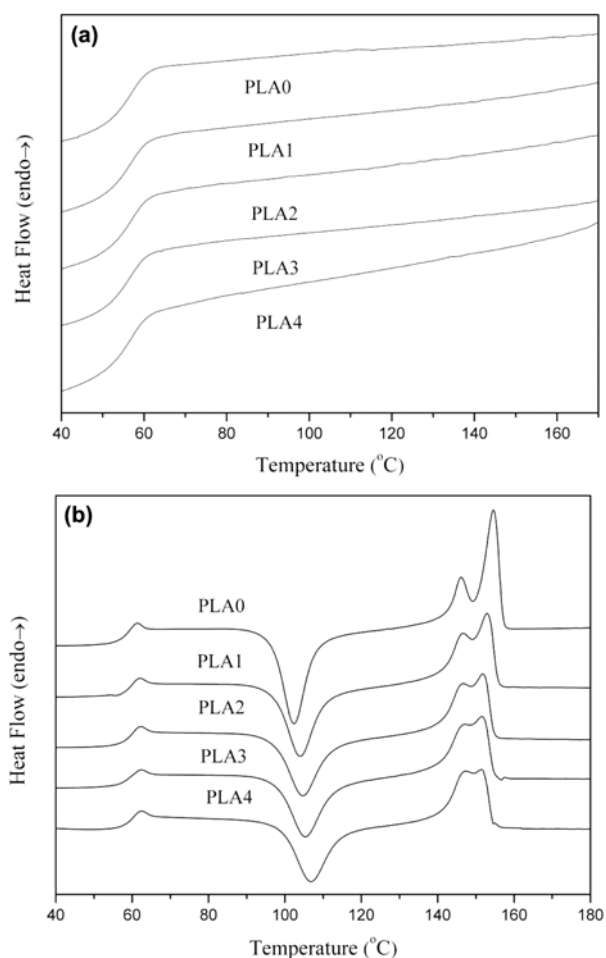
Figure 2. DSC curves of the unfoamed neat and branched PLAs: (a) cooling and (b) second heating.

Crystallization and Melting Behavior of Unfoamed Samples. It is important to verify the thermal behavior of the PLA affects by chain-branching. As can be observed in Figure 2(a), no exothermic events occurs other than the glass transition in the cooling scan. This indicates that the samples of neat and branched PLAs are difficult to crystallize from the molten state in the nonisothermal quenching process. Similar phenomena have been reported.[23] Figure 2(b) shows the second heating curves of the neat and branched PLAs. It can be seen

that T_g increased slightly in the branched PLAs compared with the neat PLA. This is due to the enhancement of the molecular chain entanglement, including the higher molecular weight and the mobility restriction on branched points. Owing to the slow crystallization rate of PLA, the exothermic peaks attributed to cold-crystallizations appear for all five samples. Furthermore, the cold crystallization temperature (T_c) increased slightly, while the cold crystallization enthalpy (ΔH_c) of the branched PLAs is lower compared with the neat PLA. It is caused by the formation of the branched molecular structure.[24] In addition, with the increase of CE content, T_c increased gradually, which indicated that with the increase of CE content, the degree of branching is increased, thereby introducing remarkable restrictions in chain mobility.[25] It is noticed in Figure 2(b), all samples displayed double melting peaks, coded as T_{m1} and T_{m2}, respectively. Multiple melting peaks are a common phenomenon for semicrystalline polymers. It has been reported that the double melting behavior of PLA is due to melt-reorganization.[26] The imperfect crystals formed in cold crystallization would reorganize into more orderly crystal structures.[27] It also can be seen that with increasing CE content, the magnitude of the low endotherm increases but that of the high endotherm decreases. This might be associated with the fact that CE can hinder crystallization of PLA as discussed previously. The details were summarized in Table II.

Rheological Properties. Linear viscoelastic properties are sensitive to the changes of macromolecular structures of polymers. In the last research, either the linear or the branched PLA is considered to obey the empirical Cox-Merz rule.[28] So dynamic rheological frequency sweeps were used to determine differences in the structures of the neat and branched PLA samples. Figure 3(a) shows their complex viscosity as a function of frequency. It can be seen that PLA0 exhibits typical Newtonian behavior in the low frequency region and small shear thinning starts up to 1 Hz that is a characteristic for linear polymers. However, the branched PLAs have much higher complex viscosities than the linear PLA. And the Newtonian zone disappear in the measured frequency range. The high viscosities for branched PLAs are caused by molecular entanglement with the increase of molecular weights and the strong shear thinning behavior is typical for crosslinked.[29] In addition to molecular entanglements, strong physical interaction between ester groups also play a role in rheological behavior

Table II. DSC Thermograms of Neat PLA and Branched PLAs

Samples	T_g (°C)	T_c (°C)	ΔH_c^a (J/g)	T_{m1} (°C)	T_{m2} (°C)	ΔH_m^a (J/g)	X_c^b (%)
PLA0	57.35	102.44	27.14	146.02	154.48	-28.25	1.18
PLA1	58.48	104.02	23.68	146.10	152.84	-24.44	1.06
PLA2	58.17	104.77	22.10	146.69	151.76	-22.61	0.54
PLA3	58.13	105.36	22.66	147.09	151.58	-22.68	0.66
PLA4	58.32	106.86	21.63	147.37	151.46	-22.46	0.83

[a]Determined from the DSC curve for the second heating. [b]$X_c(\%)=(\Delta H_m-\Delta H_c)/\Delta H_{m0}\times100$, the fusion enthalpy of 100% PLA crystalline (ΔH_{m0}) was assumed to be 93.7 J/g.
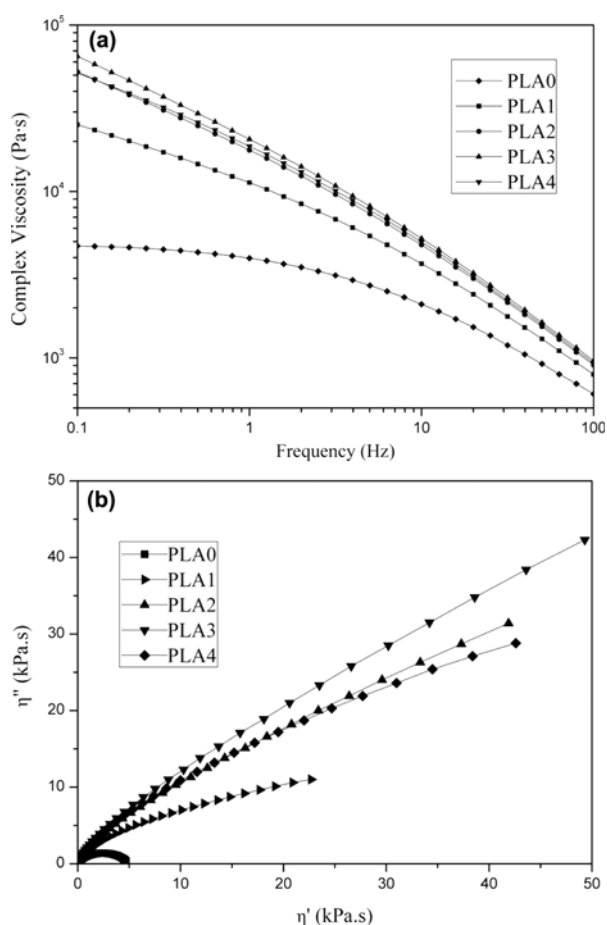
Figure 3. (a) Complex viscosities as a function of frequency and (b) Cole-Cole plots of neat and branched PLAs at 170 °C under 5% dynamic strain.

Figure 4. (a) Storage modulus (G') and (b) loss modulus (G'') of neat and branched PLAs at 170 °C under 5% dynamic strain.

of crosslinked polyesters.[30] That is, the physical bonding through ester groups may lead to the formation of pseudo-structures, which would increase with increasing molecular weight of PLA. Furthermore, the viscosity of PLA first increased with CE content and then reached equilibrium at a level around 1.0 wt% CE. Because it is more difficult to protect the material from humidity in an internal mixer (at atmospheric pressure). This is possibly an equilibrium value imposed by simultaneous chain branching through chain-end reaction and chain scission through random hydrolysis reaction.

When the imaginary part (η'') of the complex viscosity is plot against the real part (η'), a Cole-Cole plot is obtained. As shown in Figure 3(b), only linear PLA gave a symmetric arc shape. And all branched PLAs displayed significant upturning at high viscosity. It is a typical characteristic for the long chain branching polymers, due to their elastic-solid-like features caused by side chains.[31]

It is well-known that the complex viscosity can be separated into two parts, the storage modulus G' and the loss modulus G''.[31] The elastic part is represented by G', while the viscous part is described by G''. As shown in Figure 4, the increase
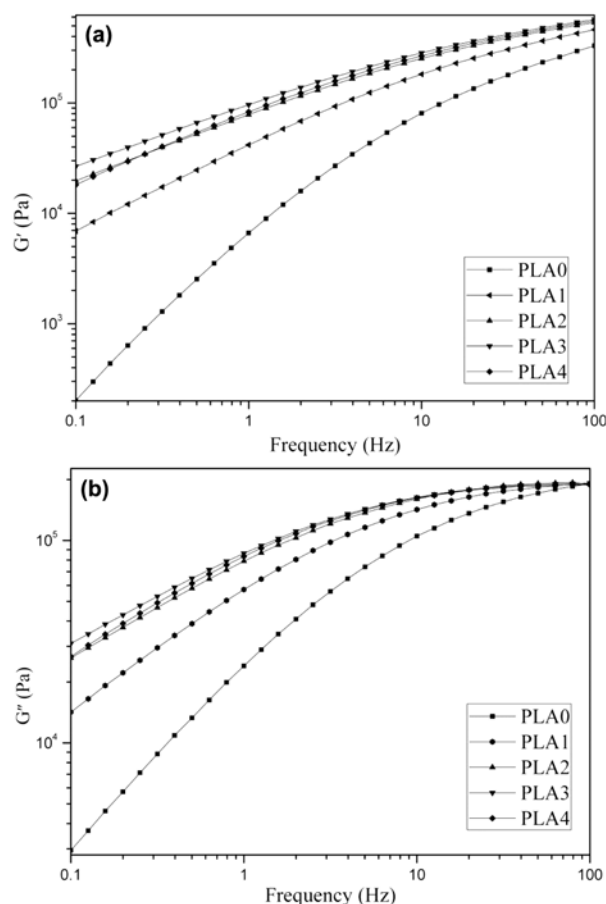
trend of G' and G'' is considered as similar as the complex viscosity. It is suggested that the branched structures could better withstand the shear strain as opposed to neat PLA. Accordingly, it could be attributed to more entanglements and the previously suggested pseudostructures through formation of physical networks at high molecular weight. On the other hand, both G' and G'' declined with the measurement frequency. And the extent of the G' change is slightly bigger than that of the G'' change with the frequency. It is known that the melt elasticity has a direct relationship with the melt strength which is an indication of the resistance for a melt to extension.

Since foaming mainly induces melt stretching, it is important to evaluate the elongational viscosity for the neat and extended PLAs. Figure 5 presents that the elongational viscosity of branched PLAs is slightly increased compare to neat PLA, and neat PLA behaves as a linear polymer exposed to axial strain. Meanwhile, branched specimens demonstrate certain strain hardening behavior which is typical characteristic of highly entangled polymer. This property in the molten state is reported to be mandatory for melt extensional process such as film blowing or foaming.[32,33] As a result, the obtained rhe-
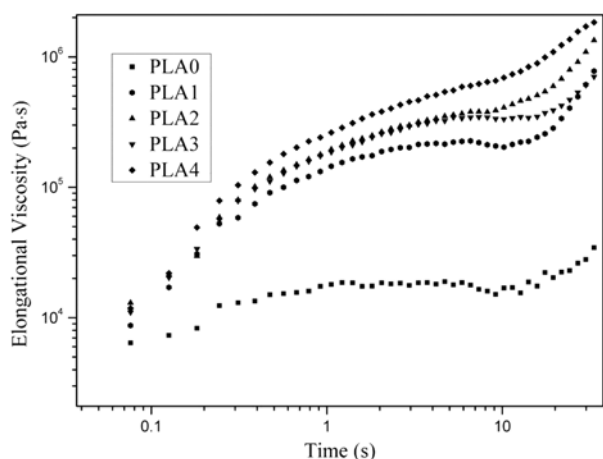
Figure 5. Elongational viscosities of neat and branched PLAs performed at 170 °C under strain rate of 0.1 s⁻¹.
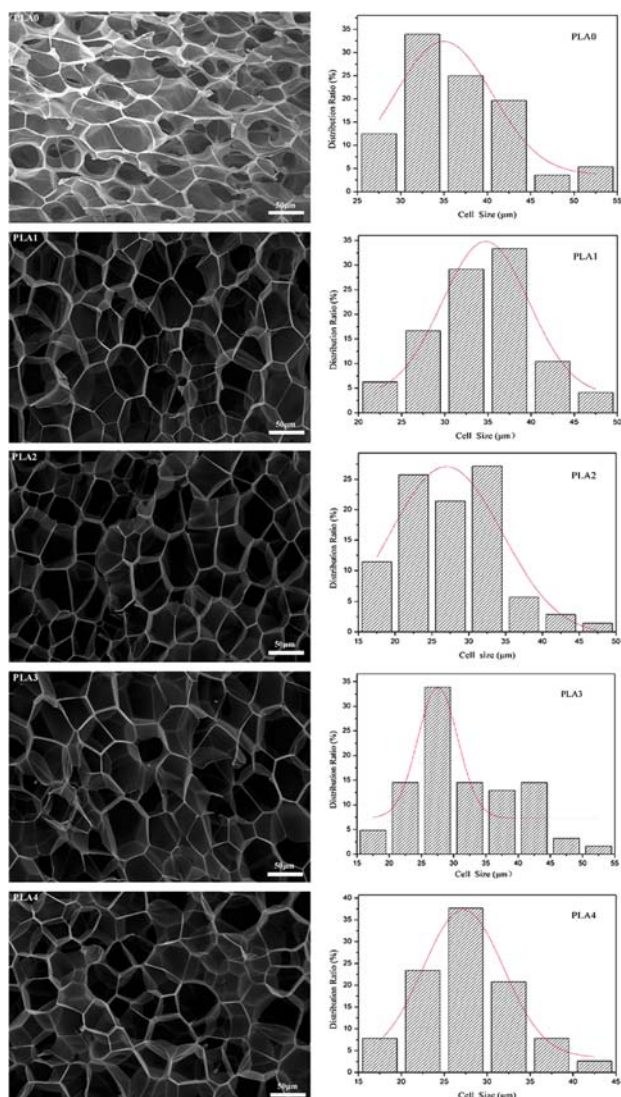

Figure 6. SEM micrographs and cell size distribution of the neat and branched PLAs.

ological improvements were expected to have a significant effect on foaming with supercritical CO_2.

Foam Processing. It has been well described that high melt viscosity at low shear rate/frequency, high shear sensitivity, and high melt strength are the characteristics of the resins suitable for foaming.[34] The effect of CE on the cell morphology of PLA foams is illustrated in Figure 6. As expected, neat PLA foam presented poor cell structure. With the different to the neat PLA, the foams of the branched PLAs exhibit uniform cell distribution, elliptical cell structure, and thin cell wall. The results of image analysis on these micrographs are listed in Table II. It can be seen that the cell coalescence and rupture are observed in the PLA foams. Meanwile, the average cell size of PLA1 is slightly less than PLA2, PLA3, and PLA4. This behavior is due to the high viscosity and stronger strain hardening of PLA2, PLA3, and PLA4 samples. Both of the two phenomena are due to the differences of the viscosity and the strain hardening of the samples. Accordingly, the resulted foams of PLA2, PLA3, and PLA4 have higher foaming grade (higher cell density), which implies that there exists optimum in foam density control by melt viscosity and elongational viscosity. Furthermore, the polystyrene segments in chain extender may accelerate nucleation.

Crystalllization and Melting Behavior of Foamed Samples. DSC scans on heating of neat and branched PLA foams are shown in Figure 7. At the time of testing, the CO_2 had

Table III. Average Cell Size, Cell Density for Foamed Neat and Branched PLAs

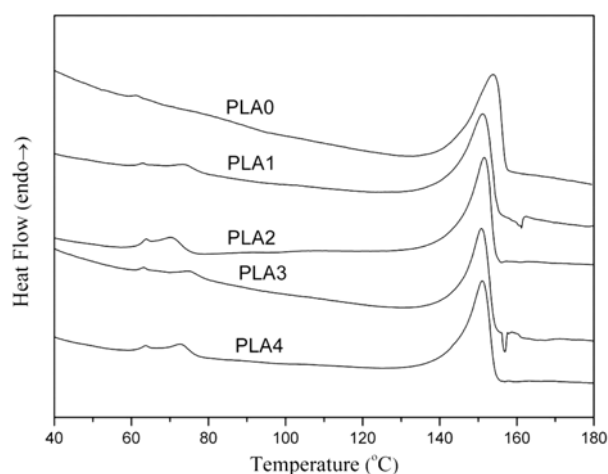| Samples	Average Cell Size (μm)	Average Cell Density ($10^7 \cdot cm^{-3}$)
PLA0	36.9	1.5
PLA1	34.3	2.7
PLA2	27.6	4.2
PLA3	28.1	3.5
PLA4	27.8	3.6

Figure 7. DSC curves of the foamed neat and branched PLAs.

completely diffused out of the samples. Thus, the DSC measurements were not affected by any CO_2 plasticization effect. It can be seen that two weak relaxation peaks appear at about 63 and 73 ^{o}C for branched PLAs, indicating that two glass transition temperatures occurs. This could be attributed to the foaming process. The samples were subjected to two thermal histories, *i.e.*, saturated in CO_2 at 12 MPa and 140 ^{o}C, foaming by decompression and quenched in ice-water bath. It is well known that CO_2 saturation and the growth of the nucleated bubbles generated the local strain field variation, which enhanced the crystallization process. However, the stress-induced arrangement was more or less incomplete due to the suddenly quenching. Thus, the two peaks occur. Furthermore, all the samples do not present any cold crystallization upon heating. This could be attributed to the aforementioned reason.

Conclusions

In present study, PLA was branched successfully using a novel type of reactive chain-extender (CE), which component is polystyrene/poly(glycidyl methacrylate) random copolymer. Based on DSC analysis, it was observed that the addition of CE increased the cold crystallization temperature, while decreased the degree of crystallinity of PLA. The branched PLAs exhibited increased complex viscosity and more pronounced shear thinning behavior, and produced obvious strain hardening, as indicated by dynamic frequency sweep measurement and elongational rheological measurement. The neat and branched PLAs foams were produced by batch foaming with Sc-CO_2. The higher complex viscosity and enlongational viscosity for the branched resins allowed the production of PLA foams with smaller cell size, higher cell density compared to plain PLA.

Supporting Information: Information is available regarding the ^{1}H NMR and GPC data of chain extender. The materials are available *via* the Internet at http://www.springer.com/13233.

References

(1) R. E. Drumright, P. R. Gruber, and D. E. Henton, *Adv. Mater.*, **12**, 1841 (2000).

(2) J. Y. Park, S. Y. Hwang, W. J. Yoon, E. S. Yoo, and S. S. Im, *Macromol. Res.*, **20**, 1300 (2012).

(3) L. T. Lim, R. Auras, and M. Rubino, *Prog. Polym. Sci.*, **33**, 820 (2008).

(4) W. T. Zhai, Y. Ko, W. L. Zhu, A. S. Wong, and C. B. Park, *Int. J. Mol. Sci.*, **10**, 5381 (2009).

(5) L. M. Mathieu, M. O. Montjovent, P. E. Bourban, D. P. Pio-

letti, and J. A. E. Manson, *J. Biomed. Mater. Res. Part A*, **75A**, 89 (2005).

(6) J. H. Lee, S. H. Park, and S. H. Kim, *Macromol. Res.*, **22**, 424 (2014).

(7) M. Sauceau, J. Fages, A. Common, C. Nikitine, and E. Rodier, *Prog. Polym. Sci.*, **36**, 749 (2011).

(8) M. Mihai, M. A. Huneault, B. D. Favis, and H. B. Li, *Macromol. Biosci.*, **7**, 907 (2007).

(9) J. H. Lee, S. H. Park, and S. H. Kim, *Macromol. Res.*, **21**, 1218 (2013).

(10) K. M. Dean, E. Petinakis, S. Meure, L. Yu, and A. Chryss, *J. Polym. Environ.*, **20**, 741 (2012).

(11) Y. W. Di, S. Iannace, E. Di Maio, and L. Nicolais, *Macromol. Mater. Eng.*, **290**, 1083 (2005).

(12) S. Pilla, S. G. Kim, G. K. Auer, S. Q. Gong, and C. B. Park, *Polym. Eng. Sci.*, **49**, 1653 (2009).

(13) L. Y. Wang, X. B. Jing, H. B. Cheng, X. L. Hu, L. X. Yang, and Y. B. Huang, *Ind. Eng. Chem. Res.*, **51**, 10731 (2012).

(14) Å. Larsen and C. Neldin, *Polym. Eng. Sci.*, **53**, 941 (2013).

(15) S. Y. Cho, H. H. Park, Y. S. Yun, and H. J. Jin, *Macromol. Res.*, **21**, 529 (2013).

(16) L. Yu, G. Toikka, K. Dean, S. Bateman, Q. Yuan, C. Filippou, and T. Nguyen, *Polym. Int.*, **62**, 759 (2013).

(17) S. Pilla, A. Kramschuster, L. Q. Yang, J. Lee, S. Q. Gong, and L. S. Turng, *Mater. Sci. Eng. C: Biomimetic Supramol. Syst.*, **29**, 1258 (2009).

(18) M. Nofar, W. Zhu, and C. B. Park, *Polymer*, **53**, 3341 (2012).

(19) K. J. Sim, S. O. Han, and Y. B. Seo, *Macromol. Res.*, **18**, 489 (2010).

(20) J. Wang, W. L. Zhu, H. T. Zhang, and C. B. Park, *Chem. Eng. Sci.*, **75**, 390 (2012).

(21) S. L. Sun, M. Y. Zhang, H. X. Zhang, and X. M. Zhang, *J. Appl. Polym. Sci.*, **122**, 2992 (2011).

(22) J. Shen, C. Zeng, and L. J. Lee, *Polymer*, **46**, 5218 (2005).

(23) D. H. S. Souza, S. V. Borges, M. L. Dias, and C. T. Andrade, *Polym. Compos.*, **33**, 555 (2012).

(24) V. Tserki, P. Matzinos, E. Pavlidou, and C. Panayiotou, *Polym. Degrad. Stab.*, **91**, 377 (2006).

(25) M. Yasuniwa, S. Tsubakihara, Y. Sugimoto, and C. Nakafuku, *J. Polym. Sci. Part B: Polym. Phys.*, **42**, 25 (2004).

(26) Y. T. Shieh and G. L. Liu, *J. Polym. Sci. Part B: Polym. Phys.*, **45**, 1870 (2007).

(27) X. Ling and J. E. Spruiell, *J. Polym. Sci. Part B: Polym. Phys.*, **44**, 3378 (2006).

(28) R. A. Mendelson, W. A. Bowles, and F. L. Finger, *J. Polym. Sci. Part A: Polym. Chem.*, **8**, 105 (1970).

(29) T. Y. Kim, D. M. Kim, W. J. Kim, T. H. Lee, and K. S. Suh, *J. Polym. Sci. Part B: Polym. Phys.*, **42**, 2813 (2004).

(30) H. G. Chae, B. C. Kim, S. S. Im, and Y. K. Han, *Polym. Eng. Sci.*, **41**, 1133 (2001).

(31) J. Tian, W. Yu, and C. Zhou, *Polymer*, **47**, 7962 (2006).

(32) G. J. Nam, J. H. Yoo, and J. W. Lee, *J. Appl. Polym. Sci.*, **96**, 1793 (2005).

(33) P. Spitael and C. W. Macosko, *Polym. Eng. Sci.*, **44**, 2090 (2004).

(34) H. Liu and J. Zhang, *J. Polym. Sci. Part B: Polym. Phys.*, **49**, 1051 (2011).