T_g Depression in Poly(L(−)-lactide) Crystallized under Partially Constrained Conditions

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ABSTRACT: A significant reduction in the glass transition temperature (T_g) is found for poly(L-(−) lactide) (PLLA), crystallized under partially constrained conditions, where the polymer is prevented from shrinking. It is proposed that the constrained crystallization process results in increasing the net free volume in the amorphous phase. This is a result of the fixed sample volume in which there is an increasing crystal volume fraction at a higher density than the amorphous fraction, depleting polymer mass from the amorphous fraction, which is not able to contract to maintain its nominal density. The T_g depression increases with increasing degree of crystallization or crystallization temperature, T_c. On the other hand, unconstrained PLLA samples (free to shrink during crystallization) exhibit the conventional trend of increasing T_g with crystallinity or T_c. Although the difference in T_g between samples prepared by the two methods could be large, as much as 30 °C, the melting point, heat of fusion, and overall degree of crystallinity in PLLA are not influenced. Finally, shear-induced crystallization does not affect any of the physical properties studied here but only modifies the crystallization rates, increasing them by enhancing nucleation.

Introduction

Poly(L(−)-lactide) (PLLA) is a biodegradable polymer studied for a wide variety of applications, from implantable medical devices to environmentally friendly packaging materials.[1−5] It is well-known that the degradation rate of PLLA in vivo or in appropriate environmental conditions depends on polymer morphology and glass transition temperature. One aspect of that characterization is given in this paper, where we relate our findings on an interesting and surprising trend in the glass transition temperature of the polymer on crystallization under constrained vs unconstrained conditions. For the purpose of this paper, the constrained conditions we studied are those of restricted volumetric contraction during crystallization. Specifically, by constrained conditions we mean those conditions under which the crystallizing polymer is nominally prevented from shrinking during crystallization by the polymer affinity to the walls of the vessel containing it. Unconstrained conditions have no constraints on one or more surface of the crystallizing polymer (e.g., an open-topped vessel, where during crystallization the polymer is free to contract from the top surface).

Previously, a number of physical factors have been shown to influence the glass transition temperature. It has been reported that organic liquids confined to nanoporous matrices[6,7] as well as thin nanoscale polymer films[8,9] have physical properties that can differ significantly from their bulk counterparts. In most reports, reduction of the glass transition temperature has been observed with a decrease in the pore size or a decrease in the film thickness approaching the average end-to-end distance of the unperturbed polymer chains. At those microscopic dimensions, events such as polymer−substrate interactions, effect of free surface, finite chain size, and interfacial energy have been shown to play key roles in determining polymer dynamics.[10−13] Unlike those studies, in the present paper we will investigate the glass transition in relatively thick films (300 μm). At this macroscopic level, physical parameters such as T_g are independent of film thickness.

In this study, the physical properties of PLLA crystallized isothermally under the constrained and unconstrained conditions are evaluated using calorimetric and X-ray diffraction methods. In addition, depolarized small-angle light scattering is used to monitor real-time crystallization kinetics in an optical shear cell apparatus to compare data generated at different crystallization temperatures as well as those obtained by quiescent and step-shear methods. We will discuss our findings of T_g depression on crystallization under the confined conditions of restricted volumetric contraction and the dependence of T_g depression on crystallization temperature.

Experimental Section

Materials. Poly(L(−)-lactide) homopolymer (hereafter, referred to as PLLA) was prepared at Ethicon by a tin-catalyzed ring-opening bulk polymerization. The polymer, after grinding and heating in vacuo to remove most of the unreacted monomer, has an inherent viscosity (IV) of 1.75 dL/g in hexafluoro-2-propanol (HFIP) at 25 °C at a concentration of 0.1 g/dL. The PLLA weight-average molecular weight, M_w, is 117 000 g/mol, with a number-average molecular weight, M_n, of 50 000 g/mol (by GPC). Prior to use, the samples were stored under high vacuum; during testing, exposure to ambient atmosphere was limited. Selected samples were examined for molecular weight and inherent viscosity reduction following the experimental procedure, and no significant reductions were found (<2%). NMR analysis at the end of crystallization cycles revealed that no monomer generation occurred during this process.

Techniques. Calorimetric results were generated on a TA Instruments differential scanning calorimeter (DSC), model 2910 MDSC, using dry nitrogen as a purge gas. A DSC pan was used without a lid, serving as our unconstrained environment for PLLA crystallization. PLLA samples crystallized in the DSC pan were free to shrink from all sides of the pan during crystallization. The heating rate was 10 °C/min.

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Table 1. Physical Properties of PLLA Films Crystallized Isothermally by Different Methods Using Quiescent and Step-Shear Conditions[a]

sample ID	crystallization conditions	T_g (°C)	T_m (°C)	ΔH_m (J/g)	% cryst [WAXD]
amorphous-1	quenched from melt in DSC cell and heated at 10 °C/min	61.5	179.0 (T_c = 110 °C) (ΔH_c = 53 J/g)	52.5	36.0
amorphous-2	annealed at 150 °C in optical cell for 120 min	52.5	179.5 (T_c = 110 °C) (ΔH_c = 55 J/g)	55.0	37.0
amorphous-3	pressed between two glass slides and quenched from the melt	56.0	179.0 (T_c = 110 °C) (ΔH_c = 54 J/g)	54.0	37.0
80c-q1	quiescent at 80 °C for 90 min	46.5	176.0	62.5	42.5
80c-2	quiescent at 80 °C for 900 min	46.0	176.0	70.0	48.0
80c-s	step shear at 80 °C for 90 min	48.0	175.5	66.0	40.5
90c-q	quiescent at 90 °C for 30 min	45.0	176.0	63.5	44.0
90c-s	step shear at 90 °C for 50 min	45.5	176.5	58.0	43.0
100c-q	quiescent at 100 °C for 30 min	48.0	178.5	59.0	42.0
100c-s	step shear at 100 °C for 25 min	47.5	178.0	60.5	41.0
105c-q1	quiescent at 105 °C for 30 min	45.5	176.0	66.0	45.0
105c-q2	quiescent at 105 °C in DSC cell/30 min	61.5	178.5	51.5	36.0
105c-s	step shear at 105 °C for 35 min	46.5	178.5	68.0	44.0
110c-q1	quiescent at 110 °C for 50 min	46.0	179.0	67.0	46.0
110c-q2	quiescent at 110 °C for 1200 min	44.5	175.0	79.0	54.0
110c-q3	quiescent at 110 °C in DSC cell/60 min	62.0	180.0	58.0	43.0
110c-s	step shear at 110 °C for 20 min	47.0	178.5	69.5	47.0
120c-q	quiescent at 120 °C for 90 min	43.0	177.5	64.0	44.0
120c-s	step shear at 120 °C for 80 min	42.0	174.0	70.3	48.5
130c-q1	quiescent at 130 °C for 140 min	44.0	178.0	69.5	48.0
130c-q2	quiescent at 130 °C in DSC cell/120 min	63.5	179.0	78.0	53.0
130c-q3	pressed and oven-annealed film; quiescent at 130 °C for 600 min under N_2	43.0	177.0	67.0	46.0
130c-s	step shear at 130 °C for 70 min	41.0	176.5	82.0	55.0
140c-q1	quiescent at 140 °C for 600 min	39.0	181.5	88.5	61.0
140c-q2	quiescent at 140 °C in DSC cell/300 min	64.5	181.0	83.0	56.5
140c-s	step shear at 140 °C for 100 min	39.5	182.0	85.0	58.0
145c-q	quiescent at 145 °C for 600 min	37.5	184.5	86.5	59.0
145c-q1	quiescent at 145 °C in DSC cell /360 min	66.5	185.0	83.5	57.5
145c-s	step shear at 145 °C for 600 min	40.0	185.0	90.0	58.5
150c-s	step shear at 150 °C for 200 min	38.0	186.5	94.5	65.0

[a] Note: All pressed and annealed samples after melting and second reheating display the same properties as sample ID amorphous-1.

The overall percent crystallinity in studied materials is determined by wide-angle X-ray diffraction (WAXD). X-ray measurements are carried out on a Siemens Hi-Star unit using Cu Kα radiation at the wavelength of 1.542 Å. Samples are mounted on the goniometer in such a way that the surface of the polymer film was positioned normal to the X-ray beam. The deconvolution of the X-ray images and the calculation of crystallinity content are conducted using the DIFFRAC PLUS software developed by Siemens.

Depolarized small-angle light scattering (SALS) transmission measurements are used to obtain real-time crystallization kinetics. A helium neon laser was the light source. The beam path consisted of a series of optical components, guiding the polarized light through the sample, to a photodetector and/or to a screen. The sample was enclosed in a Linkam CSS 450 Cambridge shearing system equipped with quartz windows. For shear-induced, nucleation-enhanced crystallization, a step shear rate of 1 s^{-1} (strain 125% for duration of 1 s with a sample thickness of about 300 μm and diameter 30 mm) was applied at the moment the sample reached the crystallization temperature. More details on the SALS apparatus and Linkam CSS 450 Cambridge shearing system can be found in our previous communications.[14,15]

Crystallization Procedure. Prior to use, the samples were stored under nitrogen. All samples were melted at 210 °C for 10 min to erase any thermal or mechanical history. For samples crystallized in the optical shear cell (constrained conditions), the upper lid of the shear cell was lowered after 5 min at the melting temperature of 210 °C to achieve a sample thickness of about 300 μm (verified after each experiment). Following the melting step, the samples were quenched to the desired crystallization temperature. They were then allowed to crystallize quiescently, or with a step shear for particular samples (noted in Table 1), until the crystallization process was completed—the kinetics were determined by SALS turbidity measurements and ultimate crystallinity determined by WAXD. Selected polymer films were made using an MTP-14 Tetrahedron compression molding press with the stainless steal plates operating under a high flow of nitrogen. The samples were melted in a mold frame at 210 °C for 5 min, and a 10 ton force was employed to produce uniform films. After melting, the mold frame was immediately brought from the compression molder to an already preheated annealing oven to conduct isothermal crystallization. It should be emphasized that for both unconstrained and constrained crystallization conditions the samples were exposed to identical thermal histories.

Results and Discussion

The physical properties of PLLA crystallized isothermally under various experimental conditions are listed in Table 1. The most important and unexpected result reported in Table 1 is the substantial reduction of T_g (by as much as 30 °C) in PLLA samples crystallized under constrained conditions vs unconstrained conditions. This behavior does not appear to be caused by any chemical change in the polymer. (NMR indicates no monomer generation; GPC and IV show no significant M_w changes.) To check whether the constrained conditions can be reproduced in a setup other than our optical cell, we prepared PLLA films by compression molding using stainless steel plates. The compression-molded samples experienced much higher nitrogen flow rates than samples in the optical cell, but this difference did not influence the T_g depression found in both cases. The thermal analysis and WAXD results for these samples, shown in Table 1, indicate that the T_g depression is not unique to the optical cell. It was also found that this effect is reversible: all T_g-depressed samples, after being remelted and scanned in the DSC in a second heating step, have glass transition temperatures that return to their unconstrained "normal" literature values. If the origin of the T_g depression was due to a chemical change in the polymer, it would not be reversible by a second DSC heating step.

The glass transition temperature of PLLA crystallized under partially constrained conditions decreases sys-

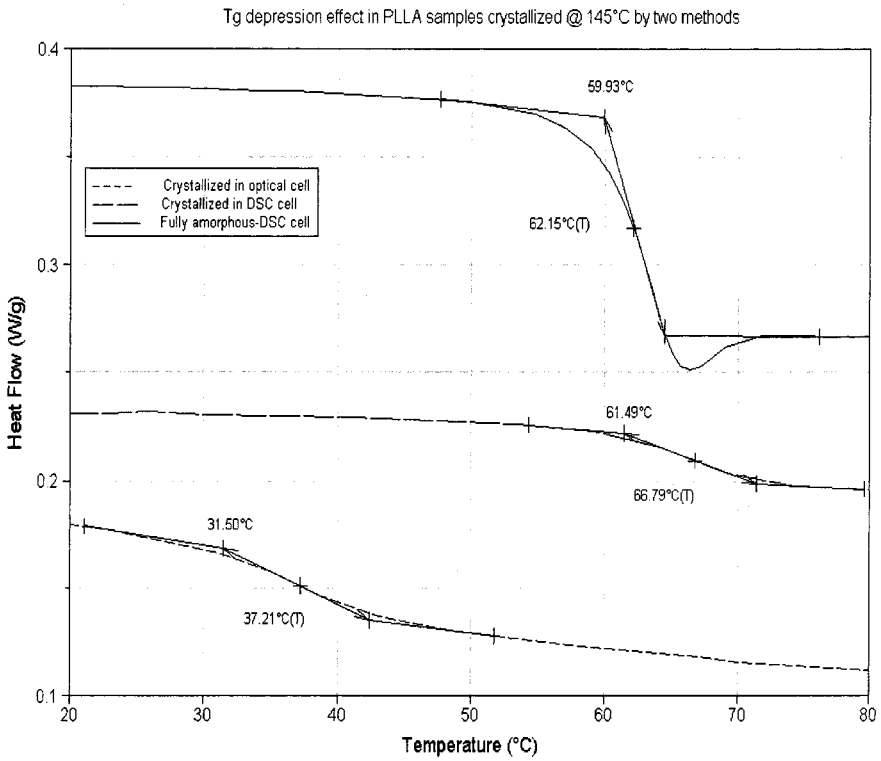

Figure 1. DSC thermograms of a T_g-depressed, constrained sample, and an unconstrained sample. The thermogram of a fully amorphous sample is also shown as a comparison.

tematically with an increase in the crystallization temperature. On the other hand, the T_g of PLLA samples crystallized under unconstrained conditions has an opposite trend with increasing T_c. An example of the T_g depression is shown in Figure 1. In this figure, we show thermograms for a T_g-depressed, constrained sample, and an unconstrained sample. Both samples were crystallized at the same isothermal T_c (145 °C) and to the same degree of crystallinity (verified by WAXD). Also in the figure, the scan of a fully amorphous sample is shown as a comparison. Between the samples crystallized under the same annealing conditions, the difference in the T_g is very large—in this case, 30 °C. Interestingly, despite the fact that T_g differs considerably depending on the crystallization method used, all other physical parameters that were measured, including the melting point and degree of crystallinity, are not affected. The constancy of the T_m is another indication that the T_g depression is not chemical in origin. In Figure 2, the T_g's of all constrained and unconstrained samples are presented as a function of T_c. The increasing difference in T_g between unconstrained and constrained samples with increasing crystallization temperature may be related to the higher overall level of crystallinity achievable at elevated temperatures. We will discuss this further below.

In general, the T_g of a polymer is unchanged or increases slightly with degree of crystallinity.[16] The argument made for the T_g increase with crystallinity is that the segmental mobility in the amorphous phase is reduced near crystal lamellae. To acquire sufficient energy to mobilize these hindered chains in a vitrified amorphous phase, a higher temperature is required, and thus a higher T_g is found. Given this well-known and widely observed T_g trend with polymer crystallinity, we suggest next an explanation of our findings of T_g depression that are at odds with the conventional observations.

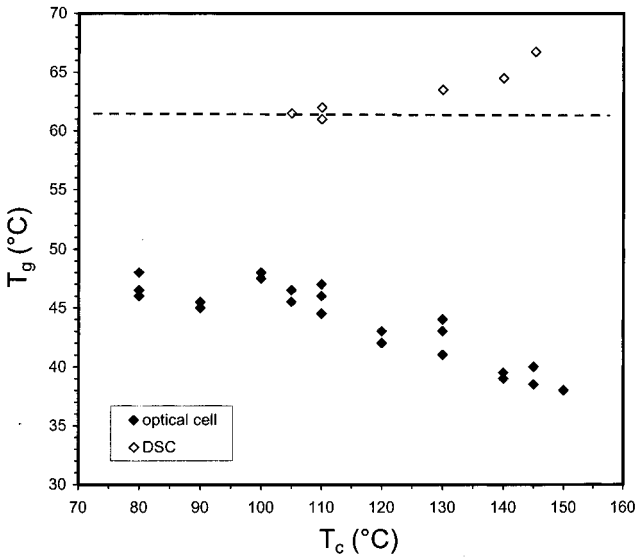

Figure 2. Glass transition temperature as a function of crystallization temperature for all constrained and unconstrained PLLA samples.

As we defined above, constrained crystallization conditions are those under which the crystallizing polymer does not contract away from the walls of its container. In this situation, provided that voids do not form in the polymer, the free volume in the amorphous phase of the polymer will increase with crystallization, as the increasing crystal volume fraction has a higher density than the amorphous fraction, depletes mass from the amorphous phase, which is not able to contract to maintain its normal density. On cooling from the crystallization temperature, the polymer vitrifies in its high-free-volume state, fixing the sample's overall volume, which is preserved when the sample is removed from the constraining environment. The crystallites

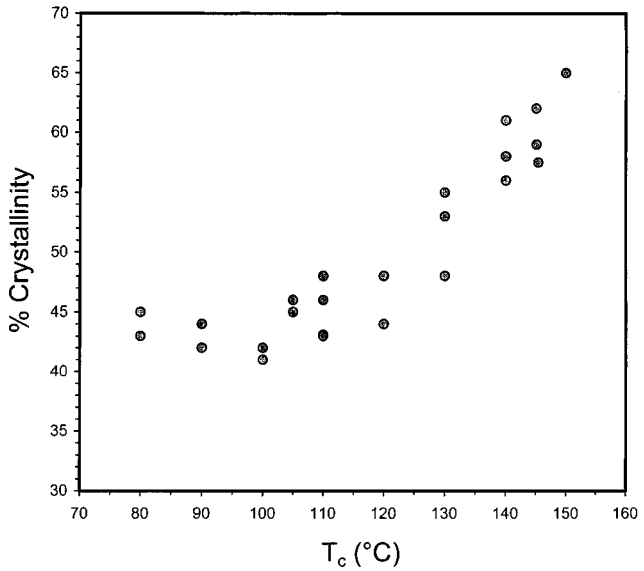

Figure 3. Degree of crystallinity as a function of crystallization temperature for all constrained and unconstrained samples.

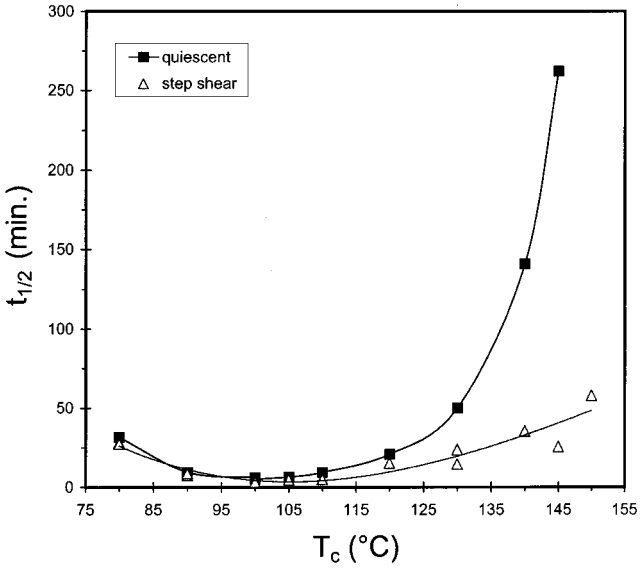

Figure 4. Crystallization half-time as a function of crystallization temperature for quiescent and sheared PLLA samples.

which span the bulk of the polymer may also act to fix the overall sample volume. Such prepared sample exhibits a depressed T_g on the first DSC heating step to above the melting point. But since the sample is unconstrained in the DSC pan, on heating above T_g and T_m, the excess free volume will relax to its equilibrium values, so that the second heating step shows the normal, unconstrained, literature T_g value.

The degree of crystallinity in PLLA is known to increase with increasing T_c.[5,16] These data for all of our constrained and unconstrained samples are shown in Figure 3. As the crystal volume fraction increases, the degree of excess free volume needed to compensate for the shrinking crystalline material increases; thus, the T_g depression increases with degree of crystallinity, or T_c.

The influence of a step shear on PLLA crystallization is to enhance the crystallization kinetics by activating nuclei. A summary of crystallization data is shown in Figure 4. The largest enhancement in PLLA crystallization kinetics is observed at the highest T_c. It is important to note that the step shear used (shear rate 1 s^{-1}, strain 125%, 1 s) produced only spherulitic morphologies, albeit with a much higher nucleation density, and not fibrillar morphologies.[14] Given these effects of shear on crystallization kinetics and spherulite density, we have not found changes in the two types of constrained samples (shear-induced and quiescent) for other physical properties—T_g, T_m, nor degree of crystallinity.

Conclusions

A significant reduction in glass transition temperature is observed in poly(L(−)-lactide) crystallized under partially constrained conditions, where the polymer is prevented from shrinking. We propose that this controlled crystallization process increases the net free volume in the amorphous phase, as the increasing crystal volume fraction has a higher density than the amorphous fraction, which is not able to contract to maintain its nominal density. The T_g depression increases with increasing degree of crystallization, %X, or crystallization temperature, T_c. On the other hand, unconstrained PLLA samples exhibit the conventional trend of increasing T_g with %X or T_c. Although the difference in T_g between samples prepared by the two methods could be large, as much as 30 °C, the melting point, heat of fusion, and overall degree of crystallinity in PLLA are not influenced. Finally, shear-induced crystallization does not affect any of the physical properties studied here but only modifies the crystallization rates, increasing them by enhancing nucleation.

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