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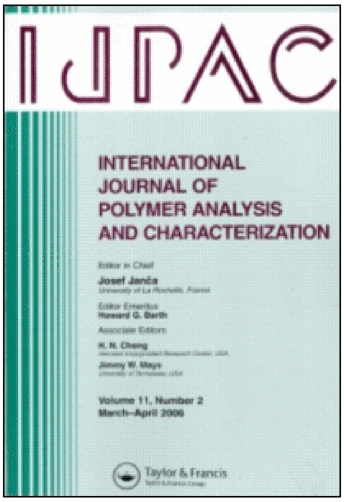

International Journal of Polymer Analysis and Characterization
Publication details, including instructions for authors and subscription information:
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Study of the Mechanical and Thermal Properties of Poly(Lactic Acid) and Poly(Ethylene Glycol) Block Copolymer with Molecular Dynamics

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Online publication date: 13 May 2010

To cite this Article Xiang, Hongzhao , Wang, Yuanliang , Yang, Weihu , Hu, Chengbo , Mu, Yuanhua and Li, Junfeng(2010) 'Study of the Mechanical and Thermal Properties of Poly(Lactic Acid) and Poly(Ethylene Glycol) Block Copolymer with Molecular Dynamics', International Journal of Polymer Analysis and Characterization, 15: 4, 235 — 244

To link to this Article: DOI: 10.1080/10236661003746405

URL: http://dx.doi.org/10.1080/10236661003746405

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International Journal of Polymer Anal. Charact., 15: 235–244, 2010
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ISSN: 1023-666X print
DOI: 10.1080/10236661003746405

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STUDY OF THE MECHANICAL AND THERMAL PROPERTIES OF POLY(LACTIC ACID) AND POLY(ETHYLENE GLYCOL) BLOCK COPOLYMER WITH MOLECULAR DYNAMICS

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In this study, the mechanical properties and glass transition temperature of PLA-PEG block copolymer were investigated by molecular dynamic simulation. The software package Discover in Materials Studio with condensed-phase optimized molecular potentials for atomistic simulation studies (COMPASS) force field was used for the simulation. To verify the validity of simulation results, PLA and PLA-PEG copolymer were prepared in this research and the glass transition temperature was measured by DSC. The simulation results showed that the random combination chain has more probability than the alternating combination chain to exist in copolymer structure. Furthermore, PLA-PEG block copolymer has better tensile strength but lower shear strength than PLA, which agree well with the theoretical results. The simulation values of T_g (PLA: 333.97 K and PLA-PEG: 326.70 K) agree well with the DSC results (PLA: 328.8 K and PLA-PEG: 321.3 K). The conclusion could be drawn from the results that molecular dynamic simulation (MDS) is a potential method for investigating the structure, mechanical properties, and glass transition temperature of PLA-PEG copolymer and may be used for other polymers and copolymers.

***Keywords*:** Block copolymer; Glass transition temperature; Molecular dynamics; PLA

INTRODUCTION

Due to highly controllable chemical and physical properties as well as a number of biologically favorable properties such as biodegradability, non-immunogenicity, and nontoxicity, block copolymers of poly(ethylene glycol) (PEG) and poly(lactic

Submitted 21 January 2010; accepted 4 March 2010.

This work is technology supported by China Academy of Engineering Physics and State Key Laboratory of Heavy Oil Processing in China University of Petroleum.

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acid) (PLA) have emerged as some of the more promising biomaterials.[1,2] The PEG block is water-soluble, conferring hydrophilicity to the copolymer backbone, while the PLA block (less hydrophilic than PEG) enables the biodegradability of the material with its hydrolytically cleavable ester moieties.[3]

The versatility of these materials showing drastically different polymer properties such as degradation rate and hydrophilicity lies in the ability to adjust them by altering the compositions of the copolymer and the size of the PEG and PLA blocks in the polymer network. It has been documented that changing the compositions and block length in PLA-PEG copolymer results in differences in mechanical properties and glass transition temperature (T_g).[4,5] In addition, diblock,[6,7] triblock,[6] multiblock,[8,9] and star-shaped PEG-PLA copolymers[10] have been developed, which have various compositions, molecular weights, and glass transition temperatures.

Glass transition is the inherent property of the amorphous polymer materials and the macro-expression of the form changing of polymer movement, which directly affects the mechanical and application properties of the polymer, so it has long been the main element of polymer physics research. Glass transition has been investigated experimentally and theoretically in the fields of materials and physics for a long time. Experimentally, the glass transition can be tracked by differential scanning calorimeter (DSC). Accordingly, T_g can be determined by an abrupt change of heat flow in the DSC thermogram.

Although the glass transition temperature of a polymer can be measured by many instruments, T_g determination is a time-consuming procedure, especially if the sample is to be kept at subzero temperatures, in anhydrous conditions, or if sampling a portion of the specimen for analysis is cumbersome.[11–13] Hence, predicting rather than directly measuring T_g when researching a polymer can be a promising and powerful tool. Moreover, predicting the mechanical property of a polymer is easier than carrying out an experiment.

The molecular dynamics (MD) method, which has been used extensively in the study of different aspects of polymer structures and properties, provides a theoretical and numerical framework for many particle problems.[11,14,15] In this article, the usability of COMPASS (condensed-phase optimized molecular potentials for atomistic simulation studies) force field in Materials Studio 4.0 was examined by mechanical property and glass transition temperature determination using molecular dynamics simulation. The theory is to determine the kink in a graph of the density versus temperature originating from the change of the thermal expansion coefficient at T_g when passing from a glassy to a rubbery system. To verify the validity of simulation results, PLA and PLA-PEG copolymer were prepared in this research and the glass transition temperature was measured by DSC.

MATERIALS AND METHODS

Materials

Tin(II) 2-ethylhexanoate (stannous octoate, $SnOct_2$, analytical reagent) was purchased from Chengdu Haihong Chemistry Reagent Factory (China). D,L-lactic acid (LA, 90% pure), polyethylene glycol (PEG, $Mw = 4{,}000$), methylene chloride,

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and tetrahydrofuran (THF) of analytical reagent (AR) grade were supplied by Chengdu Kelong Chemistry Reagent Company (China).

Preparation Methods

PLA-PEG copolymer monomer was synthesized in a two-step reaction involving the ring opening addition of lactide to PLA and the coupling of the PLA-PEG block macro-monomer. Briefly, for the synthesis of PLA-PEG copolymer, 69 g DL-lactide, 5.76 g dry PEG, and 253.2 mg $SnOct_2$ were charged to a round-bottomed flask under nitrogen atmosphere. At reflux conditions, the solution was stirred at 430 K for 6 h under the pressure of 0.095 MPa. After cooling to room temperature, the monomer product in the reaction vessel was extracted using methylene chloride and dried overnight in a vacuum oven. As a control material, PLA was prepared according to literature.[16]

Fourier Transform-Infrared (FT-IR) Spectroscopy

Copolymer samples were dissolved in THF and the films were cast directly onto transparent CaF_2 plates. The FT-IR spectra of the copolymer samples were recorded on a Spectrum-GX FT-IR spectrophotometer (PerkinElmer, USA) in the wavelength range of 4000–400 cm^{-1} at a resolution of 4 cm^{-1}.

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Nuclear Magnetic Resonance (NMR) Analysis

^1H NMR spectra were recorded on a superconducting Fourier transform NMR spectrometer AVANCE-500 (Bruker, Switzerland) at 300 K. Deuterochloroform ($CDCl_3$, Fluka Chemical, 99.8% isotopic) was used as the solvent with an internal standard of tetramethyl silane (TMS).

Viscosity-Average Molar Mass

PLA and copolymer were dissolved in tetrahydrofuran with a concentration of 0.1 g/mol. Intrinsic viscosity $[\eta]$ was measured with a Ubbelohde viscometer at 310 K, and the viscosity-average molar mass was calculated with the following Mark-Houwink equation:

$$[\eta] = \mathrm{KM}\eta^{\alpha}$$

K and α are constants that connect with the temperature. In this article, K and α are chosen as 1.04×10^{-4} and 0.75, respectively.[17]

Differential Scanning Calorimetry (DSC) Measurement

For DSC thermograms, the PLA (10 mg) and the copolymer (10 mg) samples were contained in sealed aluminum pans and placed in a Netzsch STA-449C differential scanning calorimeter. The temperature was scanned between 300 and 873 K with a heating rate of 10 K/min under the protection of argon gas. The samples were first heated from 300 to 873 K and held at that temperature for 2 min. After cooling back down to 300 K, the samples were again heated to 873 K at the rate of 10 K/min.

Simulation Methods

Molecular simulations were performed by Materials Studio 4.0 software purchased from Accelrys (San Diego, Calif., USA). The simulation methodology includes molecular mechanics (MM) and molecular dynamics (MD) calculations using the Discover module. The oligomer chains of PLA and PLA-PEG were generated with eight monomer units in isotactic tacticity and random torsion. The resulting structures were energy-minimized to remove strain in the polymer backbone and alleviate high energy close contacts. The amorphous cells were constructed based on the respective densities of the selected oligomers. The method used in constructing the amorphous cell module of MS modeling was the combined use of an algorithm developed by Theodorou and Suter[18] and the scanning method of Meirovitch.[19]

The molecular dynamics simulations were performed by the package Discover in Materials Studio. The potential energy and the elastic constant of the chosen simulation system were calculated using the COMPASS force field, one of the first ab initio force field approaches that has been parameterized and validated using the condensed-phase properties. The minimization was performed using the steepest descent approach followed by the conjugate gradient method.

The simulation systems consisted of 25 oligomer chains placed in a cubic box with periodic boundary conditions at an average temperature of 298 K. The simulations for calculation of elastic properties were run in an NVT (normal volume and temperature) ensemble at 298 K for 5 ps to shake the cell out of the unfavorable local minima that had high energies. A representative structure of PLA oligomer units is illustrated in Figure 1. Eight repeated LA units were marked with purple. Moreover, the ending configuration of PLA cubic box after molecular dynamics simulation is also shown in Figure 1.

To calculate the glass transition temperature of the copolymer, molecular simulation was performed three times by using NPT (normal pressure and temperature)

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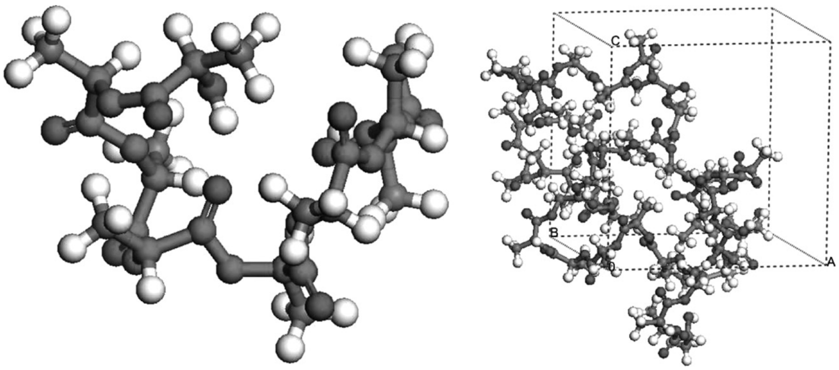

Figure 1. Simulated structure of PLA oligomer chain and the snapshot of PLA box ending configuration. (a) The oligomer chain of PLA with 8 monomer units, (b) PLA amorphous cell consisting of 25 oligomer chains.

ensemble for 200 ps in order to get a reliable average value. The temperature range for the molecular simulation is set from 200 to 440 K with an interval of 30 K. Each trajectory was sampled every 10 fs, and 10,000 structures were subject to analysis. Based on the data of molecular simulation, the values of the density of the copolymer were further extracted and discussed.

RESULTS AND DISCUSSION

Chemistry Analysis

The FT-IR spectrum of the prepared copolymer is shown in Figure 2. Many characteristic peaks of PLA are found in this figure. The peaks at 3001 cm^{-1} and 2950 cm^{-1} are assigned to the absorption peaks of C-H and CH_3, respectively. The peaks at 1760 cm^{-1} and 1189 cm^{-1} are separately attributed to the stretching vibration of C = O and C-O-C. The peak at 1459 cm^{-1} is due to the bending vibration of C-H. Meanwhile, the bending vibration peak of CH_3 is found at 1391 cm^{-1}, while the symmetric stretching vibration peak of C-O appears at 1090 cm^{-1}. Furthermore, the characteristic peaks of PEG are also found in this figure, which are the asymmetric stretching vibration peak of -OCH_2- at 2875 cm^{-1} and the bending vibration peak of -O-CH_2-CH_2-O- at 949 cm^{-1}. The FT-IR spectrum indicates the prepared copolymer belongs to the block copolymer of PLA and PEG.

^{1}H NMR is usually applied as a main method to evaluate polymer reaction products. Therefore, a typical ^{1}H NMR spectrum of PLA-PEG block copolymer is shown in Figure 3. Peak a, at around 1.5 ppm, and peak b, at about 5.1 ppm, are assigned to the protons in the methyl and methane groups of PLA, respectively.[20] In addition, peak c near 3.6 ppm is assigned to the protons in the methylene group of the repeat unit of PEG.[20] The ^{1}H NMR spectrum of the prepared copolymer also proved that the prepared copolymer is the block copolymer of PLA-PEG and this block copolymer has clear structure.

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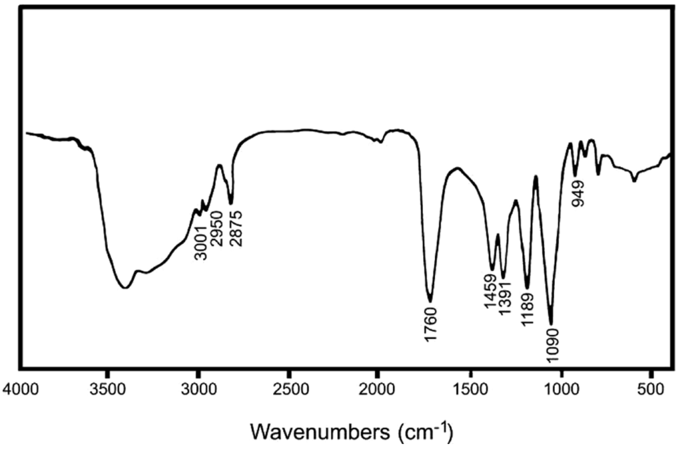

Figure 2. FT-IR spectrum of the prepared copolymer.

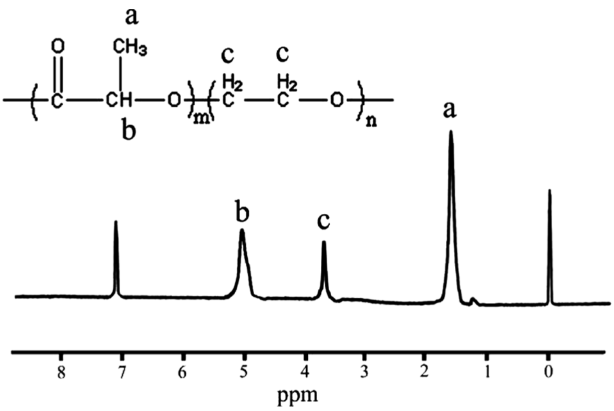

Figure 3. ^{1}H NMR spectrum of the prepared copolymer. Peak a, the methyl protons of PLA; peak b, the methane protons of PLA; peak c, the methylene protons of the repeat units (i.e., ethylene oxide) of PEG.

The viscosity-average molar masses of PLA and PLA-PEG block copolymer were calculated according to Equation (1). The calculated value of PLA was 87,419 g/mol, while PLA-PEG was 21,350 g/mol. PEG destroys the order and coherence of the PLA chain, therefore, PLA-PEG block copolymer has lower viscosity-average molar mass than PLA.

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Simulation and Calculation Results

Block copolymer is an alternating copolymer that has different chemical structure and shorter linear chain segments in structure. The combination chain consists of alternating combination chains and random combination chains. Thus, in PLA-PEG block copolymer structure, there are two kinds of possible combination chains: the alternating combination chains of PLA and PEG like -PLA-PEG-PLA-PEG- and random combination chains like -PLA-PLA-PLA-PEG-. To assess the more probable combination chain in the structure of PLA-PEG block copolymer, molecular dynamics simulation was performed with the package Discover in NVT ensemble. Figure 4 shows the snapshots of PLA-PEG copolymer box ending configuration after simulation. The calculated structure energy of PLA-PEG block copolymer with alternating combination chains after simulation is 4,507 KJ/mol, while the energy of PLA-PEG block copolymer with random combination chains is 3,841 KJ/mol. It should be noted that there is a direct correspondence between the concepts of "structure stability" and "structure energy," i.e., structure with lower energy will be more stable and vice versa. Hence, the random combination chain is more stable and has more probability to exist in the PLA-PEG block copolymer structure. Therefore, the following simulations adopt the model of PLA-PEG block copolymer with random combination as the calculation model.

Molecular dynamics simulation was also undertaken to predict the influence of PEG on PLA-PEG block copolymer mechanical properties. Table I shows the calculated effective isotropic elastic constants of PLA and PLA-PEG block copolymer after molecular dynamics simulation. The results indicate that PLA-PEG block copolymer has better tensile strength but lower shear strength than PLA, ignoring

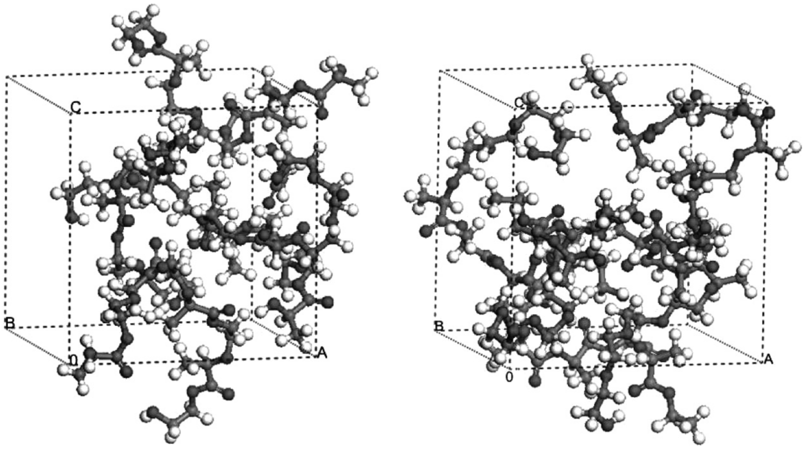

Figure 4. Snapshots of PLA-PEG copolymer box ending configuration. (a) The copolymer with alternating combination chains, (b) the copolymer with random combination chains.

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Table I. Calculated effective isotropic elastic constants of PLA and PLA-PEG block copolymer after simulation

	PLA	PLA-PEG
Tensile (GPa)	1.8340	2.7490
Poisson's ratio	0.1150	1.5970
Shear	0.8226	0.5292
Lame constants λ	0.2456	0.7704
Lame constants μ	0.8226	0.5292

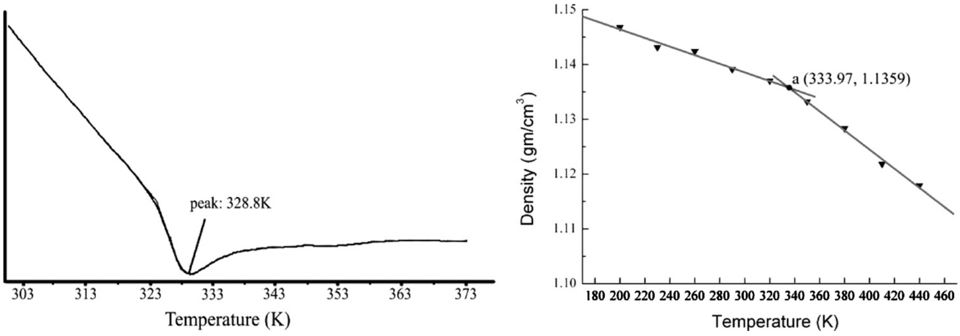

Figure 5. Tested glass transition temperature of PLA (a) and the computed curves of the density vs. temperature for PLA (b).

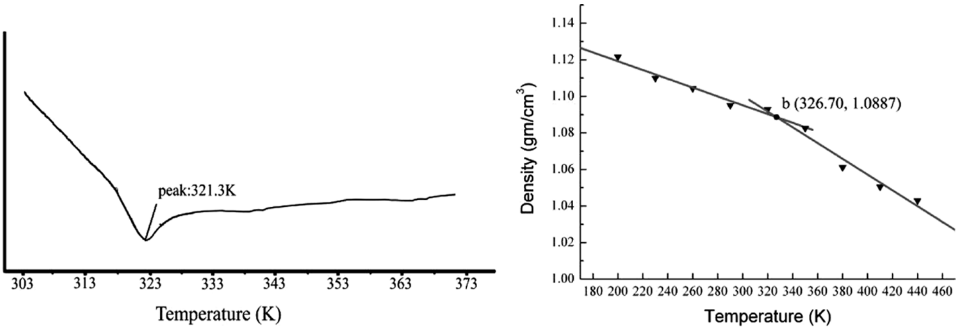

Figure 6. Tested glass transition temperature of PLA-PEG copolymer (a) and the computed curves of the density vs. temperature for PLA-PEG copolymer (b).

the influence of polymer molecular weight. In general, PEG has better tensile property than PLA and is usually used to improve the plastic property of PLA. The simulation results accorded with the practical application, which proved that the model and simulation are correct.

Glass transition occurs when a sample goes from a hard, glass-like state to a rubber-like state. The state parameters of the sample will exhibit an abrupt change within the range of the glass transition temperature. The tested glass transition temperature of PLA and the computed curves of the density versus temperature for PLA are shown in Figure 5. It can be seen from the computed curves that below 350 K, the density decreases linearly with the increase of temperature; the linear equation of this curve is $y = 1.16213–7.86667E\text{-}5 * x$. Although above 350 K, the density also decreases with the increase of temperature, the trend is more obvious, and the linear equation of this curve is $y = 1.19419–1.74667E\text{-}4 * x$. The temperature of 333.97 K at the intersection of the two linear curves is taken as the glass transition temperature of PLA. The predicted values are verified with the values from the actual glass transition temperature of PLA with same mass tested by DSC. The computed glass transition temperature is close to the tested glass transition temperature 328.8 K, which shows the simulation method and the calculated models are relatively accurate. The deviation may be due to differences in PLA structure, method of measurement, or the heating rate in DSC studies. The same simulation was performed to predict the glass transition temperature of PLA-PEG block copolymer. Figure 6 shows the tested glass transition temperature and the computed curves of the density versus temperature for PLA-PEG copolymer. The calculated glass transition temperature of PLA-PEG is 326.70 K, which is similar to the actual glass transition temperature 321.3 K.

CONCLUSIONS

Block copolymer is an alternating copolymer that has different chemical structure and shorter linear chain segments in structure. The combination chain consists of alternating combination chains and random combination chains. The changing of compositions and block length in PLA-PEG copolymer results in the differences of mechanical properties and glass transition temperature.

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In this study, molecular dynamics simulation was performed to predict the more probable combination chain in the structure of PLA-PEG block copolymer by calculating the structure energies of the copolymer with alternating combination chains and with random combination chains, respectively. The results show that the random combination chain is more stable and has more probability to exist in PLA-PEG block copolymer structure. In addition, calculated results after molecular dynamics simulation indicate that PLA-PEG block copolymer has better tensile strength but lower shear strength than PLA, which agree well with the practical application.

Although the glass transition temperature of a polymer can be measured by many instruments, T_g determination is a time-consuming procedure, especially if the sample is to be kept at subzero temperatures, in anhydrous conditions, or if sampling a portion of the specimen for analysis is cumbersome. Hence, predicting rather than directly measuring T_g when researching a polymer can be a powerful tool. In this study, the glass transition temperatures of PLA and PLA were predicted using MD simulation protocols. Calculations of T_g for the chosen systems using the COMPASS force field approach compared well with the testing data, suggesting the validity of the proposed method. Therefore, the molecular modeling approach and molecular dynamics simulation employed in this research provide good insight into the mechanical properties of a copolymer as well as a good method to predict the glass transition temperature of polymer and copolymer.

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