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CHARACTERIZATION OF POLY(LACTIC ACID) BY SIZE EXCLUSION CHROMATOGRAPHY, DIFFERENTIAL REFRACTOMETRY, LIGHT SCATTERING AND THERMAL ANALYSIS*

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A number of experimental techniques are employed to characterize physical and thermal properties of poly(lactic acid), PLA. To characterize PLA in terms of molecular mass and molecular mass distribution, size exclusion chromatography was used. The value of the specific refractive index increment was measured by differential refractometry. The thermal properties of semicrystalline PLA were measured by standard and temperature-modulated differential scanning calorimetry. The thermal stability of PLA was monitored by measuring the changes of mass using thermogravimetric analysis. The mechanical properties of amorphous PLA were measured by dynamic mechanical analysis and the results were discussed and compared with DSC in the glass transition region.

Keywords: *crystallinity, heat capacity, molecular mass, poly(lactic acid), refractive index*

Introduction

The complete characterization of polymeric materials involves the use of several techniques. Each of these techniques can serve as a basis for experiments to be used in an introductory polymer chemistry course. In this paper, various techniques used to analyze PLA will be discussed. Typical results for each technique will be given. Although there are many polymeric materials which could be used to demonstrate characterization techniques, PLA was used in this study. It is produced from corn, is biodegradable, and has many environmentally friendly applications which would be a good training for a future polymer chemist [1]. Even though the emphasis here is on thermal analysis, a thorough characterization of a polymeric material must involve the determination of the absolute molecular mass. Mass average molecular mass of the polymeric material is represented by $M_w=\Sigma(N_i M_i^2)/\Sigma(N_iM_i)$; number average molecular mass is represented by $M_n=\Sigma(N_iM_i)/\Sigma N_i$, and the polydispersity by $PD=M_w/M_n$, where N_i is the number of molecules of mass M_i [2]. The determination of the absolute molecular mass using light scattering is based on the principle that the amount of light scatterd is directly proportional to the product of the polymer molar mass (M), concentration of the polymer in solution (c), and the square of the specific refractive index increment (dn/dc): $I_{scattered}\propto Mc(dn/dc)^2$, where I is the intensity of the scattered light and n is refractivity [3]. Calorimetry allows for the determination of characteristic properties such as heat capacity at constant pressure ($C_p=(\partial H/\partial T)$ where H represents the change in heat content and T is temperature). The following other quantities are of importance: glass transition temperatures (T_g), melting transition temperatures (T_m), and heats of fusion (ΔH_f) [4]. Crystallinity, w_c, for a given crystal at a given temperature was determined as follows: $w_c=(H_a-H)/(H_a-H_c)$ where H_a is enthalpy for liquid, H_c is enthalpy for crystal, and H is experimental enthalpy from the measurements [5]. In the last few years characterization of poly(lactic acid) using thermal analysis techniques was explored extensively as indicated in the literature [6–13].

Experimental

Three different samples of poly(*L*-lactic acid) PLA were obtained from Cargill Dow Polymers, LLC, USA. The samples differed in their percentage of the *L*-isomer and *D*-isomer of lactic acid. PLA samples with a low amount of *D*-isomer of lactic acid (1.5% of *D*, PLA-L), medium *D*-isomer (8.1% of *D*, PLA-M), and high *D*-isomer (16.4% of *D*, PLA-H) were used for our study (PLA-H is amorphous and PLA-L is

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semi-crystalline [13]). The form of PLA used for each characterization procedure will be indicated.

The d*n*/d*c* for PLA was measured using a differential refractometer. The instrument that was used was an OPTILAB DSP Interferometric Refractometer manufactured by Wyatt Technology. The instrument was controlled by DNDC for windows software installed on a Dell computer system. The analysis of the data was also performed using the same computer software. Five solutions of varying concentrations of PLA-H in chloroform were prepared. The concentrations were as follows: 0.005698, 0.004748, 0.003799, 0.002849 and 0.001899 g mL^{-1}. The chloroform used to prepare the solutions and used to establish the baseline was sonicated for 10 min prior to use. The batch method was used for this experiment with a flow rate of about 0.2 mL min^{-1} based on gravity. The solutions were placed approximately 24 cm above the instrument with the waste reservoir located about 65 cm below the instrument. After the baseline was established, the input tube was placed into each solution starting with the highest concentration for about 10 min. After the last solution was used, the pure solvent was used again to reestablish the baseline. This experiment was carried out at 313 K.

The absolute molecular mass and the relative molecular mass for PLA were measured using size exclusion or gel permeation chromatography (SEC or GPC). The instrument used was a Polymer Labs GPC-120 size exclusion chromatograph. The instrument was controlled by Precision Detectors software installed on a Dell computer system. The analysis of the data was performed using the Precision Detectors software and Polymer Labs Cirrus software. The GPC-120 contained two Polymer Labs PLgel 10 μm MIXED-B columns running chloroform as the solvent at a flow rate of 1 mL min^{-1} at 313 K. The GPC contains four detectors: Precision Detectors PD2040 (static light scattering); Precision Detectors PD2000DLS (dynamic light scattering); Viscotek 220 Differential Viscometer; and a refractometer. Two injections each of PLA-H (conc.=1.869 mg mL^{-1}), PLA-M (conc.=1.942 mg mL^{-1}) and PLA-L (conc.=1.901 mg mL^{-1}) were analyzed. The samples were injected using a 5 mL syringe with an 0.2 μm filter. Approximately 2 mL of each solution was injected into a 100 μL injection loop. Polystyrene standards were used for determining relative molecular mass using a polystyrene calibration [14]. The polystyrene standards were Polymer Labs EasyCal PS1-A and PS1-B each containing five polystyrenes of varying molecular masses.

Additional experiments to determine the relative molecular mass of PLA were done using a GPC running N,N-dimethylacetamide (DMAC) containing 0.11% LiCl and 0.03% toluene-4-sulfonic acid at a temperature of 343 K. This SEC system consisted of a Knauer HPLC Pump (K-501) running at a flow rate of 1 mL min^{-1}; four Polymer Labs PLgel 10 μM columns (pore sizes of 500, 1000, 10,000 and 100,000 Å); a Knauer RI Detector (K-2301), and an Alltech 330 Column Heater. The SEC system was controlled by PSS WinGPC software installed on a Dell computer system. The analysis of the data was also performed using the same computer software. Two injections each of PLA-H (conc.=2.014 mg mL^{-1}) and PLA-M (conc.=2.073 mg mL^{-1}) were analyzed. PLA-L was not used since it was not soluble in the DMAC. The samples were injected using a 5 mL syringe with an 0.45 μm filter. Approximately 2 mL of each solution was injected into a 100 μL injection loop. Polystyrene standards were used for determining the relative molecular mass using a polystyrene calibration. The polystyrene standards were Polymer Labs EasyCal PS1-A and PS1-B each containing five polystyrenes of varying molecular masses.

Thermal analysis of PLA was carried out using three characterization techniques: TG, DSC and DMA. First, the thermal decomposition properties were studied using a TA Instruments TGA Q50 thermal gravimetric analyzer [4]. Nitrogen was used as the purge gas for both the sample and the balance. Approximately 35–40 mg of PLA was used for each analysis. The samples were heated up to 1073 K using varying heating rates (5, 20, 30 and 40 K min^{-1}). The instrument was controlled by Thermal Advantage software installed on an IBM computer system. The data was analyzed using Universal Analysis software on the same computer system.

Secondly, the heat capacity, glass and melting transition temperatures, and heat of fusion were measured for PLA by using both standard and temperature-modulated differential scanning calorimetry [4, 13]. DSC measurements were performed using a TA Instruments DSC Q1000 differential scanning calorimeter. Nitrogen was used as the purge gas at a flow rate of 10 mL min^{-1}. Approximately 5–10 mg of PLA was used for each analysis. For standard DSC, the samples were heated from 183 up to 523 K at the rate of 20 K min^{-1} using aluminum pans. For temperature modulated DSC in the quasi-isothermal mode, the samples were heated around the given temperature with a modulation amplitude of 0.5 K and a period of 100 s. For temperature modulated DSC in the standard mode, the samples were heated with an underlying heating rate of 1 K min^{-1}, modulation amplitude of 0.5 K and a period of 60 s. The instrument was controlled by Thermal Advantage software installed on an IBM computer system. The data was analyzed using Universal Analysis software on the same computer system.

Thirdly, the mechanical properties of PLA were studied using dynamic mechanical analysis. DMA experiments were performed using a TA Instruments DMA Q800 dynamic mechanical analyzer. Nitrogen was used as the air bearing gas and the furnace was cooled using liquid nitrogen. A sample of PLA-H with the dimensions of 17.27×12.46×1.77 mm was prepared using a Carver Laboratory Press heating the sample to 338 K under a pressure of $6.9\cdot10^7$ Pa. The sample was then cooled to room temperature without a controlled cooling rate. The sample was analyzed at a constant strain of 20 μm using a frequency of 1 Hz. The sample was heated from 298 up to 338 K at a heating rate of 1 K min^{-1}. The instrument was controlled by Thermal Advantage software installed on an IBM computer system. The data were analyzed using Universal Analysis software on the same computer system.

Results and discussion

OPTILAB refractometer

Complete characterization of a polymer begins with determining the specific refractive index increment (d*n*/d*c*) for the polymer in an appropriate solvent. For these experiments, chloroform was the solvent of choice because PLA is soluble in chloroform. All three forms of PLA (L, M and H) dissolved in chloroform after 2–3 h. Amorphous PLA was used for determining the d*n*/d*c* value. Figure 1 shows the resulting d*n* *vs*. concentration curve with the resulting slope, d*n*/d*c*, given as 0.0237±0.0034 mL g^{-1}.

The analysis was somewhat difficult because of the nature of the solvent. Even though the chloroform was degassed by sonication before use, there still appeared to be many air bubbles forming in the cell as indicated by the gases flowing out of the cell. The experiment was repeated a 2nd time giving similar results: 0.0240±0.0049 mL g^{-1}. The d*n*/d*c* value for PLA in chloroform is fairly small compared to other polymers such as polystyrene which has a d*n*/d*c* of 0.169 mL g^{-1} in chloroform. A small value of d*n*/d*c* makes analysis using light scattering somewhat difficult as will be discussed in the next section.

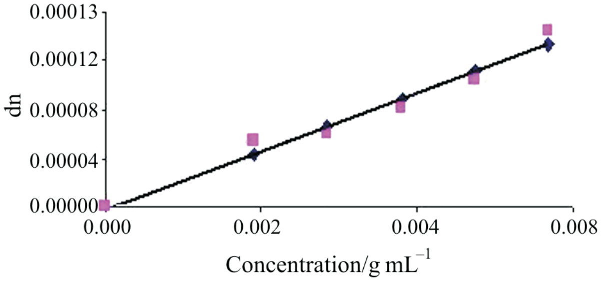

Fig. 1 d*n*/d*c* curve for PLA in chloroform

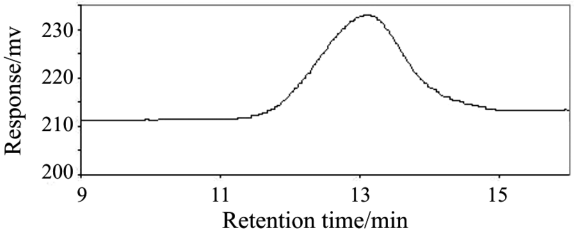

Fig. 2 Chromatogram for PLA-L in chloroform

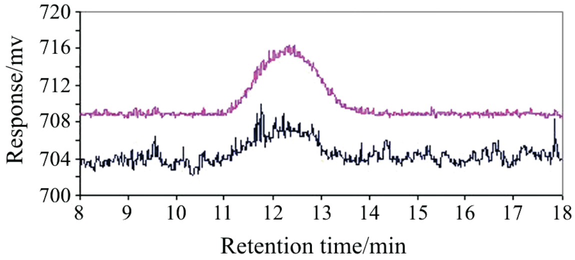

Fig. 3 Light scattering chromatogram for PLA-L

SEC or GPC

Size exclusion chromatography was used in three ways to determine the molecular mass of PLA. First, the relative molecular mass was determined for each of the three PLA samples by comparing the retention times to that of polystyrene standards using chloroform as the solvent. Figure 2 shows an example of a chromatogram obtained from the analysis of PLA-L using only the RI signal. For this sample, the following results were obtained: $M_{w,app}$ (apparent)=193,000 and M_w/M_n=1.84.

In Table 1, the $M_{w,app}$ and M_w/M_n are shown for each of the samples of PLA that were analyzed.

You should notice three significant things about the results in Table 1. First, for a given sample of PLA (L, M or H), there is good reproducibility of the $M_{w,app}$. Secondly, notice that the $M_{w,app}$ varies slightly depending upon the type of PLA. Thirdly, the polydispersity of PLA is fairly broad which makes it more difficult to analyze PLA using light scattering.

The second way that the absolute molecular mass was determined for each of the PLA samples was by analysis of the light scattering data. Figure 3 shows the light scattering chromatogram for PLA-L. The analysis of the light scattering data gives an abso-

Table 1 $M_{w,app}$ and M_w/M_n for PLA from PS calibration

Sample	$M_{w,app}$	M_w/M_n
PLA-L	193,000	1.88
PLA-L	193,000	1.84
PLA-M	224,000	1.63
PLA-M	229,000	1.78
PLA-H	208,000	1.79
PLA-H	206,000	1.76

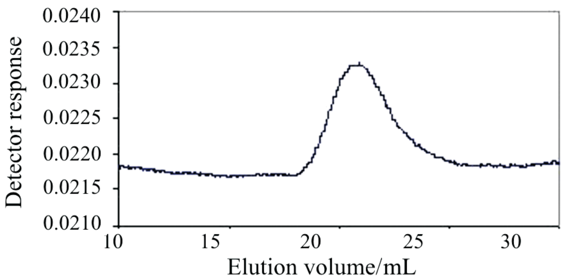

Fig. 4 Chromatogram for PLA-M in DMAC

lute molecular mass of 199,000 which is close to the value obtained from the polystyrene calibration. Notice that there is a lot of noise in the light scattering signal since the signal is weak (about 4 mV) due to a small d*n*/d*c* value. Compare this signal strength to that of a polystyrene standard of about the same concentration and molecular mass which has a signal of about 100 mV. Table 2 gives the absolute molecular mass for each of the PLA samples based upon light scattering analysis. The molecular mass for the L form agrees fairly reasonably with the data obtained from the polystyrene calibration. The M and H forms give results much higher than would be expected.

Thirdly, the relative molecular mass of PLA was measured using a GPC system with the solvent N,N-dimethylacetamide (DMAC) containing 0.11% LiCl and 0.03% toluene-4-sulfonic acid at a temperature of 343 K. Since only the M and H forms of PLA were soluble in the DMAC solvent, samples of the L form could not be used. Figure 4 shows the chromatogram obtained from one of the injections of the M form.

In comparing the retention time for the peak with that of the polystyrene standards, the following results were obtained for this sample: $M_{w,app}$=213,000 and M_w/M_n=1.58. If these results are compared with those in Table 1, you will notice fairly close agreement. In Table 3, the $M_{w,app}$ and M_w/M_n are shown for each of the samples of PLA that were analyzed in the DMAC.

Table 2 $M_{w,app}$ for PLA from light scattering

Sample	$M_{w,app}$
PLA-L	199,000
PLA-L	235,000
PLA-M	377,000
PLA-M	347,000
PLA-H	443,000
PLA-H	269,000

Table 3 $M_{w,app}$ and M_w/M_n for PLA in DMAC

Sample	$M_{w,app}$	M_w/M_n
PLA-M	213,000	1.58
PLA-M	159,000	1.64
PLA-H	115,000	1.54
PLA-H	209,000	1.70

Looking at the results in Tables 1, 2 and 3, it was concluded that the molecular mass of PLA is around 200 K with an M_w/M_n of around 1.7. It is difficult to make a more accurate assessment of the results.

Thermogravimetry (TG)

The thermal decomposition properties of PLA were studied by heating samples of PLA in a TG instrument from room temperature up to 1073 K in nitrogen. Figure 5 shows an overlay of the decomposition of the L, M and H forms of PLA with the masses being 39.045, 38.713 and 35.802 mg, respectively.

PLA is very stable up to around 583 K. At ≈584 K it begins to decompose and completes decomposition at ≈673 K. The fact that there is very little change in mass from room temperature up to 584 K indicates that the PLA is pure with no contaminates, is very dry with no solvent, and is very stable. The sharp drop in mass around 584 K shows relatively complete decomposition and that the samples were pure with no contaminates.

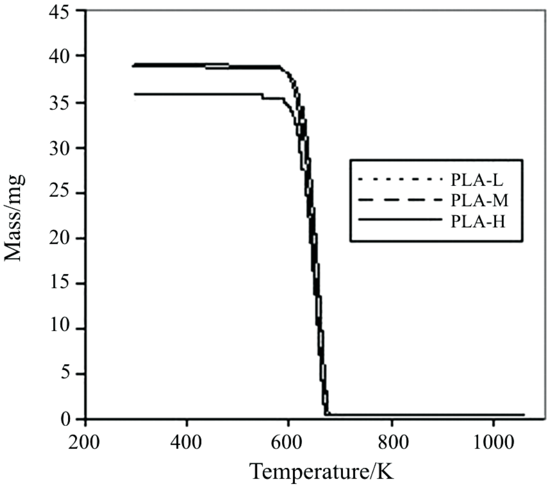

Fig. 5 Decomposition of PLA-L, M and H in N_2

Standard differential scanning calorimetry (DSC)

Figure 6 illustrates a set of DSC data showing the heat-flow rate as a function of temperature for PLA-L and PLA-H. The heat flow rate, HF, is proportional to ΔT as shown by the equation HF=$k\Delta T$. The samples were isothermally crystallized at T=418.15 K for 15 h. The data suggests that PLA-L is semicrystalline and PLA-H is amorphous under the given conditions since PLA-H shows no melting.

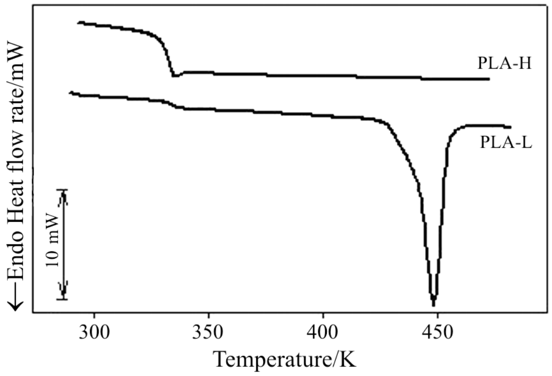

Fig. 6 Experimental DSC curves of heat flow rate as function of temperature for semi-crystalline PLA-L and amorphous PLA-H (the curves were shifted arbitrary)

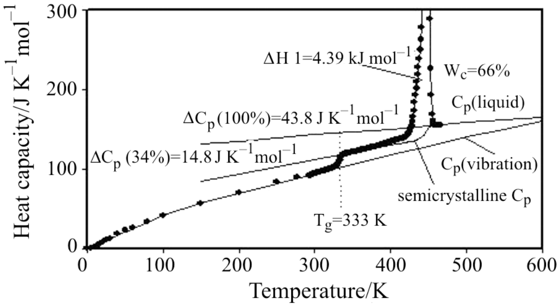

Fig. 7 Experimental and calculated heat capacities of semi-crystalline PLA-L [13]

After converting the heat-flow rate, HF, to the heat capacity using the equation $C_p=K\mathrm{HF}/q$ (where K is a calibration constant and q is the heating rate), the DSC data for PLA was analyzed. Figure 7 shows the experimental heat capacity at low temperature region from 5 to 300 K obtained from adiabatic calorimetry and found in the literature [13, 14]. The heat capacity above 300 K was measured from standard DSC. These heat capacities are shown by two equilibrium heat capacity lines: vibrational and liquid heat capacity [13]. The calculated vibrational heat capacity, C_p (vibration) and the calculated liquid heat capacity C_p (liquid) of PLA serve as base lines for thermal analysis of the semicrystalline PLA-L, as shown in Fig. 9. The heat capacity of the fully amorphous PLA-L, PLA-H and PLA-M, presented in [13] show a glass transition temperature, T_g, between 330 and 333 K, dependent on thermal history. For the semicrystalline PLA-L, the heat capacity shows the glass transition temperature, T_g, at 333 K with a ΔC_p of 14.8 J K^{-1} mol^{-1} which applies to 34% of the amorphous PLA-L. Using these two baselines, C_p (vibration) and C_p (liquid), one can calculate the changes of heat capacity at T_g for the fully amorphous sample to be 43.8 J K^{-1} mol^{-1}.

Quantitative thermal analysis allows determination of the crystallinity changes with changes in temperature. Knowing C_p (vibration), C_p (liquid), equilibrium melting temperature as 480 K, and the heat of fusion for 100% crystal as 6.554 kJ mol^{-1}, the crystallinity as a function of temperature was estimated [13]. The result of this crystallinity calculation is presented in Fig. 10 for the semicrystalline PLA-L of Fig. 7. The semicrystalline PLA-L reaches 66% crystallinity around 400 K, decreases with increasing temperature, and finally drops to zero at the melting temperature. This function of crystallinity was used to construct the heat capacity line for semicrystalline PLA (Fig. 7, semi-crystalline C_p) which separates a heat capacity from a latent heat in the melting region of apparent heat capacity. Semicrystalline C_p is calculated as follows: $w_c(T)C_p(\mathrm{vibration})+(1-w_c(T))C_p(\mathrm{liquid})$ where $w_c(T)$ is the fractional degree of crystallinity as a function of temperature (Fig. 8). Using this semicrystalline C_p, a corrected heat of fusion, 4.39 kJ mol^{-1}, was calculated for semicrystalline PLA-L. This line for semicrystalline C_p was also used for additional quantitative thermal analysis of PLA-L [13, 15].

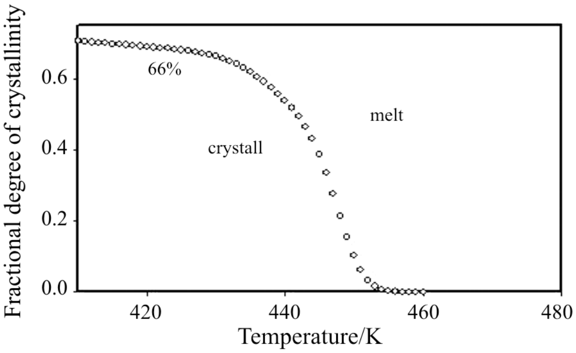

Fig. 8 Changes in crystallinity with changes in temperature for semicrystalline PLA-L

Temperature modulated differential scanning calorimetry (TMDSC)

Figure 9 shows a comparison of the total heat capacity from standard DSC and the apparent reversing heat capacity of semicrystalline PLA-L. The results

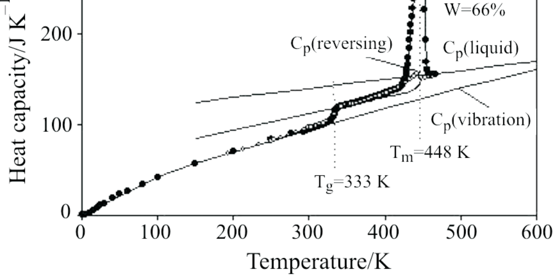

Fig. 9 Comparison of total and reversing heat capacities of PLA-L [15]

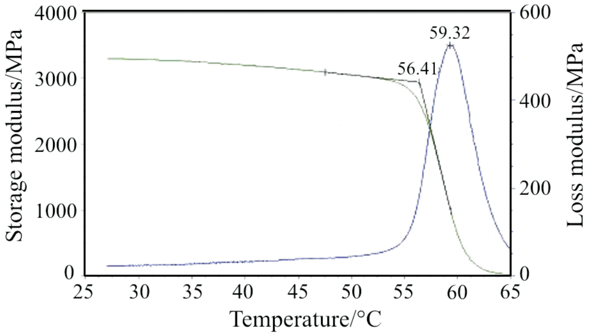

Fig. 10 Storage and loss modulus as function of temperature for PLA-H

show that the reversing heat capacity agrees with total heat capacity in all regions except the melting region. In the melting region, only a small contribution of C_p (reversing) is observed, which means that the melting process for PLA-L is mostly irreversible.

Dynamic mechanical analysis (DMA)

The mechanical properties such as the storage modulus (*E*') and the loss modulus (*E*'') were measured for the solid state of amorphous PLA-H as function of temperature and frequency using a dynamic mechanical analyzer (DMA). Figure 10 shows an example of the results for a frequency of 1 Hz. The decrease in the storage modules occurs at the glass transition region around 332 K. These results agree well with the results obtained from standard DSC which gave a value of 332.5 K.

Overall, quantitative thermal analysis is a useful approach for characterizing polymeric materials such as PLA [13, 16] as was shown by TG, DSC, TMDSC and DMA.

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References

1 R. A. Gross and B. Kalra, Science, 297 (2002) 803.
2 J. W. Mays and A. D. Puckett, Solution Characterization of Polyolefins, in Handbook of Polyolefins, C. Vasile (Editor, Marcel Dekker, Inc., New York 2000, pp. 359–377.
3 Y. Liu, S. Bo, Y. Zhu and W. Zhang, Polymer, 44 (2004) 7209.
4 B. Wunderlich, Thermal Analysis, Academic Press, Boston 1990.
5 V. B. F. Mathot, Calorimetry and Thermal Analysis of Polymers, Hanser, Munich 1994.
6 Y. Wang and J. F. Mano, J. Therm. Anal. Cal., 80 (2005) 171.
7 A. O'Connor, A. Riga and J. G. Turner, J. Therm. Anal. Cal., 76 (2004) 455.
8 J. F. Turner, A. Riga, A. O'Connor, J. Zhang and J. Collis, J. Therm. Anal. Cal., 75 (2004) 257.
9 D. Cohn and A. Hotovely-Salomon, Polymer, 46 (2005) 2068.
10 J. Huang, M. S. Lisowski, J. Runt, E. S. Hall, R. T. Ken, N. Buehler and J. S. Lin, Macromolecules, 31 (1998) 2593.
11 V. L. Hill, N. Passerini, D. Q. Craig, M. Vickers, J. Anwa and L. C. Feely, J. Therm. Anal. Cal., 54 (1998) 674.
12 J. R. Sarasua, R. E. Prud'homme, M. Wisniewski, A. Le Borgne and N. Spassky, Macromolecules, 31 (1998) 3895.
13 M. Pyda, R. C. Bopp and B. Wunderlich, J. Chem. Thermodyn., 36 (2004) 731.
14 T. G. Kulagina, B. V. Lebedev, Ye. G. Kiparisova, Ye. B. Lyndvig and I. G. Bbcrskaya, Polymer Science USSR, 24 (1982) 1702.
15 M. Pyda and B. Wunderlich, Proc. 31st NATAS Conf. in Albuquerque, NM, Sept. 22–24, M. J. Rich, Ed. 31 (2003).
16 M. Pyda, A. Buzin, R. Bopp and B. Wunderlich, Proc. 30th NATAS Conf. in Pittsburgh, PA, Sept. 23–25, K. J. Kociba and B. J. Kociba, Eds., 30 (2002) 463.

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