 DOI: 10.1002/masy.200850312

Thermal Properties of Poly(L-lactide)/Calcium Carbonate Nanocomposites

Branka Andričić, Tonka Kovačić, Sanja Perinović, Adela Grgić*

Summary: Thermal properties of nanocomposites prepared of poly(L-lactide) (PLLA) and $CaCO_3$ applying differential scanning (DSC) calorimetry and thermogravimetry (TG) were studied. Nanocomposites were prepared by extrusion process at 170 °C. DSC measurements show that $CaCO_3$ has no influence on glass transition and melting point of PLLA but lowers its cold crystallization temperature. There is no difference in glass transition temperature of PLLA before and after extrusion. High temperature thermal stability of the PLLA in the composites is poorer than neat PLLA. Kinetic parameters also indicate greater reactivity of the system upon $CaCO_3$ addition.

Keywords: activation energy; DSC; nanocomposites; Poly(L-lactide); TGA

Introduction

Most of the biodegradable polymers have two major applications: biomedical and ecological. Their typical applications in medicine are for disposable products (syringes, blood bags and catheters), materials supporting surgical operations (sutures, adhesives, sealants, fracture fixation) or drug delivery system. The minimum requirements for biomedical applications are non-toxicity, sterilizability and effectiveness.[1] The other mayor use of biodegradable polymers is to replace bio-stable plastics for maintaining the earth environment clean. Some of them are used for either of those two purposes, but some of them are applicable for both and poly(L-lactide) (PLLA) is among them. Although synthetic, PLLA is prepared from renewable agriculture-based feed stocks which are fermented to lactic acid and then polymerized. Its mechanical properties are comparable with those of polypropylene and polystyrene.[1–4] However, the properties of PLLA used for packaging can be modified and application field broadened by addition of different additives. Generally, the recommendation for biodegradable plastics is to focus on replacing non-recyclable disposable plastic products, but not those which have well established recycling system.[5] As PLLA, similar to polystyrene, is relatively brittle and stiff polymer, one of demands is to alter its mechanical properties by different plasticizers.[6–9] However, PLLA is still more expensive than conventional thermoplastics and some investigations were performed in order to low its price by adding different biodegradable fillers.[10–12] On the other side, in biomedical applications PLLA-based nanocomposites are expanding area of investigation resulting in polymeric materials with enhanced properties. Investigations were performed on PLLA/montmorilonite nanocomposites aimed to improve processability and mechanical properties of PLLA materials.[13–15] Nanocomposites of PLLA and hydroxyapatite, as osteoconducting material, were explored as the promising material for bone fracture repair.[16–18] Only some investigations were published on PLLA/calcium carbonate nanocomposites. Calcium carbonate ($CaCO_3$) used in those studies was in a crystal form of vaterite. It has been found that introduction of $CaCO_3$ in PLLA matrix improves the modulus of elasticity and the composite shows no brittle fracture.[19] Also, $CaCO_3$

Department of Organic Technology, Faculty of Chemistry and Technology, Teslina 10/V, 21000 Split, Croatia
E-mail: branka@ktf-split.hr

in PLLA nanocomposites improves the Young modulus and change the hydrolysis rate.[20] But, in contrast to hydroxyapatite and β-tricalcium phosphate calcium carbonate show very high bioresorbability and stimulate bones healing, as published on the base of performed *in vivo* studies.[21]

Wherever the PLLA/$CaCO_3$ nanocomposites are going to be used, their properties during processing at elevated temperature should be also considered.

In this work PLLA/$CaCO_3$ composite material containing nano-sized $CaCO_3$ was prepared by extrusion and the thermal properties were determined by DSC. The thermal degradation was followed by TGA and the kinetic doublet (E_a and A) of thermal degradation in nitrogen were calculated according Kissinger's equation.

Experimental Part

PLLA in granular form, with viscosity-average molecular weight (M_w) = 58700 (Biomer L9000), was supplied by Biomer (Krailing, Germany) and used after purification by precipitation using chloroform and ethanol as solvent and non-solvent, respectively. $CaCO_3$ of mean particle size of 70 nm and specific surface of 20 m^2g^{-1} (Socal U1) was supplied by Solvay Chemicals (Ebensee, Austria). PLLA and homogenized dry mixtures of PLLA and 0, 5, 12 and 20% $CaCO_3$ were extruded on Dynisco laboratory extruder (Qualitest, Canada) at 170 °C and 150 rpm.

Melting, crystallization and glass transition temperatures (T_m, T_c, and T_g, respectively) and enthalpy of melting and crystallization (ΔH_m and ΔH_c, respectively) were determined using differential scanning calorimetry (DSC-4, Perkin-Elmer, USA). The temperature range was 30 . . . 200 °C at heating/cooling rate of 10 °Cmin^{-1} and the nitrogen flow was 30 cm^3min^{-1}. Melting and crystallization characteristics were determined from the first heating and the glass transition was determined from the second heating as the midpoint temperature.

Crystalline content in PLLA (X_c) was calculated according the following equation:

$$X_c(\%) = 100(\Delta H_m + \Sigma\Delta H_c)/(93 \cdot w_{PLLA}) \quad (1)$$

where 93 (Jg^{-1}) is the enthalpy of fusion of PLLA crystals of infinite crystal thickness[10,12] and w is mass fraction of PLLA.

Thermal degradation of the composites was performed using thermobalance (TGS-2, Perkin-Elmer, USA) in the temperature range 50. . .550 °C in nitrogen flow of 30 cm^3min^{-1}, at four different heating rates: 2.5, 5, 10 and 20 °Cmin^{-1}. Characteristic temperatures of the thermal degradation, such as temperature of 5% mass loss ($T_{5\%}$), onset degradation temperature (T_{ons}) and temperature at the highest degradation rate (T_m) were determined from the thermogravimetric curves scanned at 10 °Cmin^{-1}.

In order to determine kinetic parameters of the thermal degradation of PLLA in the composites, the Kissinger's method was applied.[22] The method was derived on the basic kinetic equations for heterogeneous chemical reactions and therefore has a wide applications.[23–26]

Kissinger's method for calculating the kinetic parameters uses the temperature at which the rate of mass loss is the highest and is shown by the equation:

$$\frac{qE_a}{RT_m^2} = An(1-\alpha)_m^{n-1}\exp\left(-\frac{E_a}{RT_m}\right) \quad (2)$$

where q, E_a, R, T_m, A, α and n denotes heating rate, apparent activation energy, general gas constant, maximum degradation rate temperature, pre-exponential factor, conversion function and the reaction order, respectively. It is assumed that the degradation is first order reaction and that conversion does not depend on heating rate. Upon this assumption, the apparent activation energy and the pre-exponential factor were determined from the parameters of the straight line obtained by drawing the dependence $ln(q/T_m^2)$ vs. $1/T_m$ according to the following equation:

$$\ln(q/T_m^2) = \ln(AR/E_a) - (E_a/RT_m)$$

The method applied to the maximum rate of conversion can be considered as the

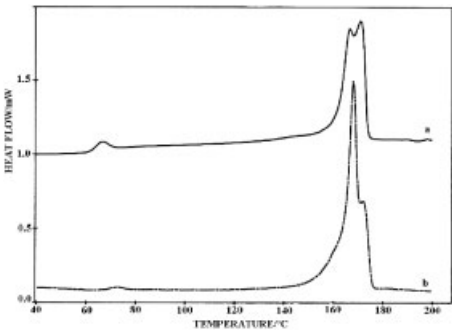

Figure 1.
DSC curves (first run) of PLLA as-received (a) and precipitated PLLA (b).

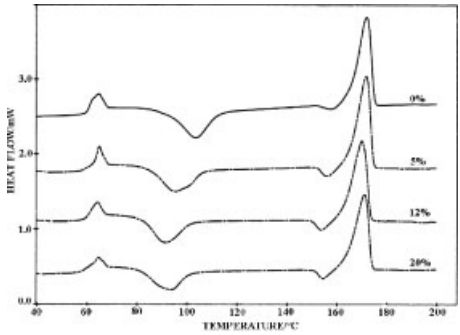

Figure 2.
DSC curves of PLLA nanocomposites with different $CaCO_3$ content.

variation of isoconversional methods such as Flynn-Wall Ozawa method, expanded Friedman method and Kissinger-Akahira-Sunose method.[24]

Results and Discussion

DSC Measurements

Figure 1 shows DSC curves of PLLA granules as-received and precipitated PLLA as well, generated during first heating. Double, overlapped melting peaks of PLLA are the result of sequence of melting and recrystallization processes, i.e. reorganization of existing crystal phase.[27,28] Double-melting behaviour exists when the crystallization temperature is relatively low.

PLLA granules and PLLA precipitate exhibit the same values of glass transition temperature and melting point, Table 1. The melting enthalpies and corresponding degrees of crystallization are different. PLLA granules as-received, formed from the molten state, exhibit lower melting enthalpy and crystallinity degree than the precipitated sample, formed from the concentrated solution of PLLA in chloroform.

DSC curves of extruded PLLA precipitate and the composites as well are shown on Figure 2. Besides T_g and T_m all of those extrudates exhibit additional transitions, such as cold crystallization (T_{cc}) and pre-melting crystallization (T_{pmc}). As seen in the figure, the degree of non-equilibrium structure was underscored by the large enthalpy relaxation peak that followed the glass transition. Also, it seems that the cooling rate in sample preparation (i.e. after extrusion) was high and only low amount of PLLA crystallizes during cooling. PLLA crystallizes mainly in the heating process and the corresponding exotherm is broader in the presence of $CaCO_3$. The curves of the second heating run are of the same shape as those of the first heating run for all samples and points out that cooling rate of 10 °C/min was still too high for complete crystallization.

The values of crystallization and melting point temperatures with corresponding enthalpies are listed in Table 2. While no significant shift of T_{pmc} and T_m of PLLA was observed upon addition of nano-sized $CaCO_3$, those particles cause decrease of T_{cc}, suggesting that $CaCO_3$ particles enhance the nucleation of PLLA crystallites during heating. That phenomenon is accompanied with an increase in crystalline fraction from 13% for pure PLLA up to 23% for the

Table 1.
Thermal properties of different PLLA forms.

PLLA	T_m	ΔH_m	T_g	X_c
	°C	J/g	°C	%
as received	163	45.6	59	49
precipitated	163	62.4	59	67

Table 2.
Melting and crystallization characteristics of PLLA/$CaCO_3$ composites from the first heating run

PLLA/$CaCO_3$	T_{cc}	ΔH_{cc}	T_{pmc}	ΔH_{pmc}	T_m	ΔH_m
	°C	J/g	°C	J/g	°C	J/g
100/0	93	−31.2	152	−1.2	164	44.4
95/5	85	−26.3	151	−4.2	164	45.4
88/12	83	−24.2	151	−3.8	164	44.3
80/20	81	−21.6	150	−2.6	163	41.3

$_{cc}$ - cold crystallization.
$_{pmc}$ - pre-melting crystallization.

composite with 20% of $CaCO_3$, Figure 3. Also, it is obvious that after extrusion of mainly crystalline PLLA precipitate (X_c = 67%) amorphous phase in PLLA dominates and cannot reach the crystalline degree of starting granules.

Fukuda et al.[20] found that in PLLA/$CaCO_3$ films cast from methylene chloride $CaCO_3$ particles induced increases of T_{cc} as the result of disturbing the nucleation of PLLA crystallites during heating. The reasons for the opposite results are either the difference in particle size or more probably the preparation method.

T_g value of pure PLLA was practically unchanged after extrusion suggesting that no observable degradation took place (Figure 4).

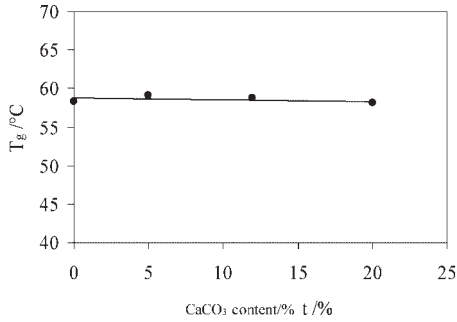

Figure 4.
Dependence of glass transition temperature of PLLA on $CaCO_3$ content.

TG Measurements

To our knowledge this is the first article concerning the thermal degradation of PLLA/$CaCO_3$ composites with aim to estimate the influence of inorganic component on the thermal degradation of PLLA in wider temperature range. During the degradation in the investigated temperature range $CaCO_3$ is thermally stable, thus the observed mass loss was attributed to PLLA only, Figure 5. PLLA almost completely decomposes in one step and the residual mass increases with $CaCO_3$ content.

The thermal degradation mechanism of PLLA above 200 °C is very complex and includes intramolecular transesterification leading to lactide and cyclic oligomers, *cis*-elimination leading to acrylic acid oligomers, and fragmentation producing acetaldehyde and carbon dioxide.[29–31] As shown in Figure 6, characteristic temperatures of the thermal degradation, such as temperature of 5% mass loss ($T_{5\%}$), onset degradation temperature (T_{ons}) and temperature at the highest degradation rate (T_{max}) strongly decrease when $CaCO_3$ was

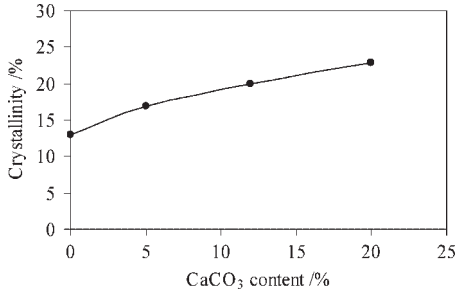

Figure 3.
Dependence of crystallinity of PLLA on $CaCO_3$ content.

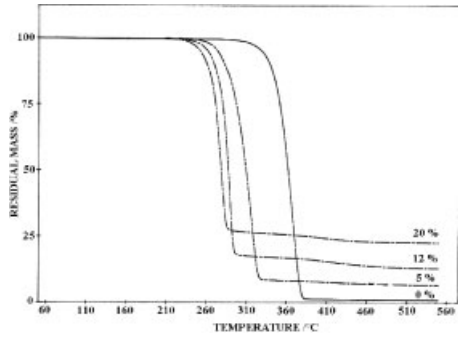

Figure 5.
Representative TG curves of PLLA nanocomposites with different CaCO at heating rate of 10 °C/min.

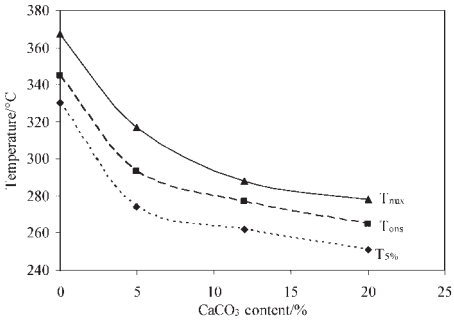

Figure 6.
Characteristics of thermal degradation of PLLA/$CaCO_3$ nanocomposites at heating rate 10 °C/min.

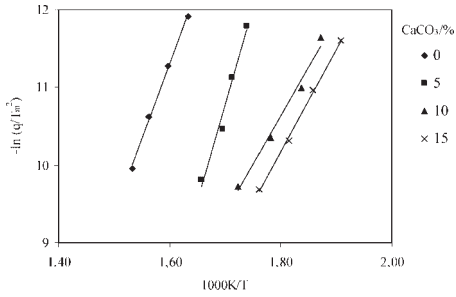

Figure 7.
TG data plotted according to Kissinger's method (T_m is the peak of DTG curve).

added. It is evident that $CaCO_3$ thermally destabilize PLLA, so it might be concluded that the PLLA/$CaCO_3$ interfaces are the possible weak points of the composites. The differences in polarity and surface free energy of PLLA ($\gamma = 37 \ldots 40\,mJ/m^2$, depending on molecular mass and casting material)[32] and $CaCO_3$ ($\gamma = 76\ mJ/m^2$)[33] might play an important role in the compatibility of the composite, enhancing the aggregation of $CaCO_3$ particles. Thus, the non-uniform dispersion of the filler in the composites changes the diffusion pathway of degradation products of PLLA and affects the thermal stability. It was known that $CaCO_3$ neutralises polymer acidity,[21] but the possible interactions of $CaCO_3$ with thermal degradation products are still unknown and should be investigated.

Apparent activation energy and pre-exponential factor of thermal degradation of PLLA/$CaCO_3$ nanocomposites according to equation (3) was determined from the slope and intercept of the straight lines, respectively, shown in Figure 7. The results obtained are listed in Table 3. However, the value of E_a of thermal degradation of pure PLLA (161 kJ/mol) is higher than reported by McNeil and Leiper[29] of 120 kJ/mol and Kopinke et al.[30] of 110 kJ/mol, but in better agreement with recent investigations of Aoyagi et al.[34] of 80–160 kJ/mol, depending on conversion. The thermal degradation of PLLA in nanocomposites is characterized with quite different values of E_a. Sample 95/5 exhibit E_a of 208 kJ/mol, and other two samples almost twice lower values. As mentioned earlier, the thermal degradation of PLLA involves different mechanisms and the presence of filler probable makes it more complex. Since the values of A are different, apparent activation energies are not comparable and should be considered with respect to pre-exponential factor A. This is not only formally mathematical demand according to the Arrhenius law, but the necessity concerning the heterogeneous reaction systems, especially when comparing them. To avoid possible misinterpretations the ratio $E_a/log\ A$ was used to characterize the reactivity of the system.[26,35,36] Generally, higher ratio $E_a/log\ A$ means the higher system stability. That ratio decreases as the $CaCO_3$ content in the nanocomposites increases and reveals that the system is less stable in the presence of $CaCO_3$. The kinetic parameters expressed as explained are also in agreement with trend in characteristic temperatures of thermal degradation presented in Figure 6.

Table 3.
Kinetic parameters of the thermal degradation of PLLA/$CaCO_3$ nanocomposites.

PLLA/$CaCO_3$	E_a	A	E_a/log A
	kJ/mol	1/min	
100/0	161	6.48×10^{12}	12.55
95/5	208	1.55×10^{18}	11.44
88/12	104	11.94×10^{9}	11.23
80/20	109	8.8×10^{9}	10.96

Conclusions

PLLA in the extruded PLLA/$CaCO_3$ nanocomposites are of low crystalline degree and additionally crystallize upon heating. Percent of crystallinity increases with $CaCO_3$ content suggesting that $CaCO_3$ enhance the crystallization process of PLLA. Chain mobility of the polymer remains unchanged, i.e. nanofiller has no effect on the glass transition temperature. PLLA in PLLA/$CaCO_3$ nanocomposites is stabile at processing conditions, although the thermal stability of the nanocomposites at high temperatures was influenced by $CaCO_3$.

[1] Y. Ikada, H. Tsuji, *Macromol. Rapid Commun.* **2000**, *21*, 117.
[2] G. Scott, D. Gilead, Eds., *Degradable Polymers, Principles and Applications*'', Chapman and Hall, London 1995.
[3] J. Lunt, *Polym. Degrad. Stab.* **1997**, *59*, 145.
[4] C. J. Weber, *Biobased Packaging Materials for the Food Industry*, KVL, Frederiksberg, Denmark **2000**.
[5] G. Robinson, Waste Management World, **2007**, Jan-Feb.77.
[6] L. V. Labrecque, R. A. Kumar, V. Davé, R. A. Gross, S. P. McCarthy, *J. Appl. Polym. Sci.* **1997**, *66*, 1507.
[7] S. Jacobsen, G. Fritz, *Polym. Eng. Sci.* **1999**, *39*, 1303.
[8] N. Ljungberg, T. Andersson, B. Wesslen, *J. Appl. Sci.* **2003**, *88*, 3239.
[9] N. Ljungberg, B. Wesslen, *Polymer*, **2003**, *44*, 7679.
[10] T. Ke, X. Sun, *J. Appl. Polym. Sci.* **2001**, *81*, 3069.
[11] B. Braun, J. R. Dorgan, D. M. Knauss, *J. Polym. Environ.* **2006**, *14*, 49.
[12] V. L. Finkenstadt, L. S. Liu, J. L. Willett, *J. Polym. Environ.* **2007**, *15*, 1.
[13] C. Thellen, C. Orroth, D. Froio, D. Zigler, J. Lucciarini, R. Farrell, N. A. D'Souza, J. A. Ratto, *Polymer*, **2005**, *46*, 11716.
[14] M. Shibata, Y. Someya, M. Orihara, M. Miyoshi, *J. Appl. Polym. Sci.* **2006**, *99*, 2594.
[15] S. Lee, C.-H. Kim, J.-K. Park, *J. Appl. Polym. Sci.* **2006**, *101*, 1664.
[16] Y. Shikinami, M. Okuno, *Biomaterials*, **1999**, *20*, 859.
[17] T. Furukawa, Y. Matsusue, T. Yasunaga, Y. Shikinami, M. Okuno, T. Nakamura, *Biomaterials*, **2000**, *21*, 889.
[18] Z. Hong, P. Zhang, C. He, X. Qiu, A. Liu, X. Chen, *Biomaterials*, **2005**, *26*, 6296.
[19] T. Kasuga, H. Maeda, K. Kato, M. Nogami, K. Hata, M. Ueda, *Biomaterials*, **1999**, *20*, 859.
[20] N. Fukuda, H. Tsuji, Y. Ohnishi, *Polym. Degrad. Stab.* **2002**, *78*, 119.
[21] N. J. Cotton, Press release, Smith & Nephew, 11/05.
[22] H. E. Kissinger, *Sci. Technol.* **1971**, *16*, 22.
[23] J.-D. Nam, J. C. Seferis, *J. Polym. Sci. Polym. Phys.* **1991**, *29*, 601.
[24] T. Ozawa, *Thermochim. Acta* **1992**, *203*, 159.
[25] T. C. Chang, K. H. Wu, C. L. Liao, S. T. Lin, G. P. Wang, *Polym. Degrad. Stab.* **1998**, *62*, 299.
[26] B. Andričić, T. Kovačić, *Polym. Degrad. Stab.* **1999**, *65*, 59.
[27] M. Yasuniwa, S. Tsubakihara, Y. Sugimoto, C. Nakafuku, *J. Polym. Sci. Polym. Phys.* **2004**, *42*, 25.
[28] M. L. Di Lorenzo, *Macromol. Symp.* **2006**, *234*, 176.
[29] I. C. McNeil, H. A. Leiper, *Polym. Degrad. Stab.* **1985**, *65*, 267.
[30] F. D. Kopinke, M. Remmler, K. Mackenzie, M. Möder, O. Wachsen, *Polym. Degrad. Stab.* **1996**, *53*, 329.
[31] O. Wachsen, K. H. Reichert, R. P. Krüger, H. Much, G. Shulz, *Polym. Degrad. Stab.* **1996**, *55*, 225.
[32] R. Smith, R. Pitrola, *J. Appl. Polym. Sci.* **2002**, *83*, 997.
[33] S. Lučić, V. Kovačević, D. E. Pacham, A. Bogner, A. Geržina, *Polym. Surf. Modif.* **2000**, *2*, 505.
[34] Y. Aoyagi, K. Yamashita, Y. Doi, *Polym. Degrad. Stab.* **2002**, *76*, 53.
[35] A. K. Galwey, M. E. Brown, *Thermochim. Acta* **1997**, *300*, 107.
[36] M. Maciejevski, *J. Therm. Anal.* **1998**, *33*, 243.

