

# Mechanical Properties and Thermal Stability of Poly(L-lactide)/Calcium Carbonate Composites

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**ABSTRACT:** Poly(L-lactide) (PLA) was melt-mixed with micrometer-sized and nanosized calcium carbonate ( $\text{CaCO}_3$ ) particles before and after modification with calcium stearate. Adhesion between the  $\text{CaCO}_3$  particles and the PLA matrix was assessed qualitatively by scanning electron microscopy observation of the fractured surface morphology of the composites. The effect of the incorporation of the  $\text{CaCO}_3$  particles on the thermal stability of the PLA-based composites was quantified by the temperatures corresponding to 5 and 50% of weight loss and the

activation energy determined through thermogravimetric analyses of the composites. The tensile strength and modulus values of the composite were improved greatly without a significant loss in the elongation at break when the nanosized  $\text{CaCO}_3$  was incorporated up to 30 wt %. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 109: 3087–3092, 2008

**Key words:** composites; thermogravimetric analysis (TGA); thermal properties; polyesters

## INTRODUCTION

Poly(L-lactide) (PLA) is one of the most important biobased polymers and is widely used in various applications. It is degraded by the cleavage of ester bonds to produce lactic acid and its oligomers, which can be metabolized by many microorganisms.<sup>1</sup> PLA is highly biocompatible<sup>2</sup> and is used for biomedical purposes, such as surgical sutures,<sup>3–5</sup> fractured bone fixation,<sup>6,7</sup> tissue engineering,<sup>8</sup> and drug-delivery systems.<sup>9,10</sup> Recently, Cargill Dow<sup>11</sup> began to produce PLA on a commercial scale under the trade name Nature Works, and the price has been reduced greatly because of the combination of biological fermentation and polymerization technologies.

Calcium carbonate ( $\text{CaCO}_3$ ) is one of the most abundant materials on our planet and has been used for various polymer composites. Recently, nanosized  $\text{CaCO}_3$  has received a lot of attention because of its wide range of potential applications and its low cost. Various methods, such as high-gravity reactive precipitation, have been developed to prepare nanosized  $\text{CaCO}_3$  particles with a narrow size distribution.<sup>12</sup>

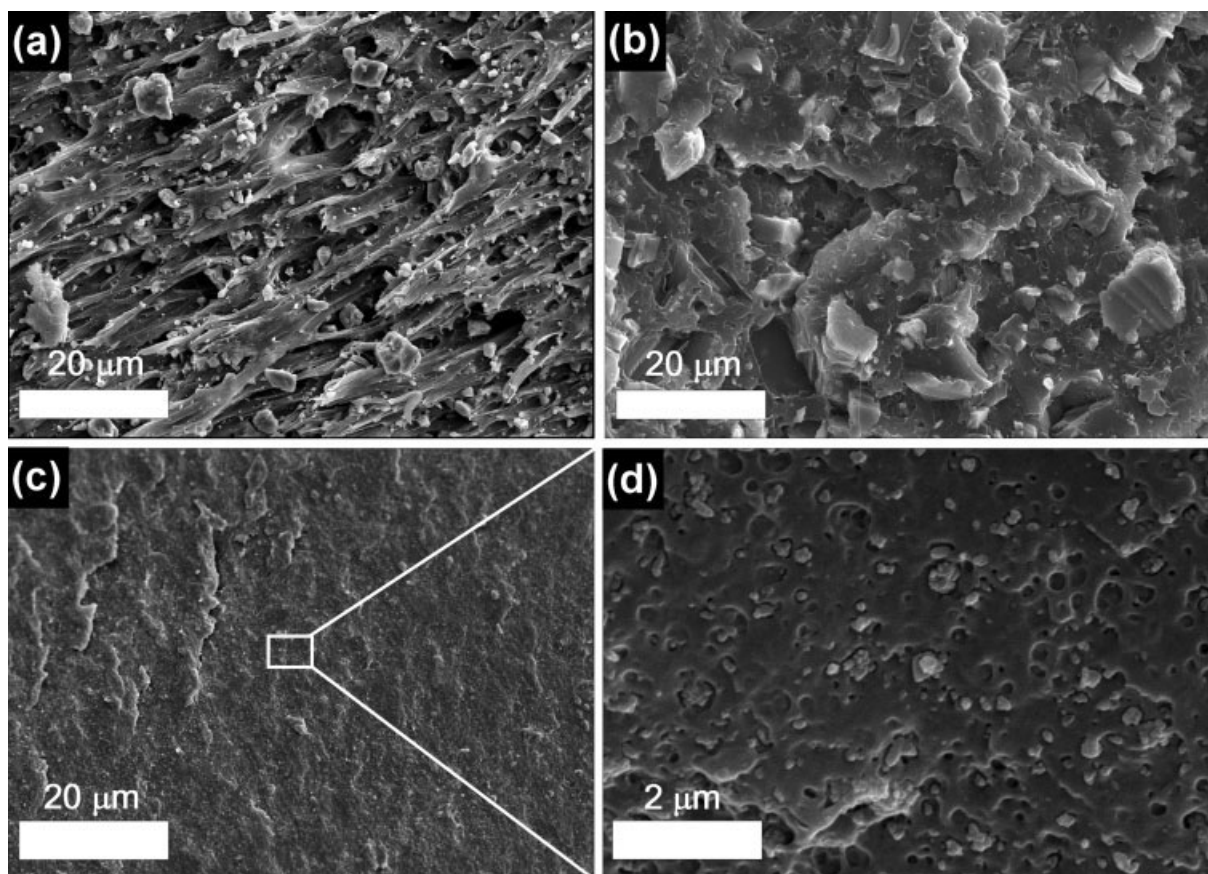
The pulverization of  $\text{CaCO}_3$  particles and treatment with organic surfactants are needed to minimize the deterioration of the mechanical properties of the resulting polymer composites. Chen et al.<sup>13</sup>

found that impact strength of polypropylene (PP) could be increased from 55 to 133 J/m by the addition of 9.2 vol % of surfactant-treated 44 nm-sized  $\text{CaCO}_3$  particles. Wang et al.<sup>14</sup> reported that the mechanical properties of PP, especially the ductility, were effectively improved because of the incorporation of nanosized  $\text{CaCO}_3$  particles treated with stearic acid by using an ultra-high-speed mixer. A variety of surface modifiers, such as fatty acids, phosphates, silanes, titanates, and zirconates, have been used to reduce the high surface energy and, thus, to avoid particle agglomeration.<sup>15–18</sup> The coated organic layer situates itself at the interface between the filler and the polymer matrix and, hence, influences the wetting and adhesion properties of the two phases involved to raise the particle–particle interactions. Consequently, coating with organic surface modifiers determines the final properties of the composite.<sup>19–21</sup> Several studies on the influence of increasing volume fractions of ground micrometer-sized  $\text{CaCO}_3$  fillers on the mechanical properties of polyolefins, especially on those of PP, have been reported.<sup>22–24</sup>

In this study, attention was directed to the investigation of the role of  $\text{CaCO}_3$  particles as reinforcing filler and as an extender for PLA composites. PLAN, PLAC, and PLAH were prepared by melt-compounding PLA with nanosized  $\text{CaCO}_3$  pristine particles 2–5  $\mu\text{m}$  in diameter, and  $\text{CaCO}_3$  particles 3–4  $\mu\text{m}$  in diameter coated with calcium stearate, respectively. The thermal stability variation of the PLA-based composites was monitored by the measurement of the temperatures corresponding to 5 and 50% weight losses ( $T_{5\%}$  and  $T_{50\%}$ , respectively) and the activation energy determined through

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**Figure 1** SEM micrographs of PLA and the PLA composites with 30 wt % loading of the solid fillers: (a) PLAC, (b) PLAH, (c) PLAN, and (d) PLAN with a higher magnification.

thermogravimetric analysis (TGA). The morphology of the fractured surface was examined with a scanning electron microscope, and the tensile properties of the composites were explored as a function of the type and content of the  $\text{CaCO}_3$  fillers.

## EXPERIMENTAL

### Materials

PLA was manufactured by Cargill Dow (Minneapolis, MN) with a weight-average molecular weight of  $2.4 \times 10^5$  (g/mol). It was dried in a vacuum oven at  $50^\circ\text{C}$  for at least 2 days.  $\text{CaCO}_3$  was purchased from Wooryong (Kangwondo, Korea). Hipflex100 (Hipflex) was purchased from Specialty Minerals Inc. (MA). YH303 was obtained from Shanghua Yaohai Nano-Tech (Shanghai, China). Both Hipflex and YH303 were coated with 1 wt % calcium stearate. The particle sizes of pristine  $\text{CaCO}_3$ , Hipflex, and YH303 were 2–5 μm, 3–4 μm, and 60–90 nm, respectively.

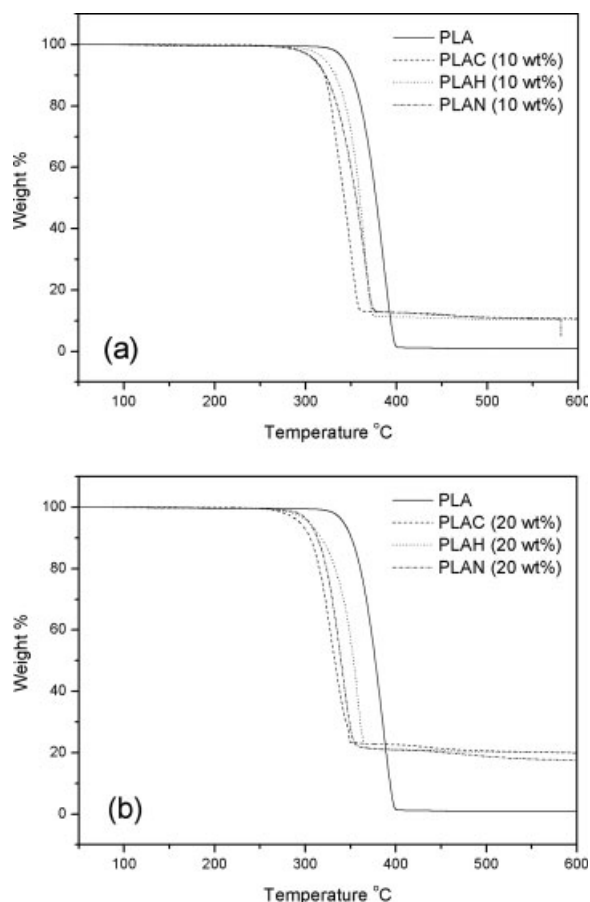
### Preparation of the composites

The PLA/ $\text{CaCO}_3$  composites with different fillers were prepared by melt-compounding with a twin-

screw extruder [Twin Extruder BA-19 (length/diameter = 40), Bautek, Korea] operated at a temperature of  $200^\circ\text{C}$  and a screw rotation rate of 300 rpm.

### Measurements

The dumbbell-shaped tensile bars were stamped out of plaques extruded from the twin-screw extruder with a cutting press according to ASTM D 638 for the tensile tests. The tensile properties were measured on an Instron no. 4462 ultimate tensile testing machine at  $20^\circ\text{C}$  and 30% humidity. The cross speed was set at 10 mm/min. At least 10 specimens were used, and the results were averaged to collect the values of the tensile properties. The morphology of the fractured surface of the specimens was examined with a scanning electron microscope (S-4300, Hitachi, Japan). The fracturing was performed while the specimen was immersed in liquid nitrogen. The fractured surfaces were coated with a Pt layer with an ion sputter (E-1030, Hitachi). The scanning electron microscopy (SEM) images were collected at an accelerating voltage of 15 kV. The thermal properties of PLA and its composites were investigated by TGA (Q50, Polymer Laboratories, United Kingdom). The



**Figure 2** TGA thermograms of the PLA, PLAC, PLAH, and PLAN composites: (a) 10 and (b) 20 wt %.

samples were heated in the temperature range of 30–800°C at heating rates of 5, 10, 20, and 40°C/min with a controlled flow rate of dry nitrogen at 60 cm<sup>3</sup>/min.

## RESULTS AND DISCUSSION

PLA was melt-compounded with nanosized CaCO<sub>3</sub>, YH303, which was made by coating 1 wt % of calcium stearate on CaCO<sub>3</sub> particles 60–90 nm in diameter to prepare PLAN. PLA was also compounded with pristine CaCO<sub>3</sub> particles 2–5 μm in diameter and with Hipflex, which was made by coating 1 wt %

calcium stearate on CaCO<sub>3</sub> particles 3–4 μm in diameter, to synthesize PLAC and PLAH, respectively.<sup>12</sup>

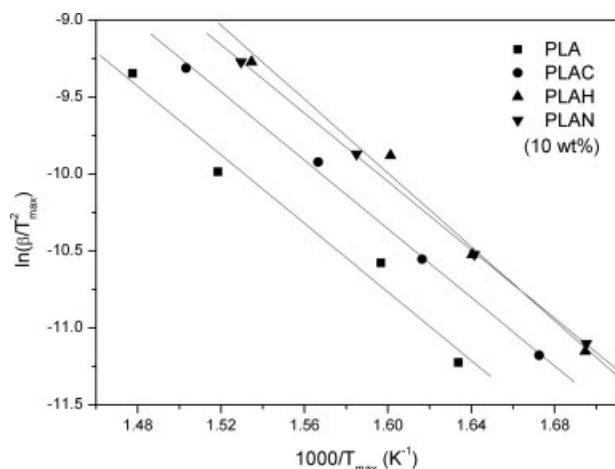
The morphology of the fractured surfaces was examined with SEM, as shown in Figure 1. The SEM micrograph of the fractured surface of the PLA composites filled with 30 wt % pristine CaCO<sub>3</sub> disclosed that many CaCO<sub>3</sub> particles protruded out and exhibited a sandlike morphology scattered on the fractured surface. Figure 1(a) reveals that plastic flow took place during the fracturing of PLAC and that distorted holes were formed around the neat CaCO<sub>3</sub> particles. This is a typical morphology of the breathable films prepared by the drawing of polyethylene (PE)/CaCO<sub>3</sub> composite films. The incompatible nature of CaCO<sub>3</sub> particles with respect to PE facilitates the detachment of the PE matrix from the solid filler and promotes the formation of distorted holes around the solid filler particles.<sup>25</sup> The numerous holes are beneficial to the breathable films used for diapers and pads.

In contrast to PLAC, the particles scattered on the fractured surface of PLAH were much smaller in number than those of PLAC, which indicated that fewer cracks propagated during the fracturing through the interface between the solid particles and the PLA matrix than in the former composite. Moreover, the Hipflex particles looked glued to the PLA matrix more evidently than the pristine CaCO<sub>3</sub> particles, as exhibited in Figure 1(b). Tiny particles are shown in Figure 1(c), which shows the fractured surface morphology of PLAN, which were due to the smaller particle size of YH303. A comparison of the morphology in Figure 1(b) with that in Figure 1(d), which is the 10× magnified image of Figure 1(c), revealed that YH303 particles were less tightly glued to the PLA matrix than the Hipflex particles, even though both YH303 and Hipflex were coated with 1 wt % calcium stearate. This was, at least in part, ascribed to the thinner coated calcium stearate layer of YH303 as compared to that of Hipflex, which was due to the larger specific surface area of the former filler and thereby to the lower compatibility of YH303 with PLA matrix.

TGA was performed for the composites, where the weight loss due to the volatilization of the degradation products was monitored as a function of

**TABLE I**  
*T*<sub>5%</sub> and *T*<sub>50%</sub> Values for PLA and the PLA/CaCO<sub>3</sub> (10 wt %) Composites as Determined from the TGA Results

β (°C/min)	PLA		PLAC		PLAH		PLAN	
	<i>T</i> <sub>5%</sub> (°C)	<i>T</i> <sub>50%</sub> (°C)	<i>T</i> <sub>5%</sub> (°C)	<i>T</i> <sub>50%</sub> (°C)	<i>T</i> <sub>5%</sub> (°C)	<i>T</i> <sub>50%</sub> (°C)	<i>T</i> <sub>5%</sub> (°C)	<i>T</i> <sub>50%</sub> (°C)
5	305.4	332.1	280.2	322.9	287.2	325.9	280.3	322.6
10	320.0	348.1	285.8	324.4	303.6	339.3	289.2	336.6
20	342.4	377.4	308.6	340.1	319.5	357.9	296.8	352.3
40	360.8	395.5	335.5	377.3	346.6	383.8	329.3	379.5



**Figure 3** Plots for the determination of the activation energies for PLA, PLAC, PLA H, and PLAN according to the Kissinger method with 10 wt %  $\text{CaCO}_3$  particles.

temperature, as shown in Figure 2. Because  $\text{CaCO}_3$  particles began to lose weight, which was caused by the dissipation of  $\text{CO}_2$  gas due to the decomposition of  $\text{CaCO}_3$ , at temperatures higher than  $600^\circ\text{C}$ , the weight loss of the composites between 300 and  $400^\circ\text{C}$  was attributed mainly to the degradation of the PLA matrix. The onset temperature of thermal degradation significantly decreased as a result of compounding with the solid fillers. Two parameters,  $T_{5\%}$  and  $T_{50\%}$ , both measured at different heating rates, are listed in Table I. Both  $T_{5\%}$  and  $T_{50\%}$  of the PLA composites were lowered because of the incorporation of Hiphlex and YH303 as well as neat  $\text{CaCO}_3$ .

The thermal stability of the polymers could be quantified by the activation energy ( $E$ ) of thermal degradation, which was determined conveniently from TGA with the equations proposed by Kissinger<sup>26</sup> and Flynn–Wall–Ozawa.<sup>27,28</sup>

The Kissinger equation can be written as

$$\ln \frac{\beta}{T_{\max}^2} = \left\{ \ln \frac{AR}{E} + \ln \left[ n(1 - \alpha_{\max})^{n-1} \right] \right\} - \frac{E}{RT_{\max}} \quad (1)$$

where  $\beta$  is the heating rate,  $T_{\max}$  is the temperature corresponding to the inflection point of the thermal degradation curves at the maximum degradation rate,  $A$  is the preexponential factor,  $\alpha_{\max}$  is the maximum conversion,  $R$  is the gas constant, and  $n$  is the reaction order. The peak temperature ( $T_{\max}$ ) was determined from the differential TGA curves. The activation energy could be calculated from the slope of  $\ln(\beta/T_{\max}^2)$  as a function of  $1/T_{\max}$ .

The Flynn–Wall–Ozawa method determines activation energy simply from the weight loss versus

**TABLE II**  
Activation Energies (kJ/mol) of the Thermal Degradation of the PLA, PLAC, PLA H, and PLAN Composites at 10 wt % Loading of the Solid Fillers

Sample	Kissinger's method	Ozawa's method (mean value)
PLA	102.5	101.3
PLAC	89.4	78.1
PLA H	94.4	93.3
PLAN	91.7	86.0

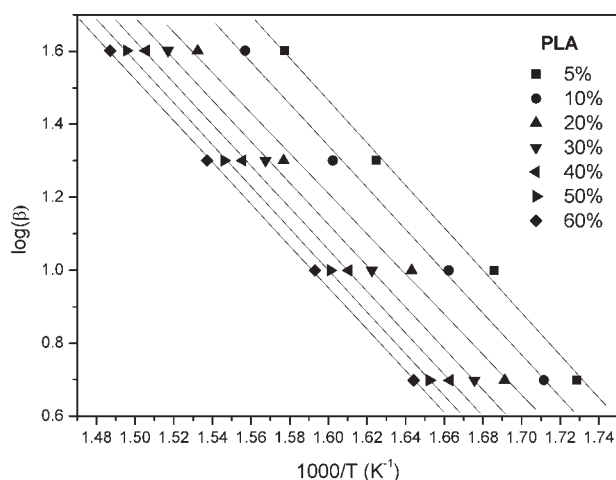
temperature data obtained at different heating rates with eq. (2):

$$\log \beta = \left[ \log \left( \frac{AE}{R} \right) - \log f(\alpha) - 2.315 \right] - 0.4567 \frac{E}{RT} \quad (2)$$

where  $\alpha$  is temperature-independent function of the conversion, that is:  $da/dt = Kf(a)$ , where  $f(a)$  depends on the mechanism of the degradation reaction and  $T$  is the absolute temperature.<sup>27</sup>

This is based on the integral method, and the activation energy can be determined without knowledge of the reaction order. Activation energy at a given conversion can be obtained from the plot of  $\log \beta$  versus  $1/T$ .

The plot of  $\ln(\beta/T_{\max}^2)$  versus  $1/T_{\max}$  according to the Kissinger's method is exemplified in Figure 3, and the results are summarized in Table II. Least squares fitting was performed on the plot of  $\log \beta$  versus  $1/T$  at different conversions to adopt the Flynn–Wall–Ozawa equation, as shown in Figure 4. The average activation energies determined at conversions of 5, 10, 20, 30, 40, 50, and 60% are tabulated in Table II. Not only the Kissinger's equation but also the Flynn–Wall–Ozawa method predicted



**Figure 4** Plots for the determination of the activation energies for PLA according to Ozawa's method.

TABLE III  
Tensile Properties of PLA and the PLA/CaCO<sub>3</sub> Composites

	Tensile modulus (GPa)	Tensile strength (MPa)	Elongation at break (%)
PLA	2.19 ± 0.5	51.5 ± 1.4	4.0 ± 0.5
PLAC (5 wt %)	2.34 ± 0.2	55.3 ± 2.1	2.7 ± 0.2
PLAC (10 wt %)	2.73 ± 0.3	58.3 ± 1.8	2.4 ± 0.2
PLAC (20 wt %)	2.64 ± 0.3	53.3 ± 1.3	1.8 ± 0.2
PLAC (30 wt %)	2.44 ± 0.2	42.3 ± 1.8	1.9 ± 0.3
PLAH (5 wt %)	2.38 ± 0.2	65.4 ± 0.7	4.8 ± 0.3
PLAH (10 wt %)	3.34 ± 0.3	60.0 ± 0.5	4.5 ± 0.2
PLAH (20 wt %)	2.97 ± 0.4	49.2 ± 0.4	3.0 ± 0.2
PLAH (30 wt %)	2.66 ± 0.4	45.0 ± 0.7	2.6 ± 0.2
PLAN (5 wt %)	2.54 ± 0.2	57.6 ± 0.7	6.3 ± 0.4
PLAN (10 wt %)	3.89 ± 0.6	63.0 ± 0.8	5.5 ± 0.2
PLAN (20 wt %)	3.25 ± 0.4	55.3 ± 1.0	4.0 ± 0.4
PLAN (30 wt %)	2.62 ± 0.5	51.6 ± 0.6	3.6 ± 0.2

that the activation energy increased in the order PLAC < PLAN < PLAH < PLA, which indicated that the incorporation of the solid fillers reduced the thermal stability of the PLA matrix. The basic nature of CaCO<sub>3</sub> may have catalyzed the depolymerization of the ester bonds of PLA, and thus, it was thought to be responsible for the reduced thermal stability. The higher activation energy of the PLAH composites in comparison to that of PLAC was attributed to the fact that the hydrophobic moiety of calcium stearate coated on CaCO<sub>3</sub> particles of Hipflex reduced the direct contact between the PLA matrix and the CaCO<sub>3</sub> moiety.

The catalytic effect on the degradation of PLA by the alkaline CaCO<sub>3</sub> moiety was more probable in PLAN than in PLAH, which led to the lower activation energy of PLAN compared to that of PLAH because YH303 was less thickly coated with calcium stearate than Hipflex at the same content of calcium stearate and because the former filler had a much larger surface area than the latter. The decreasing order of the activation energy in Table II matched the decreasing order of  $T_{5\%}$  and  $T_{50\%}$  in Table I.

The tensile modulus of the PLA composites filled with 5, 10, 20, and 30 wt % solid filler was higher than that of the neat PLA, as shown in Table III. The tensile strength rose initially and then decreased monotonously after showing a maximum as the pristine CaCO<sub>3</sub> content increased. The increase in the tensile modulus was more pronounced, and the maximum value of the tensile strength was higher when YH303 was incorporated as compared to CaCO<sub>3</sub> and Hipflex. Not only the tensile modulus but also the tensile strength of PLAN was improved without a significant loss in the elongation at break up to a YH303 content of 30 wt %.

Therefore, it can be said that the modification of CaCO<sub>3</sub> particles with calcium stearate raised the mechanical properties of the PLA-based composites. The smaller the particle size of the calcium stearate

coated CaCO<sub>3</sub> was, the more pronounced the enhancement of the mechanical properties was.

## CONCLUSIONS

PLA was melt-mixed with micrometer-sized pristine CaCO<sub>3</sub> particles and those coated with 1 wt % calcium stearate to prepare PLAC and PLAH, respectively. PLA was also melt-compounded with nanosized CaCO<sub>3</sub> particles coated with 1 wt % calcium stearate to synthesize PLAN. The coating of CaCO<sub>3</sub> with calcium stearate discernibly improved the adhesion between CaCO<sub>3</sub> and PLA. The thermal stability of PLA, as evaluated by  $T_{5\%}$ ,  $T_{50\%}$ , and the activation energy determined through TGA of the PLA/CaCO<sub>3</sub> composites decreased in the order PLA > PLAH > PLAN > PLAC because of the basic nature of CaCO<sub>3</sub>. The modification of CaCO<sub>3</sub> particles with calcium stearate enhanced the mechanical properties of the PLA-based composites. The incorporation of nanosized CaCO<sub>3</sub> improved the mechanical properties more significantly than that of micrometer-sized CaCO<sub>3</sub>, even though that adhesion between the filler and the matrix was stronger in the composites with the latter CaCO<sub>3</sub> than in those with the former CaCO<sub>3</sub> at the same content of calcium stearate.

## References

- Zhang, L.; Goh, S. H.; Lee, S. Y. *Polymer* 1998, 39, 481.
- Tsuji, H.; Ikada, Y. *Polymer* 1995, 36, 2709.
- Barrows, T. H. *Synthetic Bioabsorbable Polymers*; Technomic: Lancaster, PA, 1990; p 243.
- Hartmann, M. H. In *Biopolymers from Renewable Resources*; Kaplan, D. L., Ed.; Springer: Berlin, Germany, 1998; p 367.
- Ikada, Y.; Tsuji, H. *Macromol Rapid Commun* 2000, 21, 117.
- Zhang, X.; Goosen, M. R. A.; Wyss, U. P.; Pichora, D. J. *Macromol Sci Rev Macromol Chem Phys* 1993, 33, 81.
- Winet, H.; Bao, J. *J Biomed Mater Res* 1998, 40, 567.
- Langer, R. *Acc Chem Res* 2000, 33, 94.

9. Lewis, D. H. In *Biodegradable Polymers as Drug Release Systems*; Chasin, M.; Langer, R., Eds.; Marcel Dekker: New York, 1990; Vol. 45, p 110.
10. Bhardwaj, R.; Blanchard, J. *Int J Pharm* 1998, 170, 109.
11. Vink, E. T. H.; Rábago, K. R.; Glassener, D. A.; Gruber, P. R. *Polym Degrad Stab* 2003, 80, 403.
12. Mai, Y. W.; Yu, Z. Z. *Polymer Nanocomposites*; CRC: Boca Raton, FL, 2006.
13. Chen, C. M.; Wu, J. S.; Li, J. S.; Cheung, Y. K. *Polymer* 2002, 43, 2981.
14. Wang, G.; Chen, X. Y.; Huang, R.; Zhang, L. *J Mater Sci Lett* 2002, 21, 985.
15. Rothon, R. N. *Particulate-Filled Polymer Composites*; Rapra Technology Ltd.: Shrewsbury, UK, 2003.
16. *Mineral Fillers in Thermoplastics*; Jancar, J., Ed.; *Advances in Polymer Science* 139; Springer: Berlin, Germany, 1999.
17. *Polypropylene: Structure, Blends and Composites*; Karger-Kocsis, J., Ed.; Chapman & Hall: London, 1995.
18. Nakatsuka, T. *Molecular Characterization of Composite Interfaces*; Plenum: New York, 1985.
19. Papirer, E.; Schultz, J.; Turchi, C. *Eur Polym J* 1984, 20, 1155.
20. Fekete, E.; Pukánszky, B.; Toth, A.; Bertoti, I. *J Colloid Interface Sci* 1990, 135, 200.
21. Osman, M. A.; Suter, U. W. *Chem Mater* 2002, 14, 4408.
22. Bartczak, Z.; Argon, A. S.; Cohen, R. E.; Weinberg, M. *Polymer* 1999, 40, 2347.
23. Suwanprateeb, J. *Compos A* 2000, 31, 353.
24. Thio, Y. S.; Argon, A. S.; Cohen, R. E.; Weinberg, M. *Polymer* 2002, 43, 3661.
25. Maged, A. O.; Ayman, A.; Ulrich, W. S. *Polymer* 2004, 45, 1177.
26. Akahira, T.; Sunose, T. *Res Rep Chiba Inst Technol (Sci Technol)* 1971, 16, 22.
27. Ozawa, T. *Bull Chem Soc Jpn* 1965, 38, 1881.
28. Flynn, J. H.; Wall, L. A. *J Polym Sci Part B: Polym Lett* 1966, 4, 323.