

# Crystallization Behavior and Mechanical Properties of Poly( $\epsilon$ -Caprolactone)/Cyclodextrin Biodegradable Composites

Tungalag Dong, Takafumi Mori, Pengju Pan, Weihua Kai, Bo Zhu, Yoshio Inoue

Department of Biomolecular Engineering, Tokyo Institute of Technology, Midori-ku, Yokohama 226-8501, Japan

Received 12 May 2008; accepted 2 November 2008

DOI 10.1002/app.29628

Published online 17 February 2009 in Wiley InterScience (www.interscience.wiley.com).

**ABSTRACT:** The poly( $\epsilon$ -caprolactone) (PCL)/ $\alpha$ -cyclodextrin ( $\alpha$ -CD) inclusion complex (PCLIC) was successfully prepared, and its effect on the thermal behavior and mechanical properties of PCL was thoroughly studied. It is shown that the addition of PCLIC greatly increased the crystallization rate and thermal stability of the PCL. The Young's modulus and yield strength of PCL/PCLIC composite are about 2 and 1.3 times of the pure PCL, and the

elongation at break of the PCL/PCLIC composites kept above 350%, when the PCLIC composition is 15 wt %. It is shown that PCLIC is a good enforcing biofiller for the PCL. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 112: 2351–2357, 2009

**Key words:** crystallization; mechanical property; cyclodextrin; composite

## INTRODUCTION

Preparation of conventional composites using inorganic or natural fillers is a possible way to improve some of the properties of biodegradable polymers, such as, thermal stability, gas barrier properties, mechanical strength, melt viscosity, and biodegradability. The biodegradable composites are promising eco-friendly materials for a variety of applications. Recently, the natural filler-reinforced polymeric composites have attracted much research interest. Several kinds of natural fillers have been developed as reinforcing fillers for both thermoplastic and thermosetting matrix composites.<sup>1–3</sup> Saccharin was used as a nucleating agent for crystallization of poly(hydroxybutyrate) (PHB) and their copolymers. When it added to the melt of these polymers, their epitaxial growths were induced on its surface.<sup>4,5</sup> Starch has been shown to serve as the nucleating agent for poly(L-lactic acid) (PLLA) and poly(butylene succinate) (PBS), resulting in crystallized materials with high tensile strength.<sup>6–8</sup> Plant-derived kenaf fibers can significantly improve the crystallization rate and tensile and storage moduli of poly( $\epsilon$ -caprolactone) (PCL) and PLLA.<sup>9,10</sup>

$\alpha$ -Cyclodextrin ( $\alpha$ -CD) is an attractive material as additive for biodegradable polymer because of its excellent biocompatibility, biodegradability, solubil-

ity, and environmentally safety.<sup>11–14</sup> Furthermore, it has good nucleating ability on the crystallization of aliphatic polyesters when compared with that of the conventional nucleating agents, such as talc.<sup>15–20</sup> Since Harada et al.<sup>21–24</sup> have found that CDs form inclusion complexes (ICs) with linear polymers, the CDICs with polymers have attracted much attention because of their unique supramolecular architectures. The CDICs have been designed into polyrotaxane, hydrogel, and model materials for macromolecular recognition in biological systems.

The CDICs are also considered to be potential nanofillers for high-strength biobased materials because of their tremendous mechanical properties, nanometer-scale diameter, and high aspect ratio. Most of these, however, consist almost completely of CDICs, and there have been few studies on materials prepared using a combination of CDICs and other components. For the utilization of CDICs as the eco-friendly fillers, extensive studies have been carried out by researchers to improve miscibility,<sup>25–29</sup> biodegradability,<sup>30</sup> crystallizability,<sup>31–38</sup> and mechanical properties<sup>39–42</sup> of the biodegradable polymers. However, the research on the application of CDICs is not enough and much challenge remains, especially, in applications of CDICs as the nucleating and reinforcement agents for the biodegradable polymers. In this study, PCL, one of the typical biodegradable aliphatic polyesters was chosen to study the effects of CDICs on the crystallization and mechanical properties of PCL via simple blending. The crystallization behavior and mechanical properties of PCL blended with  $\alpha$ -CD and PCLICs were investigated by the differential scanning calorimetry

Correspondence to: Y. Inoue (inoue.y.af@m.titech.ac.jp).

Contract grant sponsors: Japan Society for the Promotion of Science.

**TABLE I**  
**Concentration and Mixing Ratio of PCL and  $\alpha$ -CD Solution Used for the Preparation of PCLICs and Host-Guest Stoichiometry of PCLICs**

Sample	Original solution		Yield	Stoichiometry of PCLIC [PCL monomeric unit]/[ $\alpha$ -CD] molar ratio
	PCL/ acetone	$\alpha$ -CD/ water		
PCLIC2	2 g/200 mL	1 g/10 mL	0.7 g	2.4 : 1
PCLIC4	2 g/200 mL	2 g/20 mL	2.4 g	4.1 : 1
PCLIC7	2 g/200 mL	4 g/40 mL	3.7 g	7.1 : 1

(DSC), dynamic mechanical thermal analysis (DMTA), and tensile test. The PCL/PCLIC composite materials are biodegradable as well as biocompatible. The Young's modulus, tensile strength, hydrophilicity, gas barrier properties, and thermal stability of the composites will be significantly improved. Based on their unique properties, the composite can be applied in packaging, bionanomaterials, and so on.

## EXPERIMENTAL SECTION

### Materials

$\alpha$ -CD was supplied by Nihon Shokuhin Kako, Tokyo, Japan. PCL ( $M_n = 1.9 \times 10^5$ ,  $M_w/M_n = 1.7$ ) was purchased from Daicel Chemical, Tokyo, Japan, and it was purified by the precipitation of chloroform solution into ethanol.

### Preparation of PCLIC

PCLIC samples were prepared by solution mixing of PCL and  $\alpha$ -CD as shown in Table I. The samples coded as PCLIC2, PCLIC4, and PCLIC7, where the numerals denote the approximate molar ratio of monomeric repeat unit of PCL to  $\alpha$ -CD molecule for PCLICs estimated by using  $^1\text{H}$  NMR spectra. To prepare PCLICs, the  $\alpha$ -CD aqueous solution was added slowly into the PCL acetone solution under vigorous stirring at 60°C for 3 h. Subsequently, the mixed solution was cooled to 25°C and continuously stirred for another 24 h. As-produced white powder was collected by filtration and then washed with acetone and water to remove the free PCL and uncomplexed  $\alpha$ -CD, respectively. Then, the final product was dried under vacuum at 60°C for 1 week.

### Preparation of PCL/PCLIC and PCL/ $\alpha$ -CD composites

The PCLICs were used as the additives to enhance the crystallization of PCL. As the particle size of the nucleating agents affects their nucleating abilities, the particle size was reduced by shattering the par-

ticles by ultrasonic disruptor (UR-200P; Tomy Seiko, Tokyo, Japan) in the suspension of acetone for 5 min at 25°C. The mixtures of PCL and PCLIC were prepared by admixing additives into a concentrated acetone solution of polymer (0.1 g/mL). The ratios of the components in the composites are listed in Table II. The solvent was then allowed to evaporate during rigorous stirring. The samples were dried at 25°C under vacuum for 3 weeks before the analysis.

The samples were molded into the rectangular film with a dimension of 100 × 40 × 0.3 mm<sup>3</sup> by pressing with a constant pressure of 10 MPa at 120°C for 3 min, and then they were aged at room temperature for 2 weeks. In the sample name, for an example, the PCL/PCLIC7-05, "05" denote the 5 wt % of  $\alpha$ -CD in the PCL/PCLIC7 composite. We also carried out the similar procedures to prepare the PCL/ $\alpha$ -CD-05 composite film.

### Measurements

#### WAXD

The wide-angle X-ray diffraction (WAXD) pattern of the sample was recorded on a Rigaku RU-200 (Rigaku, Tokyo, Japan) using Nickel-filtered Cu K $\alpha$  radiation (40 kV, 200 mA) with 2 $\theta$  ranging from 5° to 35° at a scanning rate of 3°/min.

#### $^1\text{H}$ NMR

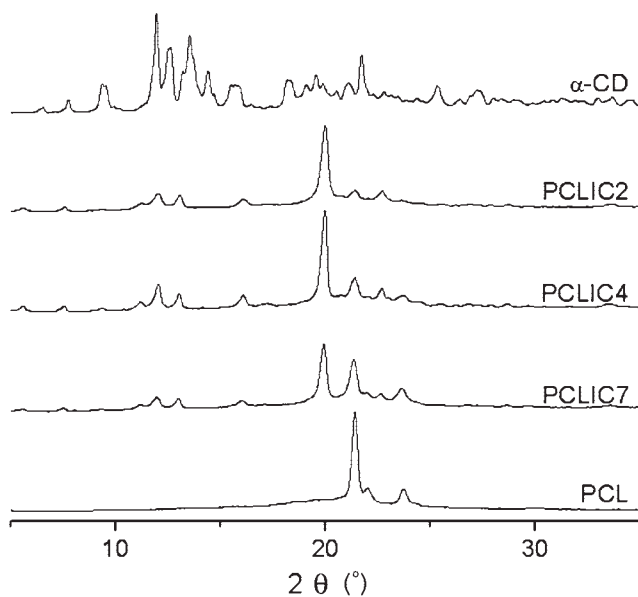
Solution  $^1\text{H}$  NMR spectra were recorded on a JEOL GSX270 NMR spectrometer (JEOL, Tokyo, Japan) in DMSO-*d*<sub>6</sub> at 80°C. The chemical shifts of the complexes were referenced to the DMSO-*d*<sub>6</sub> residual proton resonance as  $\delta = 2.5$  ppm from that of tetramethylsilane.

#### DSC

The differential scanning calorimeter Pyris Diamond DSC (Perkin-Elmer Japan, Yokohama, Japan) was used to detect the thermal transitions and also to

**TABLE II**  
**Preparation of PCL Composite Samples**

Sample	Weight percentage of composition in composite (wt %)		Weight of composition in composite (mg)	
	$\alpha$ -CD	PCLIC	PCL	PCLIC
PCL	–	–	2,000	0
PCL/ $\alpha$ -CD-05	5	–	1,900	100
PCL/PCLIC2-05	5	6.4	1,872	128
PCL/PCLIC4-05	5	12.5	1,750	250
PCL/PCLIC7-02	2	5.7	1,887	113
PCL/PCLIC7-05	5	14.2	1,717	283
PCL/PCLIC7-10	10	28.3	1,433	567
PCL/PCLIC7-15	15	42.5	1,150	850



**Figure 1** WAXD patterns of  $\alpha$ -CD, PCL, and their ICs.

monitor the rate of heat flow during nonisothermal crystallization of the sample from the molten state. In this measurement, the sample (about 8 mg) was presealed into an aluminum pan and heated from 0 to 100°C, holding for 5 min, and then cooled to 0°C at a rate of 10°C/min. Subsequently, the sample was heated to 100°C.

#### DMTA

DMTA was made on a DMS210 (Seiko Instrument, Tokyo Japan) under the tensile mode. Each test sample was 20-mm long, 10-mm wide, and ca. 0.3-mm thick. The measurement was carried out at 1 Hz at a thermal scanning rate of 2°C/min, and the temperature ranged from -100 to 100°C.

#### Tensile test

Measurement of mechanical properties of the specimen was performed at room temperature with an EZ Tester (Shimadzu, Tokyo, Japan) at a crosshead speed of 3 mm/min. All samples were cut from the sheets and shaped into dogbone-type bars (ca. 0.3-mm thickness, 4.76-mm width, and 22.25-mm length). Each value of mechanical properties reported was an average of five specimens.

## RESULT AND DISCUSSION

### Characterization of PCLIC

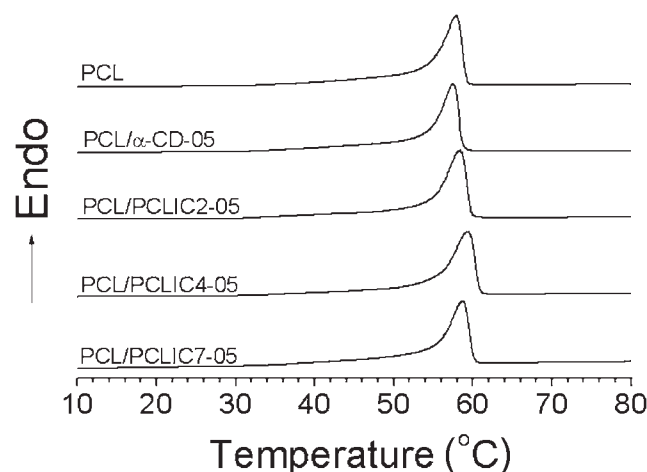
The formation of PCLIC is characterized by  $^1\text{H}$  NMR and WAXD. The host-guest stoichiometry of PCLIC is estimated by  $^1\text{H}$  NMR, and the results are shown in Table I. The ratio of the intensity of the  $\text{CH}_2$  (PCL) res-

onance at 3.98 ppm to that of the CH ( $\alpha$ -CD) one at 4.80 ppm is the corresponding molar ratio of the PCL monomeric repeat unit to  $\alpha$ -CD molecule, and it is calculated to be 2.4 : 1, 4.1 : 1, and 7.1 : 1 for the PCLIC2, PCLIC4, and PCLIC7, respectively. These results indicate that the polymer chains are partially covered by the cavities of  $\alpha$ -CD molecules in the PCLICs. The yield increases with the increasing amount of  $\alpha$ -CD/water solution, whereas the  $\alpha$ -CD content in the PCLIC decreases with the increasing amount of  $\alpha$ -CD/water solution. This result may be attributable to the decrease of PCLIC's solubility in the acetone/water solution with an increase in the water content.

Figure 1 shows the WAXD patterns of PCLICs, which are quite different from those of pure PCL and  $\alpha$ -CD, strongly supporting the IC formation between PCL and  $\alpha$ -CD. The crystalline PCL shows three prominent diffraction peaks at 21.4°, 22.0°, and 23.7°. However, two prominent peaks can be observed for each PCLIC at about 20.0° and 22.5°, which are well known to be the characteristics of  $\alpha$ -CD-based IC crystals adopting the channel structure.<sup>21-24,43-46</sup> It is obviously shown that the characteristic peaks of crystalline PCL were also observed in the WAXD patterns of PCLICs, and the relative intensity of the peak corresponding to the crystalline phase of PCL increases with decreasing the  $\alpha$ -CD content. It is indicated that there is still a PCL crystalline region outside the  $\alpha$ -CD cavity even after IC formation.

### Thermal and dynamic mechanical properties

The DSC analysis is performed to study the influences of  $\alpha$ -CD and PCLICs on the crystallization of PCL. Figure 2 shows the DSC traces of pure PCL and PCL blended with  $\alpha$ -CD and PCLICs recorded during the first heating scan, and their results are summarized in Table III. Here, the  $\alpha$ -CD content is



**Figure 2** DSC first heating-scan thermograms of PCL/ $\alpha$ -CD and PCL/PCLIC composites.

**TABLE III**  
Results of DSC First Heating and Cooling Scans for PCL, PCL/ $\alpha$ -CD, and PCL/PCLIC Composites

Sample	First heating scan		Cooling scan	
	$T_m$ ( $^{\circ}$ C)	$\Delta H_m$ for PCL (J/g) (30–70 $^{\circ}$ C) <sup>a</sup>	$T_c$ ( $^{\circ}$ C)	$\Delta H_c$ for PCL (J/g) (10–50 $^{\circ}$ C) <sup>a</sup>
PCL	57.9	75.2	22.3	–54.0
PCL/ $\alpha$ -CD-05	57.4	73.4	30.4	–52.9
PCL/PCLIC2-05	58.4	77.8	33.3	–57.3
PCL/PCLIC4-05	59.3	75.8	34.7	–53.2
PCL/PCLIC7-02	58.7	75.6	33.9	–51.9
PCL/PCLIC7-05	58.6	71.3	35.3	–52.8
PCL/PCLIC7-10	58.8	66.7	36.3	–49.3
PCL/PCLIC7-15	58.7	67.2	36.4	–41.4

<sup>a</sup> The temperature range used for determining the  $\Delta H_m$  and  $\Delta H_c$ .

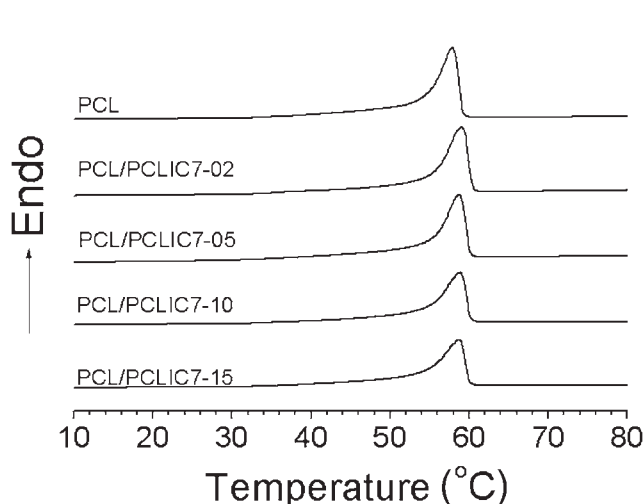
the same for all the composites, that is, 5 wt %. The  $T_m$  value of PCL in the PCL/ $\alpha$ -CD-05 composite are almost the same as that of pure PCL. After an addition of PCLIC, the  $T_m$  of PCL increases from 57.9 $^{\circ}$ C to over 58.4 $^{\circ}$ C. These results may be due to the improved perfectness of the PCL crystals with the addition of PCLICs. The fusion enthalpy,  $\Delta H_m$ , of PCL is not very sensitive to the addition of the same amount of  $\alpha$ -CD. Figure 3 shows the DSC traces of the PCL/PCLIC7 blends with various PCLIC7 contents recorded during the first heating scan. The  $T_m$  values of the PCL component in the blends are higher than that of pure PCL; however, the  $\Delta H_m$  of PCL in the blends is slightly decreased with the increase of the PCLIC7 content.

Figure 4 shows the nonisothermal crystallization behavior of PCL and PCL blended with  $\alpha$ -CD and PCLICs observed at cooling rate 10 $^{\circ}$ C/min. The DSC thermograms of these samples reveal the nucleating ability of PCLICs, as indicated by the shifts of peak

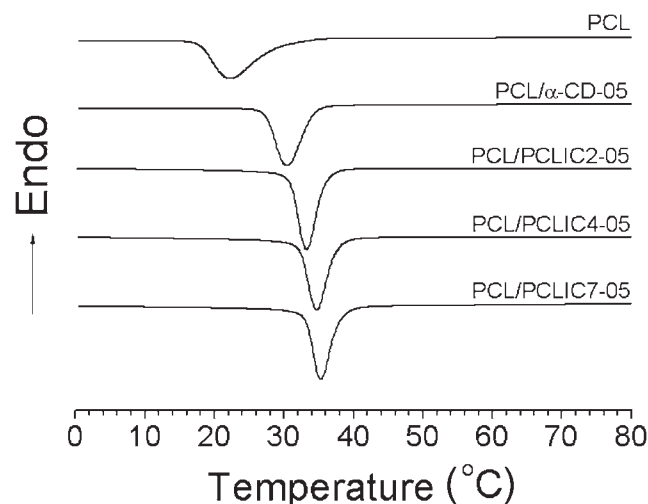
temperature of crystallization  $T_c$ , that is, the composites showed higher  $T_c$  and a narrower crystallization peak than the pure PCL. The values of  $T_c$  and corresponding crystallization enthalpies ( $\Delta H_c$ s) of PCL measured during the cooling scans are summarized in Table III. The  $T_c$  value of pure PCL is 22.3 $^{\circ}$ C, and the crystallization proceeds in a broad temperature range. After the addition of  $\alpha$ -CD, the  $T_c$  value of PCL increased from 22.3 to 30.4 $^{\circ}$ C. However, all PCLICs induce the increase in the  $T_c$  value of PCL above this temperature. Among the PCLICs, the most effective nucleating agent is PCLIC7, which increases the  $T_c$  of PCL from 22.3 to 35.3 $^{\circ}$ C. These results agree well with those in our previous studies<sup>15–20</sup> that the  $\alpha$ -CD in the complex state is more effective for promoting the crystallization of polymer than the free-state  $\alpha$ -CD.

Figure 5 shows the nonisothermal crystallization behavior of PCL and PCL/PCLIC7 composites. The  $T_c$  of PCL component in the composites increased with the increase of PCLIC7 content. The most significant nucleating effect is observed for the PCL/PCLIC7-15 composite, in which PCL crystallized in the most narrow temperature range and showed the highest  $T_c$  value, 36.4 $^{\circ}$ C. It is 14.1 $^{\circ}$ C higher than that of pure PCL. These results indicate that PCLIC7 greatly enhances the crystallization of PCL.

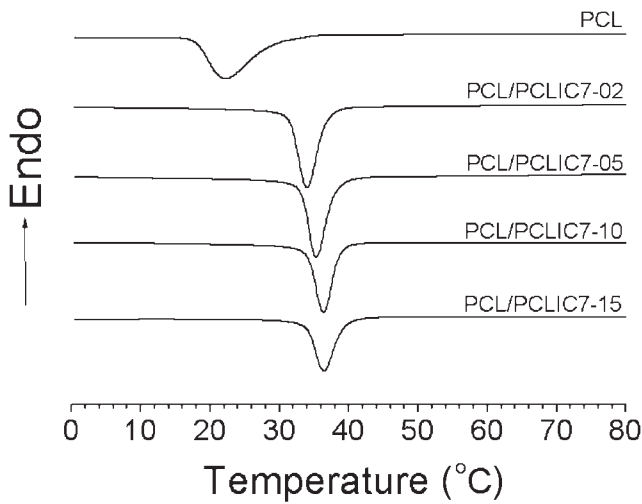
Figure 6 depicts the dynamic mechanical spectra of pure PCL, PCL/ $\alpha$ -CD-05, PCL/PCLIC7-05, and PCL/PCLIC7-15. As seen in Figure 6(a), for each system, with increasing temperature, the storage modulus ( $E'$ ) varied very little in the first section of the curve (the first plateau zone). Then, a sharp decrease is observed, which is attributable to the change in the segmental mobility related to the glass transition. After a second plateau zone, the value of  $E'$  decreased drastically again because of the melting of the crystalline phase.



**Figure 3** DSC first heating-scan thermograms of PCL and PCL/PCLIC7 composites.

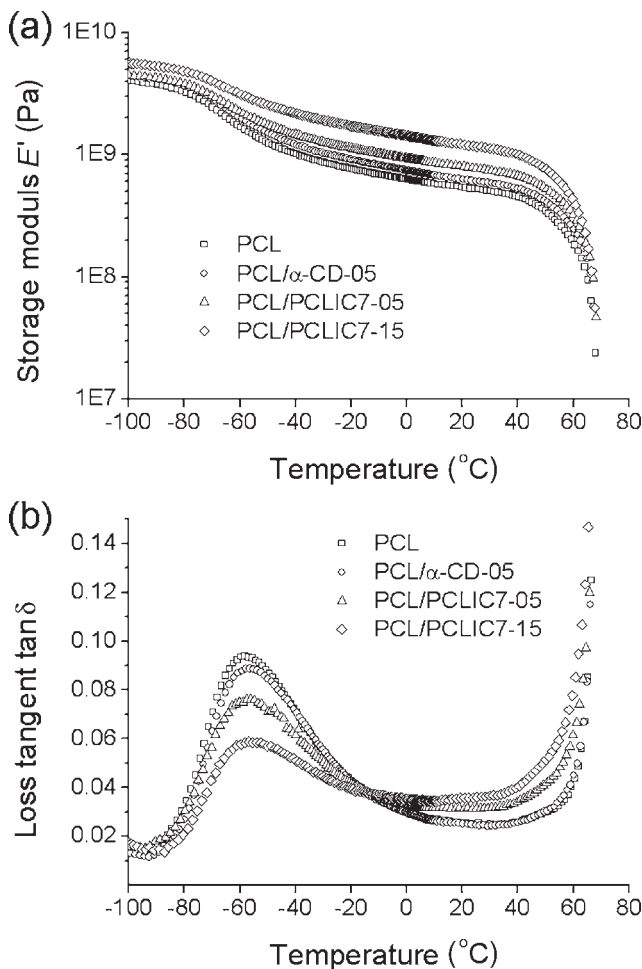


**Figure 4** DSC cooling-scan thermograms of PCL/ $\alpha$ -CD and PCL/PCLIC composites.



**Figure 5** DSC cooling-scan thermograms of PCL and PCL/PCLIC7 composites.

Comparing the storage modulus of pure PCL with those of the PCL composite samples, it is clear that in the first and the second plateau zone, the storage

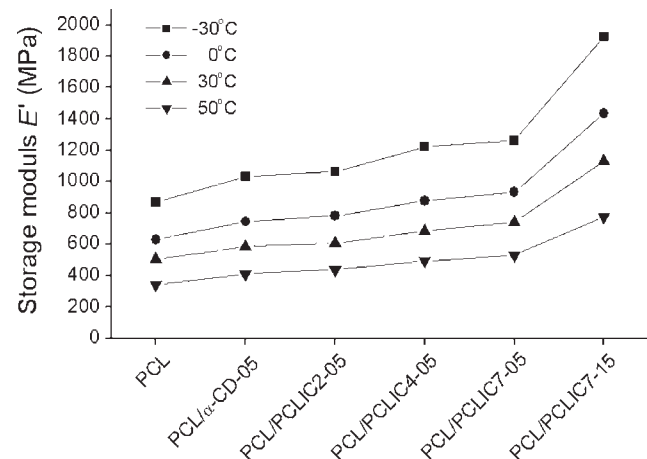


**Figure 6** Temperature dependence of (a) storage modulus ( $E'$ ) and (b) loss tangent ( $\tan \delta$ ) of PCL samples.

modulus of the composite is higher than that of pure PCL. The values of the storage modulus,  $E'$ , for pure PCL and PCL composites at  $-30$ ,  $0$ ,  $30$ , and  $50^\circ\text{C}$ , as the representative values, are shown in Figure 7. It is obvious that the  $E'$  value of PCL increased with the increase of the  $\alpha$ -CD content, and the  $E'$  of PCL increased with the PCLIC content at a certain  $\alpha$ -CD contents.

Figure 6(b) displays the loss tangent ( $\tan \delta$ ) of pure PCL and its composites. In the lower temperature region, a more intense peak due to the  $\alpha$ -transition appears at about  $-60^\circ\text{C}$  for PCL. This peak is associated with the main glass transition in the amorphous domains of PCL. Another strong dissipation corresponding to the melting of the PCL crystalline phase occurs, where the steep drop in the elastic modulus is distinct. For the PCL composite samples, the  $\alpha$ -transition peak becomes broader than that of PCL and it slightly shifts to the higher temperature region, indicating that the glass transition temperature of PCL in its composite samples increases. The intensity of  $\alpha$ -transition peak is slightly reduced for the PCL/ $\alpha$ -CD-05 composite, whereas it decreases significantly for the PCL/PCLIC7-05 composite. The intensity of the  $\alpha$ -transition peak of the PCL/PCLIC7-15 composite is greatly reduced and became very broad.

These results clearly show that the incorporation of PCLIC into the PCL matrix results in a remarkable increase in stiffness and a decrease in  $\tan \delta$ . For all PCL/PCLIC composites, the enhancement of  $E'$  can be seen over the investigated temperature range when compared with pure PCL, indicating that the addition of PCLIC induces a reinforcement effect. In fact, the composites of PCL with PCLICs are the composites of PCL with  $\alpha$ -CD. However, in the PCL/PCLIC composites, the  $\alpha$ -CDs are threaded on the PCL chains and they aggregated to form the channel columns. The aggregations of  $\alpha$ -CD act as



**Figure 7** Dynamic mechanical properties of PCL, PCL/ $\alpha$ -CD, and PCL/PCLIC composites.

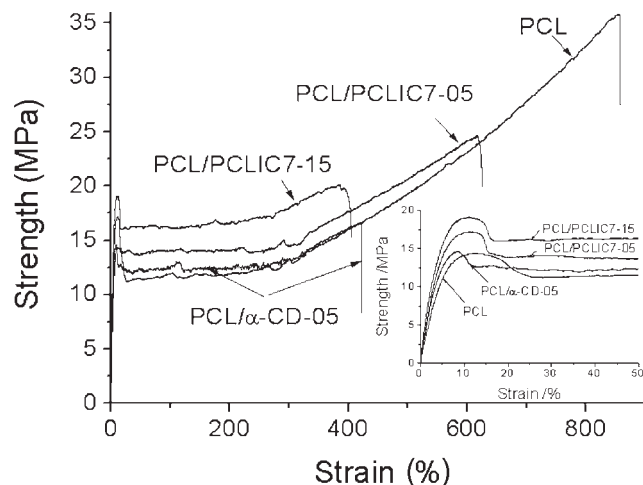
hard domains, resulting in the increase of storage modulus and glass transition temperature of the PCL.

### Mechanical properties

Mechanical properties of PCL and its composites, such as elongation at break ( $\epsilon_b$ ), Young's modulus ( $E$ ), and yield strength ( $\sigma_y$ ), of all the samples are evaluated from the stress-strain curves. The representative stress-strain curves are shown in Figure 8, and the results are summarized in Table IV.

As shown in Figure 8, PCL is able to undergo large deformation with significantly large elongation at break, but it showed relatively low  $E$  and  $\sigma_y$  values. The  $E$  and  $\sigma_y$  values of PCL/PCLIC7-15 are improved to about 2 and 1.3 times of those of pure PCL, respectively. Furthermore, its elongation at break is still above 350%. So, the addition of PCLIC7 greatly increased the Young's modulus and yield strength of PCL, whereas the addition of PCLIC7 did not much hamper its elongation.

The  $E$  and  $\sigma_y$  values of PCL are slightly increased by an addition of pure  $\alpha$ -CD. It is clear that the value of  $\epsilon_b$  of PCL/ $\alpha$ -CD-05 is much lower than that of PCL/PCLIC7-05, and the yield deformation of PCL/ $\alpha$ -CD-05 is also much smaller than that of pure PCL and PCL/PCLIC7-15. The values of  $E$  and  $\sigma_y$  of composites increased with the increase of PCLIC contents, when the weight percentage of  $\alpha$ -CD component is 5 wt %. The  $\epsilon_b$  values of the composites decreased with the increase of PCLIC contents. Also, it is seen that with the addition of PCLIC7, the PCL kept the larger deformation, and the values of  $E'$  and  $\sigma_y$  of PCL greatly increased with the increase of PCLIC7 content, although the crystallinity of PCL is slightly decreased. The structural analysis indicates that the PCLIC is a rodlike rigid molecule, forming



**Figure 8** Strain-stress curves of PCL, PCL/ $\alpha$ -CD, and PCL/PCLIC composites.

**TABLE IV**  
Results of Tensile Tests for PCL and PCL Composites

Sample	Young's modulus /MPa	Yield stress /MPa	Elongation at break /%
PCL	246 $\pm$ 5	14.49 $\pm$ 0.20	955 $\pm$ 79
PCL/ $\alpha$ -CD-05	306 $\pm$ 4	14.64 $\pm$ 0.05	544 $\pm$ 90
PCL/PCLIC2-05	281 $\pm$ 12	16.05 $\pm$ 0.05	802 $\pm$ 50
PCL/PCLIC4-05	312 $\pm$ 17	16.76 $\pm$ 0.18	709 $\pm$ 21
PCL/PCLIC7-02	300 $\pm$ 9	16.30 $\pm$ 0.12	638 $\pm$ 88
PCL/PCLIC7-05	323 $\pm$ 11	17.23 $\pm$ 0.05	565 $\pm$ 84
PCL/PCLIC7-10	451 $\pm$ 14	18.47 $\pm$ 0.16	380 $\pm$ 70
PCL/PCLIC7-15	486 $\pm$ 18	19.80 $\pm$ 0.13	390 $\pm$ 35

linear channel of several hundred to thousand nanometers length. The long polymer chains are found to be partially included inside the  $\alpha$ -CD cavities, and the uncovered parts of PCL are still crystallizable. The uncovered parts of PCL may crystallize with PCL matrix together in the molding process. It is possible that the PCLIC and polymer matrix are in good adhesion, which leads to better stress transfer between the matrix and the reinforcing fillers.

### CONCLUSION

Compared with PCL and pure  $\alpha$ -CD, the biodegradable composites of PCL and  $\alpha$ -CD in the state of complex give excellent thermal and mechanical properties. The physical properties of the PCL/PCLIC composites are different from those of PCL/ $\alpha$ -CD composite. In the PCL/PCLIC composite,  $\alpha$ -CDs are threaded on the PCL chains and they aggregated to form the channel columns. The threaded  $\alpha$ -CDs act as the hard domains for the PCL/PCLIC composites, resulting in the increase of storage modulus and glass transition temperature of bulk PCL. It is thought that the PCLIC is a good enforcing filler for the PCL.

### References

- Mohanty, A. K.; Misra, M.; Drzal, L. T. *J Polym Environ* 2002, 10, 19.
- Mohanty, A. K.; Misra, M.; Hinrichsen, G. *Macromol Mater Eng* 2000, 276, 1.
- Huda, M. S.; Mohanty, A. K.; Drzal, L. T.; Schut, E.; Misra, M. *J Mater Sci* 2005, 40, 4221.
- Withey, R. E.; Hay, J. N. *Polymer* 1999, 40, 5147.
- Black, S. N.; Dobbs, B.; Dempsey, P. S.; Davey, R. J. *J Mater Sci Lett* 1990, 9, 51.
- Ke, T.; Sun, X. *J Appl Polym Sci* 2003, 89, 1203.
- Ohkita, T.; Lee, S.-H. *J Appl Polym Sci* 2005, 97, 1107.
- Lai, S.-M.; Huang, C.-K.; Shen, H.-F. *J Appl Polym Sci* 2005, 97, 257.
- Pan, P.; Zhu, B.; Dong, T.; Serizawa, S.; Iji, M.; Inoue, Y. *J Appl Polym Sci* 2008, 107, 3512.
- Pan, P.; Zhu, B.; Kai, W.; Serizawa, S.; Iji, M.; Inoue, Y. *J Appl Polym Sci* 2007, 105, 1511.
- Bender, M. L.; Komiyama, M. *Cyclodextrin Chemistry*; Springer-Verlag: Berlin, 1978.

12. Szejtli, J. Cyclodextrins and Their Inclusion Complexes; Akademiai Kiado: Budapest, 1982.
13. Inoue, Y. *Ann Rep NMR Spectrosc* 1993, 27, 59.
14. Davis, M. E.; Brewster, M. E. *Nat Rev* 2004, 3, 1023.
15. He, Y.; Inoue, Y. *Biomacromolecules* 2003, 4, 1865.
16. He, Y.; Inoue, Y. *J Polym Sci Part B: Polym Phys* 2004, 42, 3461.
17. Dong, T.; He, Y.; Zhu, B.; Shin, K.; Inoue, Y. *Macromolecules* 2005, 38, 7736.
18. Dong, T.; Shin, K.; Zhu, B.; Inoue, Y. *Macromolecules* 2006, 39, 2427.
19. Dong, T.; Kai, W.; Pan, P.; Cao, A.; Inoue, Y. *Macromolecules* 2007, 40, 7244.
20. Dong, T.; Kai, W.; Inoue, Y. *Macromolecules* 2007, 40, 8285.
21. Harada, A.; Kamach, M. *Macromolecules* 1990, 23, 2821.
22. Harada, A.; Li, J.; Kamachi, M. *Nature* 1992, 356, 325.
23. Harada, A.; Nishiyama, T.; Kawaguchi, Y.; Okada, M.; Kamachi, M. *Macromolecules* 1997, 30, 7115.
24. Harada, A.; Okada, M.; Kawaguchi, Y. *Chem Lett* 2005, 34, 542.
25. Rusa, C. C.; Tonelli, A. E. *Macromolecules* 2000, 33, 5321.
26. Shuai, X.; Porbeni, F. E.; Wei, M.; Shin, I. D.; Tonelli, A. E. *Macromolecules* 2001, 34, 7355.
27. Rusa, C. C.; Wei, M.; Shuai, X.; Bullions, T. A.; Wang, X.; Rusa, M.; Uyar, T.; Tonelli, A. E. *J Polym Sci Part B: Polym Phys* 2004, 42, 4207.
28. Shuai, X.; Porbeni, F. E.; Wei, M.; Bullions, T.; Tonelli, A. E. *Macromolecules* 2002, 35, 3126.
29. Jia, X.; Wang, X.; Tonelli, A. E.; White, J. L. *Macromolecules* 2005, 38, 2775.
30. Shuai, X.; Wei, M.; Porbeni, F. E.; Bullions, T. A.; Tonelli, A. E. *Biomacromolecules* 2002, 3, 201.
31. Wei, M.; Shuai, X.; Tonelli, A. E. *Biomacromolecules* 2003, 4, 783.
32. Shuai, X.; Porbeni, F. E.; Wei, M.; Bullions, T.; Tonelli, A. E. *Macromolecules* 2002, 35, 2401.
33. Wei, M.; Davis, W.; Urban, B.; Song, Y.; Porbeni, F. E.; Wang, X.; White, J. L.; Balik, C. M.; Rusa, C. C.; Fox, J.; Tonelli, A. E. *Macromolecules* 2002, 35, 8039.
34. Rusa, C. C.; Wei, M.; Bullions, T. A.; Rusa, M.; Gomez, M. A.; Porbeni, F. E.; Wang, X.; Shin, I. D.; Balik, C. M.; White, J. L.; Tonelli, A. E. *Cryst Growth Des* 2004, 4, 1431.
35. Rusa, M.; Wang, X.; Tonelli, A. E. *Macromolecules* 2004, 37, 6898.
36. Rusa, C. C.; Rusa, M.; Gomez, M.; Shin, I. D.; Fox, J. D.; Tonelli, A. E. *Macromolecules* 2004, 37, 7992.
37. Martinez, G.; Gomez, M. A.; Villar-Rodil, S.; Garrido, L.; Tonelli, A. E.; Balik, C. M. *J Polym Sci Part A: Polym Chem* 2007, 45, 2503.
38. Vedula, J.; Tonelli, A. E. *J Polym Sci Part B: Polym Phys* 2007, 45, 735.
39. Vogel, R.; Tändler, B.; Häussler, L.; Jehnichen, D.; Brünig, H. *Macromol Biosci* 2006, 6, 730.
40. Wang, X. S.; Kim, H. K.; Fujita, Y.; Sudo, A.; Nishida, H.; Endo, T. *Macromolecules* 2006, 39, 1046.
41. Araki, J.; Ito, K. *Soft Matter* 2007, 3, 1456.
42. Araki, J.; Kataoka, T.; Katsuyama, N.; Teramoto, A.; Ito, K.; Abe, K. *Polymer* 2006, 47, 8241.
43. Huang, L.; Allen, E.; Tonelli, A. E. *Polymer* 1998, 39, 4857.
44. Dong, T.; He, Y.; Shin, K.; Inoue, Y. *Macromol Biosci* 2004, 4, 1084.
45. McMullan, R. K.; Saenger, W.; Fayos, J.; Mootz, D. *Carbohydr Res* 1973, 31, 37.
46. Takeo, K.; Kuge, T. *Agric Biol Chem* 1970, 34, 1787.