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β-Cyclodextrin과 Polylactic Acid간의 포접화합물 제조 및 특성 분석

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Preparation and Characterization of Inclusion Complex between β-Cyclodextrin and Polylactic Acid

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Abstract: The inclusion complexes (ICs) between polylactic acid (PLA) and β-cyclodextrin (CD) were prepared by co-precipitation method in this work. The orthogonal experiments were designed to investigate the influence of different factors on the formation of inclusion complexes. The results suggested that the optimum scheme of inclusion compounds could be obtained when the feeding ratio of CD to PLA (wt%) was 20:1, stirring speed was 6 kr/min and the stirring time was 30 min. The structures and properties of the inclusion complexes were characterized by ^{1}H NMR, FTIR, DSC, FT-Raman, XRD and TGA. The DSC results demonstrated that the crystallization behavior of the inclusion complexes nearly disappeared. It was found that β-CD-PLA inclusion complex had a better thermal stability compared with the neat PLA. The model of the inclusion complexes was proposed on the basis of XRD, ^{1}H NMR and DSC results.

Keywords: β-cyclodextrin, polylactic acid, co-precipitation method, inclusion complex, properties.

Introduction

In the recent years, polymer inclusion complexes with cyclodextrins have received much attention due to some properties such as crystallization performance,[1] degradation,[2] thermal-stability property[3] and have exhibited potential applications in bio-pharmaceutical industry such as tissue engineering,[4] drug controlled release carrier,[5] and functional polymer based composite materials.[6]

Cyclodextrins are a series of cyclic oligosaccharides containing 6, 7, or 8 D (+)-glucose unites linked by α-1, 4-linkages, namely α-, β-, and γ-CD respectively. CD molecule possesses a unique structure like truncated cone including hydrophilic outer surface and hydrophobic cavity with the capacity to accommodate different guest molecules.[1-3,5,6] In aqueous solution, the slightly apolar CD cavity is occupied by energetically unfavored water moleculars which are easily replaced by appropriate guest molecules with less polar.[7] The guests may be hydrophilic or hydrophobic small molecules and polymer macromolecules, which can form inclusion complexes with cyclodextrins. Since Harada *et al*.[8] reported linear polyethylene glycol with different molecular weights could form necklace-like inclusion complexes with α-CD named polypseudorotaxanes in 1990, many cyclodextrin inclusion complexes with polymers have been prepared in the past decades. Tallury *et al*.[9] discovered conductive polymers such as polyanilines (PANI) could form the "host-guest" inclusion structures with β-cyclodextrins, and studied the interactions between polyanilines and β-cyclodextrins in their inclusion complexes via molecular dynamics simulations; Sajadi Tabassi *et al*.[10] prepared the inclusion complexes of the water-soluble triblock copolymer PCL-PEG-PCL with α-CD; Semsarzadeh[11] also produced an inclusion complex between PDMS and γ-CD at room temperature in the presence of light and in the absence of mixing. As is known, the formation of ICs between CD and guest molecules such as monomer or polymer chains mainly depends on the van der Waals forces, hydrophobic interactions,

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and hydrogen bonding between CD rings. Moreover, if polymer chains are encapsulated in the hydrophobic cavities of cyclodextrins with good crystallization, it is supposed that the host-guest interactions between them may change the crystallization performance, degradation and thermodynamics properties of polymers.

Polylactic acid (PLA) is a synthetic biodegradable polyester, and exhibits excellent biocompatibility and bioresorbability, thus represents potentials in many aspects such as orthopedics, drug delivery and scaffolds and so on.[12-14] However, PLA based materials always have few bioactive functional groups, which greatly restrict its applications in high performance composite material and sophisticated engineering industries. The introduction of good water-soluble cyclodextrins (CDs) threaded on polymer chains could not only improve the hydrophilcity of polymer surface, but also show some effect on its crystallization, degradation and thermostability performances. He *et al*.[15] observed the PEO side chains are confined in the α-CD channels and their original crystallization properties are lost owing to the formation of inclusion complexation in the research of α-CD inclusion interaction with comblike PEO grafted polymers. Dong *et al*.[16] similarly found that the formation of α-cyclodextrin inclusion complexes would contribute to the enhancement of crystallization for several semicrystalline aliphatic polymers such as PEG, PBS and PCL. Li *et al*.[17] also discovered the inclusion complexes between PCL-PTHF-PCL triblock copolymer and cyclodextrins including α-CD, β-CD and γ-CD showed better thermal stability than their free components. To our best knowledge, although the PLA based composite materials with cyclodextrins were reported by other groups before, however the comprehensive and detailed studies on microstructures and performance of CD inclusion complexes with PLA had been rarely given so far.[18,19] In this work, the β-CD-PLA inclusion complexes were successfully prepared. Then, the microstructures and the properties of ICs were investigated by ^{1}H NMR, XRD, TGA and DSC. Finally, the proposed inclusion model of the composite was given based on stoichiometric analysis. These results would provide meaningful information on how to effectively control the actual inclusion ratios between cyclodextrin and PLA to improve the crystallization properties.

Experimental

Materials. β-cyclodextrin, analytically pure, was purchased from Tianjin Guangfu Fine Chemical Industry Research Institute (China); L-Lactic acid monomer (85-90 wt%) was obtained from Tianjin Chemical Reagent Factory Co., LTD (China); Stannous(II) octoate ($SnOct_2$) was purchased from Aldrich. Normal analytical pure chloroform, methanol and ethanol were used without further purification.

Preparation of PLA. A certain amount of latic acid was added into a round flask equipped with a magnetic stirrer, then the flask was heated and evacuated. The dehydration process followed in all cases (80 ºC, 16 kPa, 4 h). Followed by this step, 0.5 wt% of $SnOct_2$ (the amount was based on the initial addition of LA) was added dropwise in the flask, and then the reaction temperature was increased to 170 ºC and held for 10 h. The mixture was cooled to room temperature and the products were purified by precipitation from chloroform with methanol. Finally, the powder was dried at 55 ºC in a vacuum oven for 48 h.

Preparation of Inclusion Complexes. A general procedure of preparation of β-CD inclusion complexes with PLA (β-CD-PLA ICs) was as follows: PLA were dissolved in chloroform, the PLA solution was dropwise added into the β-CD saturated aqueous solution with strongly stirring at room temperature for predetermined intervals, and the mixture turned turbid. Then the solution was allowed to stand for 48 h. The precipitate was collected by filtration and washed by $CHCl_3$/heat distilled water three times to remove uncovered PLA and free β-CD, respectively. The products were dried at 50 ºC for 48 h.

Characterization. Fourier transform infrared spectra were performed using Nicolet 380 spectrometer (USA). The spectra were collected from 4000 to 400 cm^{-1} with a resolution of 4 cm^{-1} over 32 scans. All the samples were dried in vacuum oven at 60 ºC for 24 h before testing.

^{1}H NMR spectra were recorded on INOVA 400 MHz spectrometer (VARIAN, Co., LTD, USA) in the solvent DMSO-d_6 at room temperature.

GPC measurements were performed to determine molecular weight using Agilent-1100 (US) HPLC system equipped with a TSK gel Super HZM-M column and THF as solvent at 40 ºC.

FT-Raman spectra were collected on Bruker Vertex 70 spectrometer (Germany) at the resolution of 4 cm^{-1} over 32 scans.

X-ray diffraction patterns were recorded with X-ray diffractometer (Philips X' Pert, Netherland), using CuK_α X-ray source at λ=0.1540 nm (50 Kv, 35 mA). Diffraction spectra were obtained over 2θ range of 5-40º with a step interval of 0.1 º/s. Samples of 5-8 mg were operated from the injection

mold. Before testing, the samples were dried to a constant weight at 55 ºC in a vacuum oven.

Thermogravimetric analysis was conducted on TA Q600 thermal-gravimetric analyzer (USA). 5 mg of samples were performed by heating from room temperature to 700 ºC at a heating speed of 10 ºC/min on the condition of a nitrogen flow.

Differential scanning calorimetry measurements were performed with NETZSH differential scanning calorimeter (DSC-204, Germany). Samples of 6 mg were performed by heating from room temperature to 200 ºC at a heating rate of 10 ºC/min under a nitrogen flow.

Results and Discussion

Characterization of PLA. The products of polymerization were characterized by ^{1}H NMR. As shown in Figure 1, the proton peak signals at 1.5 and 5.2 ppm were assigned to CH_3 and CH of PLA block, respectively, which were consistent with the reports in the literature.[20] The molecular weights of samples were determined by GPC measurements. According to GPC (Figure 2), the weight-average molecular weight (M_w) of PLA was 5390 g/mol. The PDI value was 1.341, which indicated a narrow molecular weight distribution.

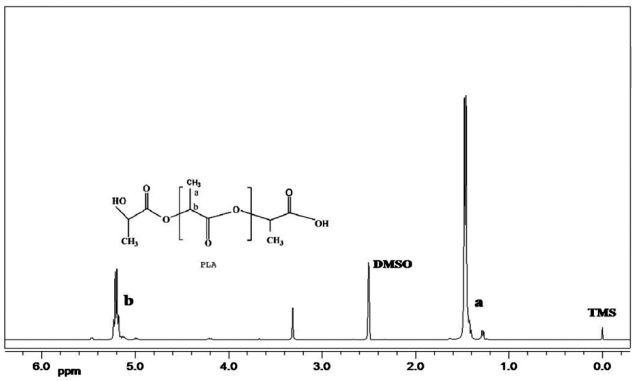

Figure 1. ^{1}H NMR spectra of the synthesized PLA.

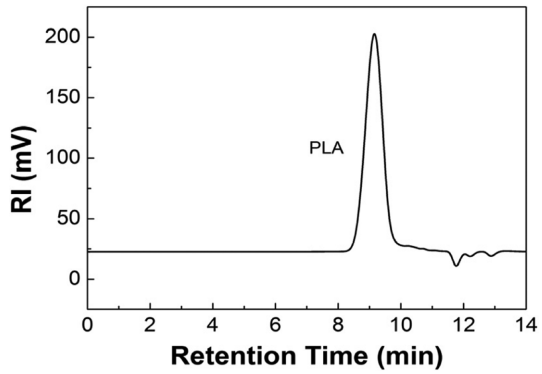

Figure 2. GPC measurement of the synthesized PLA.

Preparation of β-CD-PLA ICs. The orthogonal experiment methods were used to investigate the influences of ratios of CD to PLA, stirring time and stirring speed on the preparation of inclusion complexes. 0.10 g of PLA (M_w=5390) was used to carry out orthogonal experiments. β-CD was used with its saturated solution. Experimental factors levels were shown as Table 1. The range analysis results using the encapsulation rate as objective function were given in Table 2. The results reveled that the feeding ratio between β-CD and PLA had the greatest influence on the formation of ICs. The optimum schemes were as follows: feeding ratio 20:1, stirring speed 6 kr·min^{-1} and stirring time 30 min, respectively.

Characterization of β-CD-PLA ICs. Figure 3 illustrated the FTIR spectra of β-CD-PLA inclusion complex, pure PLA and β-CD, respectively. Seen from Figure 3(a), the characteristic absorbing peak near 1762.95 cm^{-1} corresponding to the

Table 1. Orthogonal Factor Levels of β-CD Inclusion Complexes with PLA at Room Temperature

Level	(A) Feeding ratio[a]	(B) Stirring speed (kr·min^{-1})	(C) Inclusion time (min)
1	5:1	3	10
2	10:1	6	20
3	20: 1	9	30

[a]Feeding ratio was noted as the mass ratio between β-CD and PLA.

Table 2. Orthogonal Tests and Range Analysis Results of β-CD Inclusion Complexes with PLA

Level	A	B	C	Encapsulation rate[a] (%)
1	1	1	1	4.03
2	1	2	2	9.7
3	1	3	3	7.547
4	2	1	3	9.3
5	2	2	1	9.6
6	2	3	2	9.2
7	3	1	2	9.1
8	3	2	3	12.439
9	3	3	1	9.5
K1	7.092	7.477	7.710	
K2	9.367	10.580	9.333	
K3	10.346	8.749	9.762	
R	3.251	3.103	2.052	

[a]Encapsulation rate was calculated by using the formula: ER%= (W_{ICs}–W_{PLA})/W_{PLA}; ER–encapsulation rate, W_{ICs}–mass of inclusion complexes, W_{PLA}–initial mass of PLA.

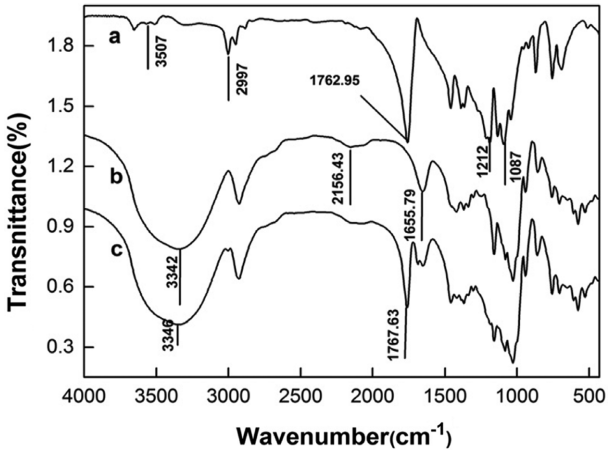

Figure 3. FTIR spectra of (a) pure PLA; (b) β-CD; (c) β-CD-PLA IC.

C=O stretching vibration, and the peak located at 3507 cm^{-1} assigned to hydroxyl group (OH) of PLA were observed; the spectral regions between 1087 and 1212 cm^{-1} were believed to the C-O-C stretching vibration.[21-23] Compared with PLA, in addition to characteristic peaks of β-CD functional groups at 3342, 1655.79 and 2156.43 cm^{-1} [24] observed in IC, the peak assigned to OH stretching vibration at 3507 cm^{-1} was almost disappeared in ICs; Meanwhile, the peak at 1767.63 cm^{-1} corresponding to the C=O stretching vibration of PLA segments, which shifted by 4.7 cm^{-1} to a higher frequency, was obviously reduced from Figure 3(c). The analysis results indicated that the hydrogen bonds had formed between the hydroxyl groups of β-CD and the carbonyl groups of PLA in the complexes or the morphological change of CDs from the cage to the channel structures might affect the strength of the CD self-association in ICs.[25,26]

Figure 4 showed the ^{1}H NMR spectra of β-CD-PLA inclusion complexes compared with PLA and β-CD. The proton peak signals at 1.5 and 5.2 ppm assigned to PLA (Figure 4(a)), 3.2~5.0 ppm (H-1, 2~6) corresponding to β-CD were obviously observed (Figure 4(b)); meanwhile, the characteristic proton peaks of PLA and β-CD in inclusion complexes were clearly discovered. This indicated that inclusion complexation between PLA and β-CD was formed.[27] The host-guest stoichiometry (i.e. CD: PLA, mol: mol) of ICs could be calculated by the integration of NMR resonances belonging to CD blocks at 4.83 ppm and to PLA blocks at 1.5 ppm.[27-29] It is known that β-CD molecule possesses the unique structure of a torus where H-3 and H-5 protons are located inside the cavity, while H-2 and H-4 are outside the torus; if β-CD can form inclusion complexes with PLA, the chemical shifts of the proton H-3 or H-5 will change at a certain extent because of the short-distance intermolecular interactions and hydrogen bond effects. From Figure 4(c), the peaks responding to H-3 and H-5 of β-CD molecular shifted slightly to a high frequency, in comparison to the spectrum line b, which also accounted for the formation of a channel-type structure in the inclusion complexes. Three β-CD-PLA inclusion complexes with different CD contents were successfully prepared (Table 3).

Table 3. Compositions of β-CD-PLA ICs and CD Contents Calculated from ^{1}H NMR

Samples	CD/PLA (mol)	CD content (wt%)
β-CD-PLA IC 1	1.749:1	31.02
β-CD-PLA IC 2	0.296:1	7.071
β-CD-PLA IC 3	0.523:1	11.38

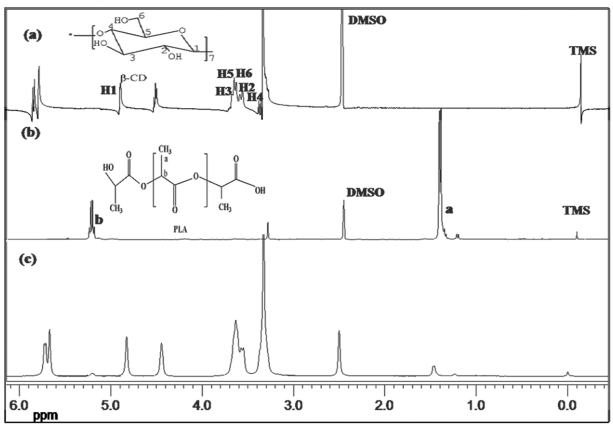

Figure 4. ^{1}H NMR spectra of (a) β-CD; (b) PLA; (c) β-CD-PLA IC in DMSO-d_6.

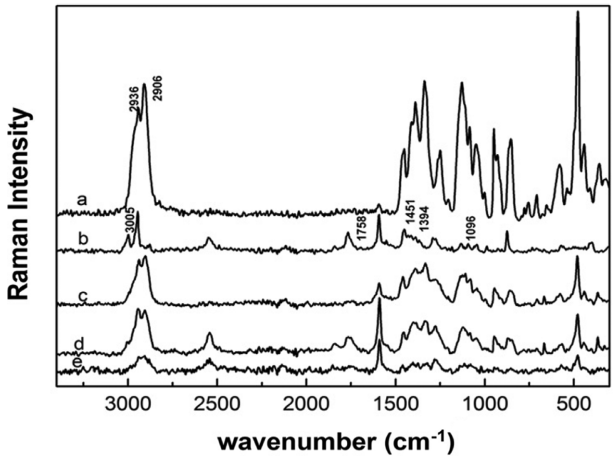

Figure 5. FT-Raman spectra of (a) β-CD; (b) PLA; (c) β-CD-PLA IC 1; (d) β-CD-PLA IC 2; (e) β-CD-PLA IC 3.

The FT-Raman spectra of (a) β-CD, (b) PLA, (c) β-CD-PLA IC 1, (d) β-CD-PLA IC 2, and (e) β-CD-PLA IC 3 was showed in Figure 5, respectively. From spectrum line of PLA, the characteristic peaks at near 3005 cm^{-1} ($\nu_{as\ CH3}$), 1758 cm^{-1} ($\nu_{C=O}$), 1293 cm^{-1} (CH in plane bending), 1096 cm^{-1} (O-C-O ester group stretching) were obviously observed. Compared with pure PLA, the asymmetric CH_3 stretching vibration bands were almost absent and meanwhile a slightly weak and broadened vibration mode of C=O at near 1760 cm^{-1} was observed in the spectrum of inclusion complexes (Figure 5(c), (d) and (e)). The findings were consistent with the relevant literatures.[30,31] With respect to β-CD, its typical absorption peaks were observed at 500-1450, 2906, and 2942 cm^{-1} in the inclusion complexes, but the overall peaks of ICs along with slightly Raman-shift to downfield were crippled, which were not also different characteristic peaks superimposed both two pure species.[32] The results indicated the hydrogen bonds developed between the host-guest molecules and PLA chains with β-CD hydrophobic cavities formed a new supramolecular structure, which were in agreement with those of the FTIR spectra.

The formation of the β-CD-PLA ICs was strongly supported by XRD. As illustrated in Figure 6, the typical diffraction peaks for pure PLA at 2θ=16.6, 19.1, 22.5, and 14.9° were clearly observed while major peaks of β-CD appeared at 6.53, 9.3, 12.7 and 23.1°, respectively which were consistent with the literatures.[33,34] It can be found that the XRD pattern of β-CD-PLA ICs is totally different from that of PLA and β-CD. Compared with pure PLA, with the content of the added β-CD increasing, the peaks of ICs were dramaticlly weaken and tightened. Meanwhile, the characteristic peaks for β-CD at 2θ=6.53 and 9.3° in the inclusion complexes were nearly not seen. The patterns of the β-CD-PLA ICs were similar to that of the inclusion complex between β-CD and PPG,[35] PDXL,[36] PDMS,[37] which had been reported to have the columnar structure. Therefore, the ICs of PLA with β-CD also likely assumed a columnar structure.

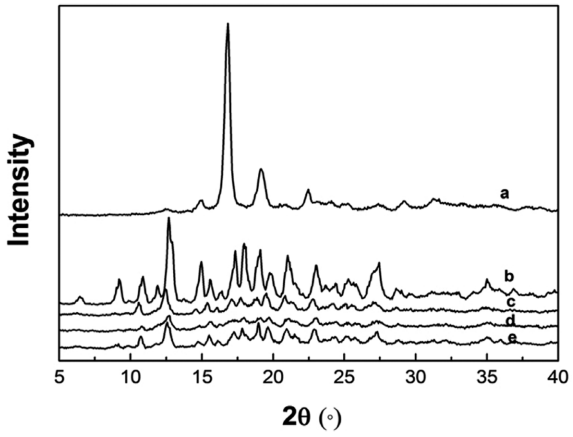

Figure 6. XRD patterns of (a) PLA; (b) β-CD; (c) β-CD-PLA IC 1; (d) β-CD-PLA IC 2; (e) β-CD-PLA IC 3.

Thermal Properties of β-CD-PLA ICs. TGA is often used to test thermal stability and to examine the residual mass of the composite at high temperature.[38,39] Referring to TGA curves of PLA, β-CD and ICs up to 700 °C in Figure 7, It was found that PLA started to decompose at 260.2 °C, while the β-CD-PLA ICs showed a higher decomposition temperature (276.4 °C) than pure PLA (260.2 °C). However, with the content of β-CD increasing, the thermal-stability of ICs would be improved and the β-CD-PLA IC1 exhibited the better thermal property compared to other inclusion complexes. Depending on the TGA curves, the contents of both PLA and β-CD in ICs and the decomposition temperature (T_d) of ICs could be also estimated, as listed in Table 4. From these data in Table 4, it could be obviously observed that the compositions of ICs determined from TGA curves were in good agreement with the results by

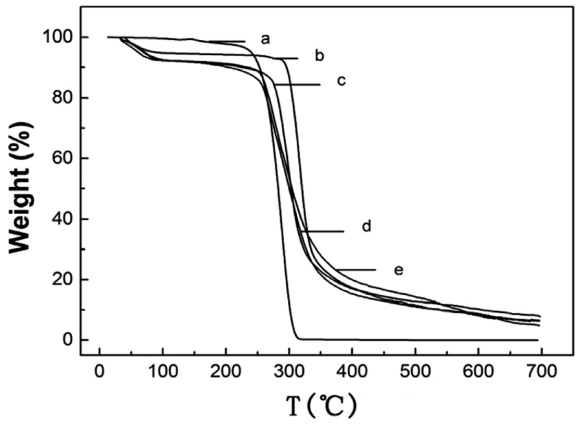

Figure 7. TGA curves of (a) PLA; (b) β-CD; (c) β-CD-PLA IC 1; (d) β-CD-PLA IC 2; (e) β-CD-PLA IC 3.

Table 4. Thermal Decomposition Temperature of β-CD-PLA Inclusion Complexes and CD Contents in ICs Determined by TGA

Samples	T_d (onset) (°C)	T_d (peak) (°C)	CD content (wt%)
PLA	260.2	285.58	-
β-CD	288.6	309.6	-
β-CD-PLA IC 1	276.4	300.32	28.14
β-CD-PLA IC 2	270.6	298.10	6.32
β-CD-PLA IC 3	271.2	296.41	11.07

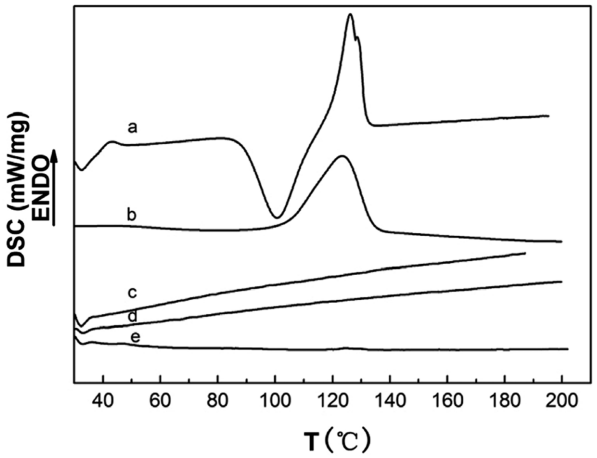

Figure 8. DSC curves of (a) PLA; (b) β-CD; (c) β-CD-PLA IC 1; (d) β-CD-PLA IC 2; (e) β-CD-PLA IC 3.

the ^{1}H NMR as in Table 3; the T_d values of ICs increased by 10-15 ℃ as compared with pure PLA. In general, the analysis results demonstrated that the CD component inside polymer-CD ICs would enhance the thermal stability of the polymer chains to a certain extent such as nylon 6,[38] polyisoprene,[39] or the capped PLA chain was more preferably stabilized by the formation of β-CD-PLA inclusion compound than free components.

The DSC patterns of PLA, β-CD and β-CD-PLA ICs were shown separately in Figure 8. It could be observed that an endothermic peak of pure PLA appeared at 128.3 ℃ and a cold crystallization peak stood at nearly 100 ℃, while β-CD had only an endothermic peak at 130.1 ℃ (Figure 8(a) and (b)). The inclusion complexes with different CD contents showed no any crystallization peak from the DSC curves (Figure 8(c), (d) and (e)), indicating that the original crystalline polymer phase was absent in the complex. The relevant findings were also reported in the literatures.[40,41] The analysis results testified that every PLA chain with small molecular weight could be easily included in the channels by the CD lattice, which had been changed from a cage configuration to a complete "head to head" columnar structure, and affected the vibration behavior of the polymer chain mode and enhanced its steric hindrance effects, thus led to the absence of crystallization performance of ICs.[42,43]

The Proposed Structure Model of β-CD-PLA ICs. The above characterization results obtained in this work imply that inclusion complexes can be formed between PLA and β-CD. From both ^{1}H NMR and DSC results, it is reasonable to postulate that PLA chains can be included and covered by β-CD

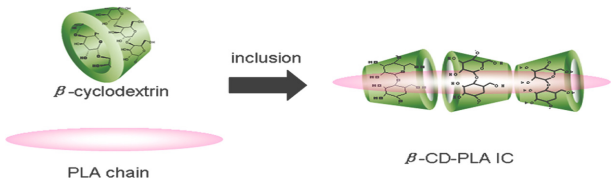

Figure 9. Proposed structure of β-CD-PLA IC.

mostly, only little PLA chains are free, as shown in Figure 9. This can explain the fact that the β-CD-PLA ICs present no thermal transitions while the neat PLA show thermal transitions in DSC studies.

Conclusions

The inclusion complexes between β-CD with PLA were successful obtained via co-precipitation method. The range analysis results of orthogonal experiment revealed that the feeding ratios between β-CD and PLA could seriously impact the encapsulation rate of ICs. From the ^{1}H NMR and FT-Raman spectra, β-CD cavities had self-assembly been threaded on the PLA chains, which formed a stable and complete host-guest supermolecular structure. In view of the thermal properties, the inclusion complexes demonstrated a better thermal stability and simultaneously the crystallization performance of ICs had disappeared. Fianally, the model of ICs was given on the basis of XRD, HNMR and DSC results.

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