

Preparation of Hydrophobic Chitosan Using Complexation Method for PLA/Chitosan Blend

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Abstract

In this study, dioctyl sulfosuccinate-chitosan complex was prepared by a mechanical mixing of aqueous chitosan with sodium dioctyl sulfosuccinate. As a result, hydrophobic chitosan was achieved. Characterizations of the complex were carried out including XRD, TGA, and FT-IR in order to follow changes in the chitosan structure. Thus produced chitosan complex was hydrophobic and anticipated to be compatible with PLA. Solution blending of PLA and hydrophobic chitosan was then conducted. Characterization techniques including XRD and FT-IR were employed to investigate the structure of the polymer blend. FTIR spectra showed that changes in the fingerprint of the chitosan amide band in the blend were observed, indicating compatibility between hydrophobic chitosan and PLA. In a similar manner, hydrophobic chitosan exhibited broader degradation profile when compared to virgin chitosan, arising from the interaction between hydrophobic chitosan and PLA.

Key words : Hydrophobic chitosan, Dioctyl sulfosuccinate-chitosan complex, PLA/hydrophobic chitosan blend

Introduction

Poly(lactic acid) (PLA) is an aliphatic polyester. It is a biodegradable and compostable thermoplastic derived from renewable resources, such as starch and sugar cane.⁽¹⁾ PLA is synthesized by direct condensation polymerization of the lactic acid monomers or by ring opening polymerization of lactide monomer.⁽²⁾ PLA is compostable, and thus perfectly suitable for consumer goods and packaging applications. At present, PLA is far more expensive than conventional olefin plastics. Moreover, processing of PLA is related to several parameters in order to achieve desirable properties. So far, properties of PLA based packaging such as mechanical properties are inferior to petroleum based packaging. Interest in the improvement of properties, as well as cost reduction has been received great attention. Attractive routes to achieve these aims include the development of composites and polymer blends.^(3,4) However, compatibility problems arising from poor interactions between added filler or a different polymer and PLA matrix need to be overcome in order to meet requirements. A promising candidate

for modifying PLA properties is chitosan. Chitosan, a biodegradable derived from renewable resources is produced from deacetylation of chitin with a degree of deacetylation higher than 75%. The main problem associated with the preparation of chitosan/PLA blend is the incompatibility between hydrophilic chitosan and hydrophobic PLA. In order to enhance the compatibility, hydrophobicity modifications of chitosan have been taken into consideration.

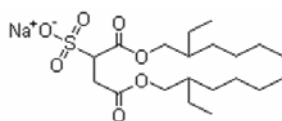
In this study, the preparation of hydrophobic chitosan using the complexation method was investigated, and the obtained hydrophobic chitosan was then employed for the preparation of PLA/chitosan blend. PLA/chitosan blend was prepared by solution blending technique. Characterizations of PLA/hydrophobic chitosan blend composition were presented.

Materials and Experimental Procedures

Materials

Chitosan flake (Mw = 800,000) was bought from Ebase Co. Ltd (Thailand) and it was pulverized with a particle size of about 0.5 mm

prior to use. Its viscosity (η) measured by Brookfield viscometer (at 25°C, speed 100 rpm) was found to be 138.6cps. Methanol was purchased from SK chemicals Ulsan, Korea. Toluene and acetic acid were purchased from Labscan Asia Co. Ltd, Thailand. Poly(lactic acid) (PLA 2002D) under the trade name of NatureWorks with a melt index of 4-8 g/10minutes was bought from a local supplier. Sodium dioctyl sulfosuccinate, an ionic surfactant, was commercial grade and kindly provided by Worldtex Commercial, Co. Ltd. Its structure is represented in Scheme 1. Commercial grade dimethylene chloride was bought from a local supplier.



Scheme 1. Structure of dioctylsulfosuccinate

Methods

Preparation of Dioctyl Sulfosuccinate-Chitosan Complex (DSS-CTS)

5 g (1% (w/v)) chitosan (CTS) in 500 ml of 1% (v/v) acetic acid solution was prepared. Then, 5 g of sodium dioctyl sulfosuccinate (DSS) equivalent to 1:1 wt ratio was slowly added under continuous homogenization for 30 minutes and left standing overnight. The insoluble DSS-CTS complex was filtrated and dried freely in open air. Prior to blending, the DSS-CTS complex was swollen in dimethylene chloride and ground using a blender. In a similar manner, DSS-CTS complexes of 3: 1 and 5: 1 DSS to CTS ratios were prepared.

Preparation of PLA/DSS-CTS Blend

Blends of PLA with DSS 3-CTS 1 were prepared by solution method using dimethylene chloride as a solvent. First, PLA was dissolved in dimethylene chloride. The calculated amount of ground DSS-CTS was admixed and stirred to obtain uniform dispersion. The mixture was cast onto petri disk to allow dimethylene chloride to freely evaporate. In this study, PLA/DSS-CTS blends having the weight ratios of PLA to DSS-CTS of 100:0, 95:5, 90:10, 85:15 and 80:20) were obtained. The obtained blends were kept in a desiccator prior to characterizations.

Characterization Techniques

FT-IR spectroscopy was employed to characterize the DSS-CTS complex. FTIR spectra measured on KBR pellet samples were recorded on Fourier Transform Infrared Spectrometer, PerkinElmer, with 32 scans at a resolution of 4 cm^{-1} . Thermal behavior of virgin chitosan, DSS-CTS complex, as-received PLA, and PLA/DSS-CTS blend was evaluated by TGA technique (METTER TOA/SDTA 851e). A heating rate of 10°C min^{-1} under nitrogen atmosphere over the temperature range of 30–750°C was set. Sample weights of 5-10 mg were employed for this measurement. X-ray diffraction data were used to observe the crystal structure of the chitosan and DSS-CTS complex. XRD patterns were obtained on Philips PW 3710 X-ray diffractometer. The X-ray source was Cu $K\alpha$ with a voltage of 40 kv and a current of 30 mv. The measurement was in the scanning range of 5–40° at a scanning speed of 50 s^{-1} .

Results and Discussion

Characterizations of DSS-CTS Complex

It is obviously noticeable that DSS-CTS complex is wax-like in appearance. This wax-like complex is found floating in water, indicating that DSS-CTS complex exhibits hydrophobicity. Characterizations were carried out to witness changes in hydrophilic-hydrophobic characteristic of chitosan as follows:

TGA derivative curves of virgin chitosan, DSS 3: CTS 1 are presented in Figure 1. Virgin chitosan exhibits the degradation temperature (T_d) of 316°C. Loss of bound moisture is obviously observed at 108°C, indicating the hydrophilic characteristic of chitosan. In case of DSS-CTS, the complex exhibits the two T_d values at 238°C and 316°C, corresponding to the degradation temperatures of dodecylsulfosuccinate and chitosan, respectively. When considering the degradation region of dodecylsulfosuccinate, a wide gap between the onset temperature and the end point temperature is discerned. This is derived from the interaction between sulfosuccinate SO_3^- group and the chitosan NH_3^+ group. As a result, DSS-CTS complex was successfully obtained.

XRD patterns of virgin chitosan and DSS modified chitosans are illustrated in Figure 2. The XRD pattern of virgin chitosan exhibits broad diffraction peaks at $2\theta = 10.0^\circ$ and 19° which are

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typical fingerprints of semi-crystalline chitosan.⁽⁵⁾ For the modified chitosan, peak intensity at $2\theta = 19^\circ$ notably decreases, indicating that the degree of chitosan crystallinity was partially destroyed due to the interruption of hydrogen.

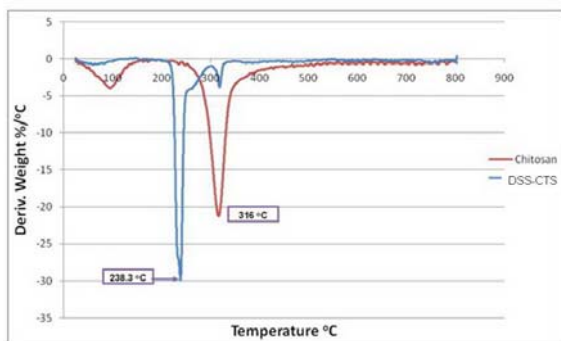


Figure 1. TGA derivative curves of virgin chitosan, and DSS 3 : CTS 1 complex

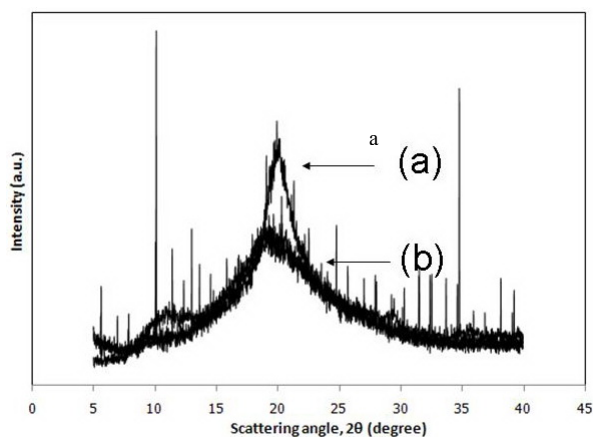


Figure 2. XRD patterns for virgin chitosan and DSS-CTS complex (a) virgin chitosan; (b) DSS 3 : CTS 1

FTIR spectroscopy was used to characterize the chitosan-dodecylsulfosuccinate interaction. Figure 3 shows the FTIR spectrum of virgin chitosan and DSS-CTS complex (DSS 3 : CTS 1). The chitosan amine band at 1608 cm^{-1} shows up clearly. It is interesting that the absorption peak of DSS-CTS at 1608 cm^{-1} corresponding to the chitosan NH_2 band exhibits narrower peak when compared to virgin chitosan (Figure 3a). This phenomenon is derived from the interruption of intermolecular hydrogen bonding arising from the interaction between chitosan NH_2 group and DSS carbonyl ($\text{C}=\text{O}$) group. The complexation between chitosan and DSS can be drawn as shown in Figure 4.

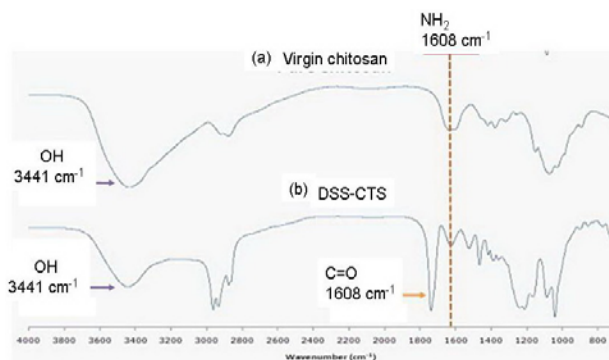


Figure 3. FTIR spectra of virgin chitosan (a) and modified chitosan DSS 3 : CTS 1(b)

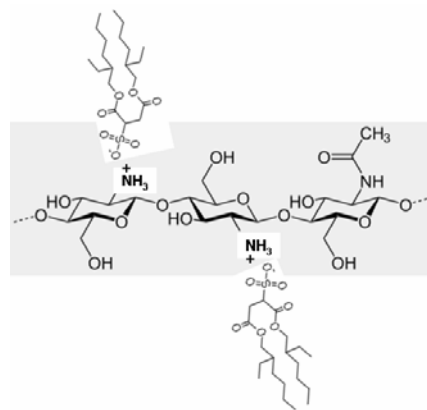


Figure 4. The complexation between chitosan and DSS.

The decrease in hydroxyl band intensity in a region of 3441 cm^{-1} also indicates the decreasing availability of the chitosan hydroxyl group, further confirming changes in the property of chitosan from hydrophilicity to hydrophobicity.

Characterizations of PLA/DSS-CTS Blend

TGA derivative curves of virgin PLA and PLA/DSS-CTS blends (PLA/DSS-CTS 95:5, PLA/DSS-CTS 90:10, PLA/DSS-CTS 85:15 and PLA/DSS-CTS 80:20) are shown in Figure 5. According to TGA curves, virgin PLA begins to degrade at 380°C . PLA/DSS-CTS 95:5 exhibits a degradation profile similar to pure PLA, while other PLA/DSS-CTS blends exhibit two degradation steps (PLA/DSS-CTS 90:10 at 265°C and 355°C , PLA/DSS-CTS 85:15 at 240°C and 342°C , PLA/DSS-CTS 80:20 at 238°C and 341°C). For blends, the degradation profiles in the region of DSS-CTS component are broader when compared to the profile of DSS-CTS complex, arising from the interaction phenomenon between DSS-CTS component and PLA matrix.

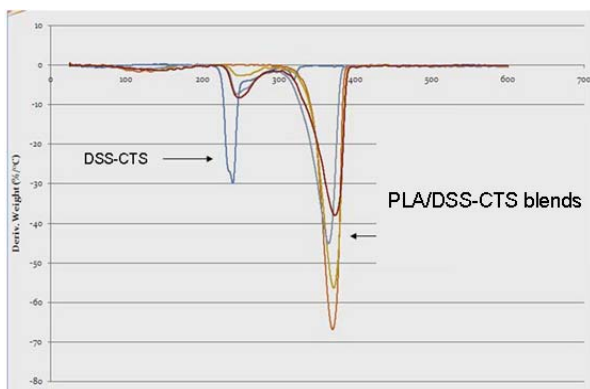


Figure 5. TGA derivative curves for pure PLA and PLA/DSS-CTS blends (PLA/DSS-CTS 95:5, PLA/ DSS-CTS 90:10, PLA/ DSS-CTS 85:15 and PLA/ DSS-CTS 80:20).

FTIR spectroscopy was used to characterize the interaction between PLA/DSS-CTS blends. Figure 6 shows the FTIR spectra of PLA 90 : DSS-CTS 10 and PLA 80 :DSS-CTS 20 blends. The characteristic carbonyl stretching of PLA at 1751 cm^{-1} is observed in all cases. It is interesting that the absorption peak of DSS-CTS at 1608 cm^{-1} corresponding to the chitosan NH_2 band exhibits broader peak when compared to free DSS-CTS (Figure 3). This is indicative of the intermolecular hydrogen bonding interaction arising from the interaction between the DSS-CTS NH_2 group and PLA carbonyl ($\text{C}=\text{O}$) group. Change in the IR fingerprint of the chitosan NH_2 band is believed to be induced by the close proximity between PLA matrix and DSS-CTS component. The evidence of hydrogen bonding indirectly indicates that DSS-CTS is compatible with PLA matrix.

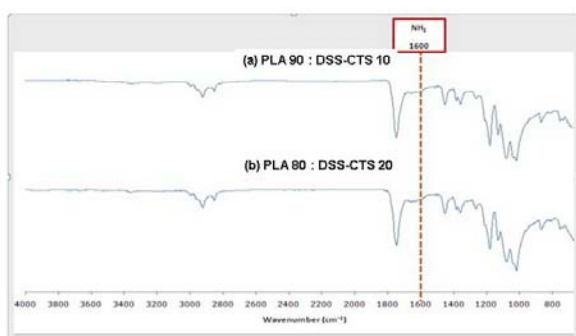


Figure 6. FTIR spectra of PLA 90 : DSS-CTS 10 and PLA 80 :DSS-CTS 20 blends

Conclusions

Hydrophobic chitosan was successfully prepared. Several techniques were employed to confirm the structural change from hydrophilicity to hydrophobicity. The obtained hydrophobic chitosan was blended into polylactic acid using solution mixing. The results showed that hydrophobic chitosan was compatible with polylactic acid due to its hydrophobic similarity.

Acknowledgements

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