

CHAPTER V

CHITOSAN OLIGO/POLYESTER NANOCOMPOSITE

Abstract

Chitosan oligo/polyester nanocomposite is proposed. In the first step, the packing structure of chitosan was opened via ionic interaction with carboxylic acid. The intercalation of carboxylic acid in chitosan layer was qualitatively analyzed by wide angle X-ray diffraction (WAXD) and the amount of chitosan carboxylate was determined by thermogravimetric analysis (TGA). In the second step, ethylene glycol was reacted directly with suspension of chitosan-carboxylate to achieve the esterification with diacid molecules as confirmed by Fourier transform infrared spectroscopy (FTIR). The work confirms the oligo/polyester formation in chitosan-dicarboxylate layer which is a model nanocomposite mimicking the natural crustacean shell of chitosan and protein system.

Keywords: Chitosan-carboxylate, Chitosan nanocomposite, Oligo/polyester-nanocomposite, Chitin-chitosan

Introduction

Nanocomposite is a type of composites containing filler that has at least one dimension in the range of nanometer, i.e. a billionth of a meter. At present, nanocomposites are produced by metal particles, colloids, and smectic-clay minerals. As nanotechnology has received much attention to develop novel polymeric materials, nanocomposite becomes an expectation for unique materials with desired properties under the concept of material hybridization. Various nanocomposites have been reported, for example, nylon 6-clay nanocomposites (Usuki *et al.*, 1993), polyimide-silica hybrid (Mascia and Kioul (1995)). It is important to note that the production of nanocomposite requires a material which offers a nanometer scale for intercalation of other material.

Clay or montmorillonite is a typical and ideal material to serve the composite at nano-scaled hybridization. The fact is that montmorillonite supplies 1 nm thickness of planar structure of anionic silicate layer which can form ionic interaction with other molecules and stabilized in the layer. Referring to nanocomposite of clay to provide nanocomposite, crustacean shell is an ideal structure of nanocomposite found in nature.

Chitin-chitosan is the second most naturally abundant copolymer of (β -1,4-linked-2-acetamido-deoxy-D-glucopyranose) and (β -1,4-linked-2-amino-deoxy-D-glucopyranose). Chitin-chitosan is networked by the strong inter-intra hydrogen bonds resulting in the problems of difficult dissolution in water and organic solvents. This also brings chitin-chitosan to perform as a thermosetting polymer even though structurally, it is a thermoplastic one. The packing structure of chitosan chain aligned in layer by layer to give the X-ray diffraction peaks at 9° and $19^\circ 2\theta$.

It is important to note that inorganic compounds of Na^+ -montmorillonite and chitosan have a common packing structure. For example, Na^+ -montmorillonite consists of an alumina-silica anionic layer protonated with sodium ion, whereas chitosan has the amino group to accept proton species. The packing structure of Na^+ -montmorillonite gives 2θ peak at 7.4° while that of chitosan is at 9° . Thus, chitosan might provide an organic layer similar to that of clay for inorganic layer.

In order to achieve chitosan oligo/polyester nanocomposite, the important point is to open chitosan layer with some ionic interaction. Here, we focus on the organic layer belonging to chitosan and the possibility to initiate the open layered structure and the intercalation with other polymer chains.

The present work proposes the use of chitosan-carboxylate salt. The work also confirms the oligo/polyester formation in chitosan-carboxylate layer which is a model nanocomposite mimicking the natural crustacean shell of chitosan and protein system.

Experimental Section

Materials. Chitosan with a degree of deacetylation (%DD) of 85 was supplied from the SEAFRESH (Lab) Company Limited, Bangkok, Thailand. Hydrochloric acid and acetone were purchased from Carlo Erba Regenti, Italy. Sodium-montmorillonite was the product of Southern Clay Product, Inc., USA. Adipic acid and ethylene glycol were obtained from Fluka Chemika, Switzerland.

Procedures. Qualitative and quantitative FTIR were obtained from a Bruker Equinox 55/S with 32 scans at a resolution of 4 cm^{-1} . A frequency range of $4000\text{-}400\text{ cm}^{-1}$ was observed using a deuterated triglycinesulfate detector (DTGS) with a specific detectivity, D^* , of $1 \times 10^9\text{ cm.Hz}^{1/2}\text{ w}^{-1}$. A Dupont thermal gravimetric analyzer was applied using an air with a flowing rate of 20 mL/min and heating rate of 10°C/min from room temperature to 900°C . X-ray diffraction patterns were obtained from a Rigaku RINT 2000, using $\text{CuK}\alpha$ ($\lambda=0.154\text{ nm}$) as an X-ray source with 2θ of $2\text{-}90^\circ$ operating at 40 kV , 30 mA with Ni filler.

Preparation of chitosan oligo/polyester nanocomposites. Chitosan solutions with concentration 1 \% (w/v) were prepared by dissolving chitosan 1 g in 100 mL of carboxylic acid. Chitosan solutions were reprecipitated in acetone to obtain chitosan salt. Chitosan salt was stirred in 1 N hydrochloric acid at 50°C for 1 h . Ethylene glycol 0.4 g (7 mmol) was added to chitosan suspension and the mixture was stirred at 150°C under nitrogen for 5 h . The solution was concentrated and dropped in methanol to obtain a brownish viscous product. The crude product was

washed with methanol and water several times before drying in vacuo. The characterizations were achieved by FTIR, TGA and XRD.

Results and Discussion

Formation of Chitosan Open Layer Structure Via Chitosan-Dicarboxylate Salt

In general chitosan shows the XRD pattern at $9^\circ 2\theta$ and $19^\circ 2\theta$ implying the packing structure based on inter and intra-molecular hydrogen bonds. The approach to produce chitosan based nanocomposites, thus, might possibly be either by intercalating other molecules into chitosan layer or intercalating chitosan molecules into other organic or inorganic layer. The present work focuses on the intercalation of polymer chain into chitosan layer.

In order to obtain chitosan nanocomposite, we have to open the layer of chitosan. By changing chitosan into chitosan salt, it can be expected that the hydrogen bond might be interrupted thus loosening the packing structure. WAXD technique is applied to clarify the changes in packing structure as a result from the interaction of carboxylic acid with amino groups in chitosan chains. Figure 1 shows the XRD pattern of chitosan with various types of carboxylic acid, i.e., monocarboxylic acid (Figure 1(b)-1(c)) and dicarboxylic acid (Figure 1(d)-1(g)) comparing with pure chitosan (Figure 1(a)). Chitosan salt obtained from all dicarboxylic acids show a new peak at $6^\circ 2\theta$ implying the layer of chitosan was expanded from 1 nm to 1.5 nm. However, in the case of chitosan salt from acetic acid the peak at $6^\circ 2\theta$ was not clearly observed. We speculated that dicarboxylic acid not only functions as a protonation species but is also intercalated in chitosan packing structure to open the layer.

The interaction at molecular level between polymer chains might induce the changes in vibrational modes which can be observed by FTIR. Figure 2 verifies how carboxylic acid interacted with clay. It was found that chitosan acetate (Figure 2(b)) and chitosan adipate (Figure 2(c)) show a new peak at 1410 cm^{-1} referring to the symmetric carboxylate ($-\text{COO}^-$) and the peak at 1610 cm^{-1} to the asymmetric ($-\text{NH}_3^+$). This suggests the possibility that chitosan is in the protonated form with carboxylic acid as illustrated in Scheme I.

TGA is applied to observe the weight loss relating to the carboxylic acids intercalated in chitosan layer. Figure 3 shows the different degradation temperature between pure chitosan (Figure 3(a)) and chitosan adipate (Figure 3(b)). It was found that pure chitosan shows only single degradation step between 200°C and 300°C but chitosan adipate gives the broad degradation range between 200°C and 530°C.

Esterification of Chitosan-Dicarboxylate

As carboxylic acid, either monocarboxylic or di-carboxylic acid, is successfully introduced into chitosan layer, we carried out the esterification by adding a certain amount of ethylene glycol into the system. Here, the successful esterification will bring polymer chain in intercalated chitosan layer to give the nanocomposite as shown in Scheme I. Esterification can be identified from the ester peak appearing separately from that of chitosan carboxylate salt. Figure 4 shows the FTIR spectra of the chitosan acetate protonated form with acetic acid (Figure 4(b)) and chitosan adipate (Figure 4(c)) after esterification comparing with pure chitosan (Figure 4(a)). It was found that after esterification only chitosan adipate gave peak of ester at 1730 cm^{-1} and 2980 cm^{-1} belonging to the ester group and long alkyl chain, respectively. Although we need to clarify the molecular weight of ester formed, the peaks at 2980 cm^{-1} suggested the alkyl chain intercalated in chitosan layer, either the ester species is oligomer or polymer. The peak 1730 cm^{-1} shows the interaction in clay layer to conclude that oligo or polyester chains are in the layer. For other chitosan dicarboxylate, the peak at 1730 cm^{-1} and 2980 cm^{-1} were also identified. This implied that chitosan protonated with dicarboxylic acid allows polymerization with ethylene glycol to obtain oligo/polyester in chitosan layer.

In order to evaluate the intercalation of oligo/polyester into chitosan layer, WAXD technique was used to observe the change in packing structure. Figure 5 shows the XRD pattern of the nanocomposites obtained from various chitosan carboxylate salts. It was found that chitosan nanocomposite obtained from chitosan monocarboxylate after the reaction with ethylene glycol (Figure 5(a) and 5(b)) retains the same XRD pattern as the starting chitosan salt. However, in the case of chitosan nanocomposite obtained from chitosan dicarboxylate, there is a new broad

peak between $10^\circ 2\theta$ and $20^\circ 2\theta$ implying the amorphous based structure. Considering the neat purification steps of the products which exclude the ester species out of the surface of chitosan, we conclude that the polyester chains are formed in chitosan layer resulting in chitosan polyester nanocomposite.

Thermogravimetry analysis was further applied to determine the weight loss between 500°C and 650°C referring to oligo/polyester degradation. Figure 6 demonstrates the degradation of chitosan adipate and chitosan adipate after treating with ethylene glycol. Chitosan salt shows degradation temperature between 200°C and 400°C under air atmosphere (Figure 6(a)). In the case of chitosan adipate after polymerization with ethylene glycol, there is a new degradation step from 500°C to 650°C implying the existence of oligo/polyester in chitosan layer. It should be noted that the result implied that the amount of oligo/polyester introduced into chitosan layer might be as high as 30 wt%.

Conclusions

The interaction of carboxylic acid is a useful approach to destroy chitosan packing structure. The peak of carboxylate ($-\text{COO}^-$) at 1410 cm^{-1} and amine salt ($-\text{NH}_3^+$) at 1610 cm^{-1} observed by FTIR suggested the carboxylic acid embedded in chitosan layer by ionic interaction. Dicarboxylic acid was intercalated into chitosan layer as evidenced from the change in XRD pattern. In the case of chitosan-dicarboxylate, the polymerization with diol to obtain polyester as identified from FTIR, XRD supported a novel type of chitosan polyester nanocomposite. The present work succeeded in obtaining a biomimic structure of chitosan polyester nanocomposite to crab shells which consist of the layer of chitosan, cuticle, and protein stabilized by various minerals.

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References

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Scheme I

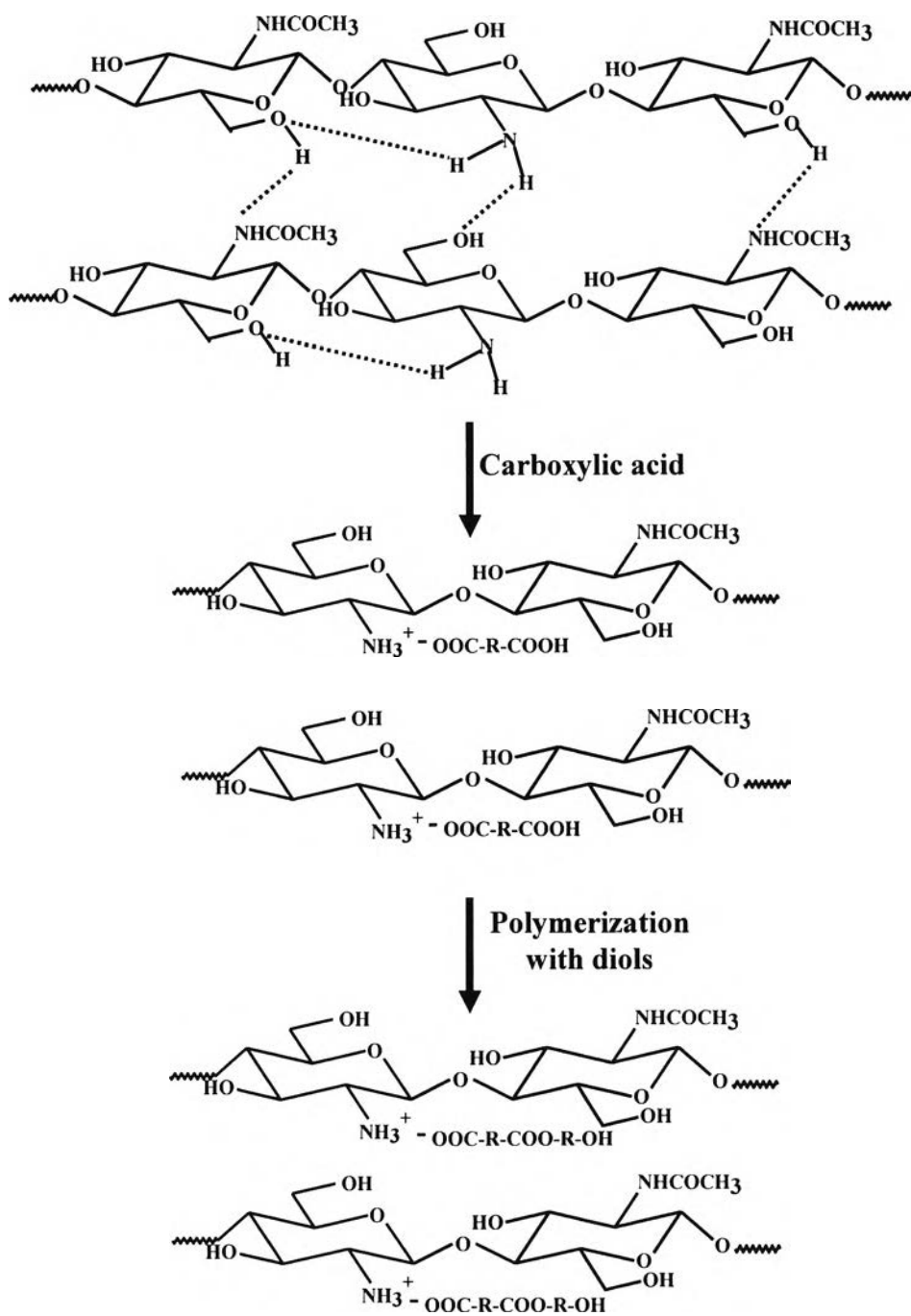


Figure Captions

- Figure 1.** XRD patterns of pure chitosan (a) and chitosan with various types of carboxylic acid: formic acid (b), acetic acid (c), malonic acid (d), succinic acid (e), adipic acid (f), and sebacic acid (g).
- Figure 2.** FTIR spectra of pure chitosan (a), chitosan acetate (b), and chitosan adipate (c).
- Figure 3.** Degradation temperature of pure chitosan (a), and chitosan-adipate (b).
- Figure 4.** FTIR spectra of pure chitosan (a), chitosan acetate protonated form with acetic acid (b), and chitosan adipate after esterification (c).
- Figure 5.** XRD pattern of pure chitosan (a) and nanocomposites obtained from various chitosan carboxylate salts: formic acid (b), acetic acid (c), malonic acid (d), succinic acid (e), adipic acid (f), and sebacic acid (g).
- Figure 6.** Degradation of chitosan adipate (a), and chitosan adipate after the reaction with ethylene glycol (b).

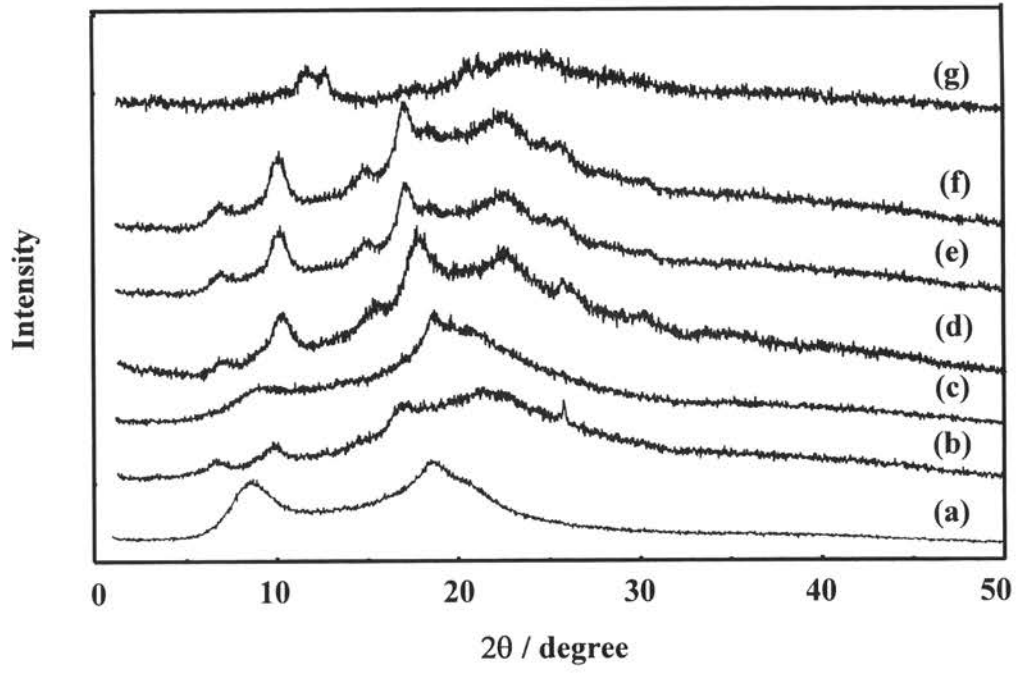


Figure 1.

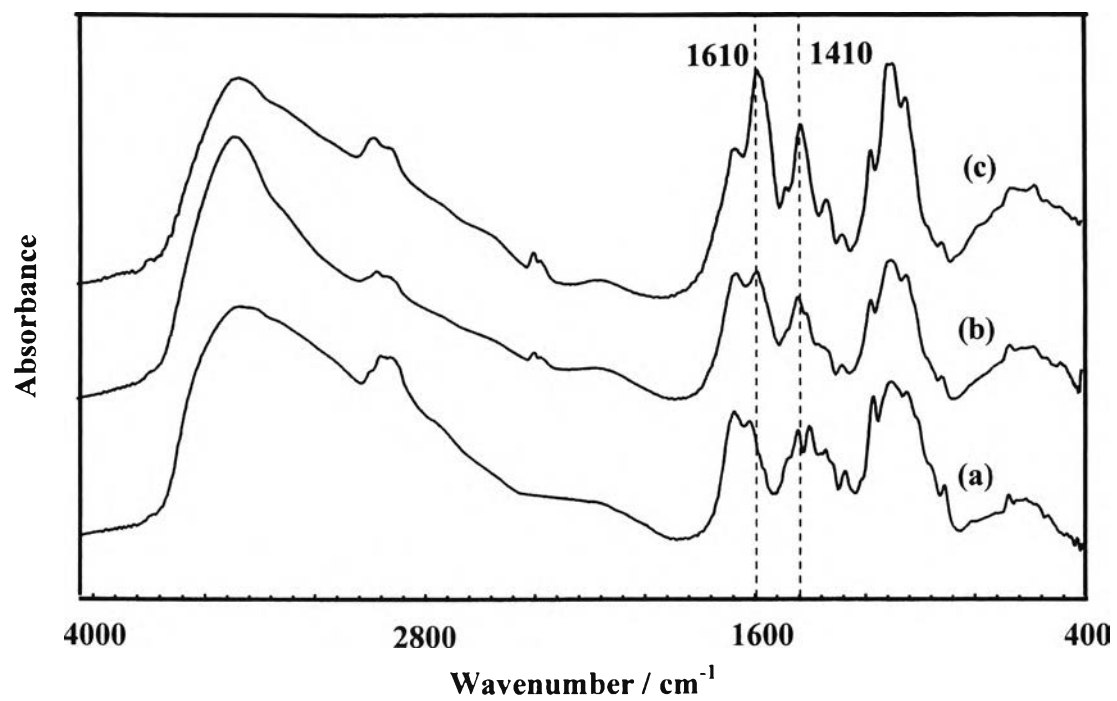


Figure 2.

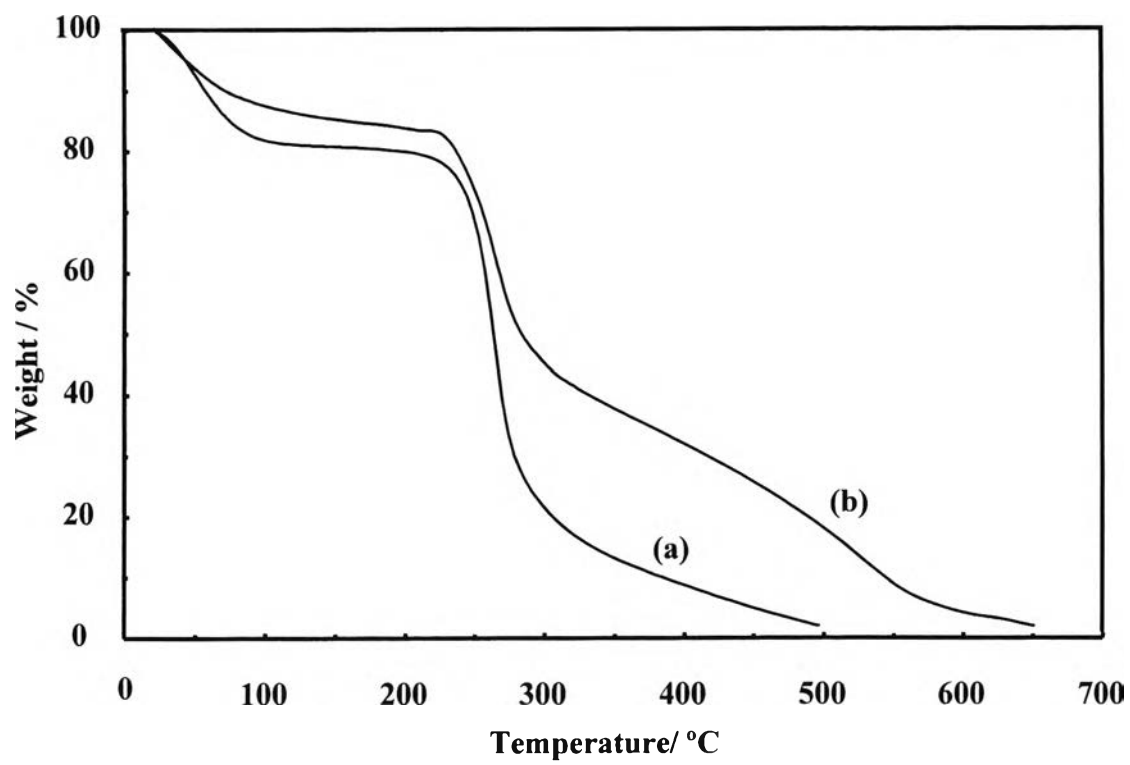


Figure 3.

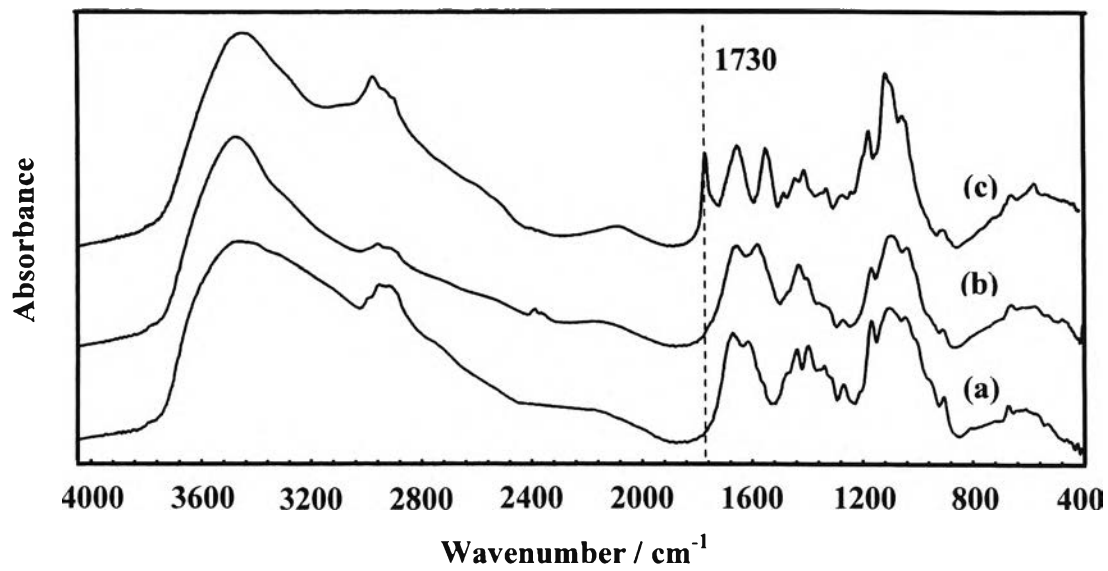


Figure 4.

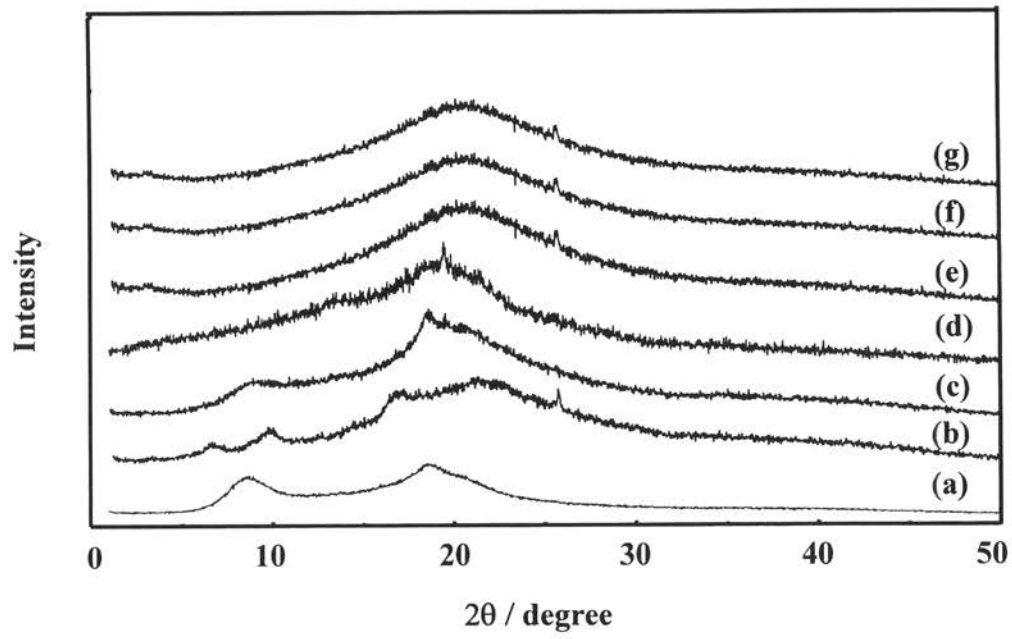


Figure 5.

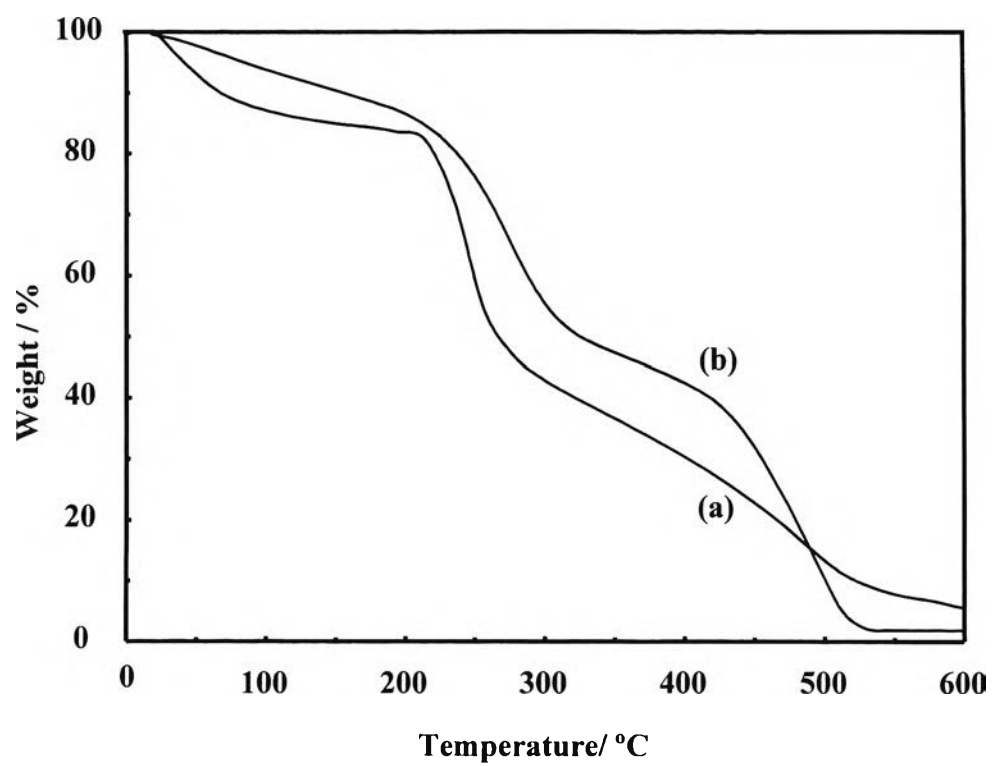


Figure 6.