CHAPTER III
INTERCALATION EFFICIENCY OF CHITOSAN FOR NANOCOMPOSITE FORMATION WITH ORGANOCLAY

Abstract

Nanocomposite of chitosan-clay prepared by mixing organoclay with chitosan acid solution was proposed. Chitosan was intercalated in the form of a carboxylic salt in the clay layer as confirmed by Fourier transform infrared spectra (FTIR). The wide angle X-ray diffraction (WAXD) showed the change in basal spacing of clay from 1.5 to 1.8 nm after chitosan intercalation. Thermogravimetric analysis technique (TGA) showed the effective amount of chitosan intercalated in clay was saturated at only 10-15 % even though the amount of chitosan carboxylic acid solution was 50 times to that of clay. Intercalation of chitosan was significant when the nanocomposite was prepared from the system of clay and chitosan in dicarboxylic acid solution. The chain length of carboxylic acid is a factor governing the intercalation efficiency as evidenced from the chitosan clay nanocomposite obtained from chitosan adipic acid solution which showed that intercalated amount was 25 % and the d-spacing of clay was 2.7 nm.

Keywords: Nanocomposite, Chitosan intercalation, Chitosan carboxylic acid solution, Chitosan-clay nanocomposite, Sodium montmorillonite, Chitin-chitosan

Introduction

Composites are materials which combine two or more distinct structurally complementary substances resulting in properties that do not exist in the individual components (Giannelis *et al.*, 1996). Most composites are well known as light-weight but strong materials under the hybridized system of organic polymer matrix with inorganic reinforced fiber. The applications of composites are found in, for example, electronic circuit board, car parts, housing or construction parts, etc.

Considering the structure of the composites, the reinforced inorganic materials are usually in micrometer to millimeter size resulting in heterogeneous phase mixing. For the past decades, it has been known that, when the size and length of the complementary phases are in nanometer, the composites will show the miscibility and give the unique properties in nano-level such as the selective gas barrier, electrical conductivity, etc. Thus, the production of reinforced material under the nanometer size and the nano-scale dispersion is challenged through various composites. Nanocomposites are developed by using metal particles, colloids, and smectic-clay minerals. For example, Usuki *et al.* (1993) proposed the system of nylon 6-clay nanocomposites using polymer melt intercalation process of caprolactam, whereas Mascia and Kioul (1995) demonstrated the polyimide-silica hybrid nanocomposites by common solvent process of polyamic acid and *N,N*-dimethylacetamide.

It is known that smectic-clay gives the silicate layer at a nanometer size. When the clay is protonated with amines, the clay layer will open up to allow the intercalation of polymer chains. Messermith *et al.* (1995) used organic modified silicate layers with 12-aminododecanoic acid for preparation of caprolactone-clay nanocomposite and declared that the molecular weight and size of crystalline of poly(caprolactone) generated depended on the content of the silicate directly. The barrier properties to prevent water vapor transmission of poly(caprolactone) nanocomposite dramatically increased with small content of silicate layers. Up to now, there have been a number of reports about using modified silicate for polymer-clay nanocomposites, such as nylon 6 (Watari *et al.*, 1997), polyimide (Yano *et al.*, 1997), and epoxy (Pinnavaia *et al.*, 1996).

It is important to point out that, the supra-structure of crustacean shells are a good model of natural nanocomposite consisting multi-component of polysaccharide, magnesium and calcium based inorganic minerals, keratin, proteins, etc. The most attractive properties of the shells can be referred to the strength and the hardness with the biodegradability as known in the cases of crab and shrimp shells. Here, we pay our attention to develop artificial nanocomposites at molecular level by mimicking the natural structure of those shells.

The polysaccharide in crustacean shells is known as chitin-chitosan aminosaccharide copolymer. The science of chitin-chitosan has been developed for decades to find the specific chemical and biochemical properties such as polyelectrolyticity, metal ion chelation, antimicrobial activity, etc. Chitin-chitosan copolymer chains are aligned in the layer with d-spacing at $9°$ 2θ and $19°$ 2θ as determined by X-ray analysis. Considering the d-spacing of chitin-chitosan which resembles that of clay, the possibility to modify chitin-chitosan for nanocomposites can be expected.

As chitosan unit has the amino group to be protonated, changing clay to be organo-clay by chitosan is an approach for nanocomposite. In previous work, Breen *et al.* (1999) demonstrated that positively charged polymers can be intercalated in smectite clays under cationic exchange mechanism. It can be expected that protonated chitosan in carboxylic acid solution might be intercalated to Na^+-montmorillonite via cationic exchange process too. Margarita *et al.* (2003) prepared chitosan nanocomposite by using acetic acid and found that the clay layer was opened up from 1.20 to 2.09 nm under the chitosan feeding weight 10 times that of clay. Although the work showed the successful intercalation of chitosan into clay layer, the nanocomposite structure and the factors governing the intercalation process have not been reported.

The present work focuses on the intercalating efficiency of chitosan into clay layer by demonstrating the role of carboxylic acid as a solvent for chitosan, the type of carboxylic acid (monocarboxylic acid and dicarboxylic acid), the effective intercalated amount of chitosan in clay layer, the changes in clay layer structure related to the intercalated chitosan, and the thermal stability of clay-chitosan nanocomposites.
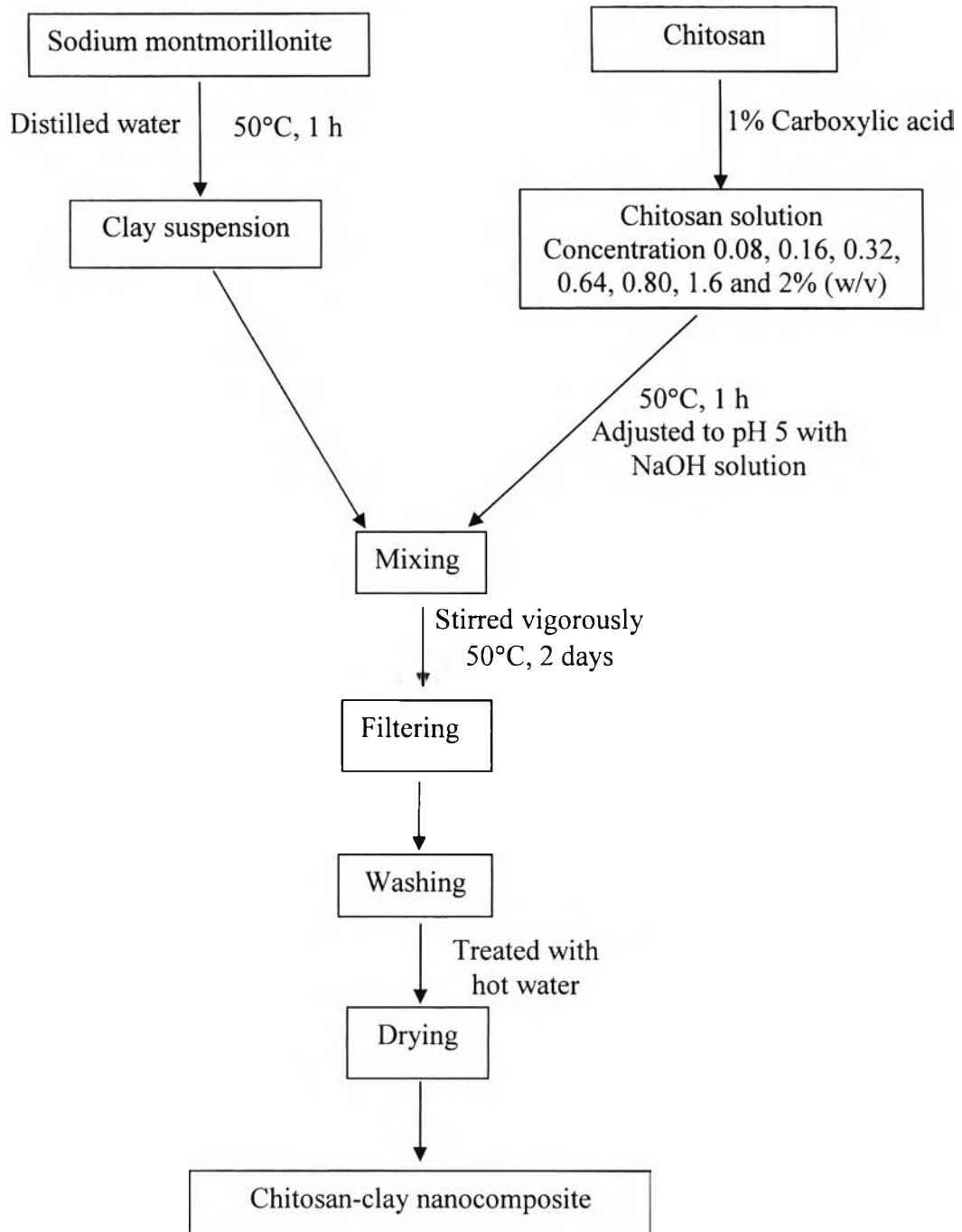
Experimental Section

Materials. Chitosan ($Mv = 7 \times 10^6$) with a degree of deacetylation (%DD) of 85 was supplied from the SEAFRESH (Lab) Company Limited, Bangkok, Thailand. Acetic acid, hydrochloric acid and ethanol were purchased from Carlo Erba Regenti, Italy. Sodium-montmorillonite was the product of Southern Clay Product. Inc., USA. Sodium hydroxide was from Labscan Co., Inc., Thailand. Adipic acid, malonic acid, succinic acid, and ethylene glycol were obtained from Fluka Chemika, Switzerland. All chemicals were used without further purification.

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 4000-400 cm^{-1} was observed using a deuterated triglycinesulfate detector (DTGS) with a specific detectivity, $D*$, of 1×10^9 $cm.Hz^{1/2}$ w^{-1}. A Dupont thermal gravimetric analyzer was applied under air flow with a rate of 20 mL/min and a heating rate of 10°C/min from room temperature to 900°C. X-ray diffraction patterns were obtained from a Rigaku RINT 2000, using CuK_α ($\lambda=0.154$ nm) with Ni filter as an X-ray source and scanning 2θ for 2°-90° at 40 kV, 30 mA.

Preparation of chitosan-clay intercalation and nanocomposite composition (Chart 1). Dicarboxylic acids, i.e., malonic acid, succinic acid, and adipic acid, were prepared as aqueous solutions 1% (w/v). Chitosan was dissolved in dicarboxylic acid solutions in the concentrations of 0.08, 0.16, 0.32, 0.64, 0.80, 1.6 and 2% (w/v). Na^+-montmorillonite 0.5 g was suspended in 25 mL deionized water. The chitosan solutions were adjusted to pH 5 by 1 N NaOH before being mixed with the clay suspension. Each chitosan solution was added to clay suspension and stirred at 50°C for 2 days using the weight ratios of 0.04:1, 0.08:1, 0.16:1, 0.32:1, 0.4:1, 0.8:1 and 1:1. The precipitate was collected and washed thoroughly with purified water and methanol for five times and dried under vacuum before use.

Chart 1

Sodium montmorillonite → (Distilled water, 50°C, 1 h) → Clay suspension

Chitosan → (1% Carboxylic acid) → Chitosan solution, Concentration 0.08, 0.16, 0.32, 0.64, 0.80, 1.6 and 2% (w/v)

Clay suspension and Chitosan solution (50°C, 1 h, Adjusted to pH 5 with NaOH solution) → Mixing

Mixing → (Stirred vigorously, 50°C, 2 days) → Filtering

Filtering → Washing

Washing → (Treated with hot water) → Drying

Drying → Chitosan-clay nanocomposite

Results and Discussion

Intercalation of chitosan in clay layer

In general chitosan shows the wide angle X-ray diffraction at 9° 2θ and 19° 2θ referring to the packing structure with 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 proposes clay nanocomposite under the interaction of amino group in chitosan unit with clay.

In order to achieve the complete intercalation and avoid structural alteration of Na^+-montmorillonite, the pH value of each chitosan solution was adjusted to 5 before being added to the clay suspension. Based on the pK_a (6.3) of the primary amine groups in the chitosan, more than 95% of the amine groups should be protonated at the final pH value (pH 5) of the chitosan-clay mixture. In such condition, the intercalation might be mainly controlled by a cationic exchange mechanism due to the coulombic interactions between the positive $-NH_3^+$ groups of chitosan and the negative charges in the clay structure.

As it is known that the interaction at molecular level between polymer chains might induce the changes in vibrational modes observed by FTIR, the present work applied this technique to verify how chitosan interacted with clay. Figure 1 shows a series of chitosan patterns after treating with Na^+-montmorillonite in various types of dicarboxylic acid solutions (Figure 1(d)-(g)). Chitosan in formic acid and acetic acid solutions (Figure 1(b)-(c)) was also studied to compare the differences in interaction between mono-carboxylic acid and dicarboxylic acid solutions. Na^+-montmorillonite gives vibrational band of the silicate as follows; v_{OH} for Al, Mg(OH) at 3635 cm^{-1}, and v_{SiO} of Si-O-Si ~ 1050 cm^{-1}. There are major peaks of saccharide unit, i.e., v_{CO} of C-O-C ~ 1075 cm^{-1}, pyranose ring ~ 890 cm^{-1}; and v_{OH} ~ 3356 cm^{-1}, which overlap with the broad peak of the silicate around 1050 cm^{-1}. However, the peak at 1560 cm^{-1} is useful to confirm the existence of chitosan as it corresponds to the deformation vibration of the protonated amine group in chitosan. The result implied that the amino group of chitosan was in protonated form and contributed the electrostatic interaction between amine and negatively charged silicate on clay surface. It should be noted that in the cases of chitosan in succinic acid and adipic

acid solutions, there is a new peak at 1720 cm^{-1}. This referred to the v_{CO} stretching band of carboxylated ions. The result is relevant to that of Magarita *et al.* (2003) to conclude that a double layer of chitosan associated by carboxylate ion might form in clay layer. Figure 2 shows the differences in FTIR spectra of chitosan-clay in the case of using chitosan in adipic acid mixing with clay. It was found that when the feeding amount of chitosan adipic acid solution was increased from the ratio of 0.16:1 to 20:1 (chitosan:clay), the band at 1720 cm^{-1} attributed to the v_{CO} stretching band of carboxylated ions appeared distinctly which also supported the possibility that chitosan formed association of two chains induced by the adipic acid molecules.

When the intercalating of chitosan into clay layer occurred, the packing structure of clay layer will change. WAXD technique is applied to clarify the changes in packing structure as a result of chitosan and clay interaction. Figure 3 shows the XRD pattern of chitosan-clay nanocomposite in various types of carboxylic solution (Figure 3(b)-(g)) comparing with pure Na^{+}- montmorillonite (Figure 3(a)). In general, Na^{+}- montmorillonite shows the d-spacing of about 12Å. When the carbon chain of carboxylic acid is increased, the d-spacing increases. For example, chitosan in acetic acid and malonic acid gives the d-spacing of 14Å and 15Å respectively, while the one in adipic acid shows the d-spacing of 18.5Å. Figure 3 leads to two important issues for discussion. The first is that chitosan might be intercalated effectively in clay to form nanocomposites. The second is that carboxylic acid molecules might be intercalated together with chitosan chains, as a result, the longer the chain length of carboxylic acid, the greater value of d-spacing of clay. This speculation can also be confirmed by TGA (see Discussion in Figure 4) which showed that chitosan-clay prepared from adipic acid solution gave significant weight loss referring to the amount of chitosan and adipic acid in clay. However, for sebacic acid system, it was found that the composite obtained showed a d-spacing less than that of the one from adipic acid solution (Figure 3(f)). This might be related to the fact that the chain length is too long to induce the intercalation in clay. Combining the WAXD results with the significant peak (1720 cm^{-1}) observed by FTIR, we speculated that chitosan in adipic acid solution might be an optimal condition to accomplish the double layer structure of chitosan with adipic acid molecules and expand the clay channel from 12Å to 18Å.

Figure 4 demonstrates the degradation of a series of Na^+-montmorillonite after treating with chitosan in various dicarboxylic acids when the feed ratio of chitosan solution was fixed at the ratio of 2:1 (chitosan:clay). It is known that chitosan shows the degradation temperature between 200°C and 400°C (Figure 4(h)) under air atmosphere whereas clay gives a long range of degradation from 100°C to 600°C due to its moisture contents and some inorganic salts. All nanocomposites show the degradation step from 200°C to 400°C referring to the weight loss of chitosan and some inorganic content in clay. For clay nanocomposite prepared from chitosan adipic acid solution, chitosan-adipate was introduced into clay for more than 25 wt% (Figure 4(g)).

Considering the intercalated amount of chitosan and dicarboxylic acid in clay, it is important to clarify the effective amount of chitosan intercalated into clay when the feed ratio of chitosan is varied. Figure 5 shows the results for chitosan in malonic, acetic and adipic acids under the feed ratios of the chitosan to clay from 0.02 to 50 times. It was found that, in the case of 0.02-50 times feed ratios, chitosan content averaged 6-15 wt% for all dicarboxylic acids. Chitosan adipate nanocomposite showed a significant intercalated amount of chitosan and adipic acid of 27 wt%, when the feed ratio is above 20 times to clay. This implies that the chitosan might be introduced into clay layer favorably when chitosan is dissolved in adipic acid. Figure 6 shows the d-spacing for chitosan-clay obtained from chitosan in malonic, acetic and adipic acids under the feed ratios of the chitosan solution to clay from 0.02 to 50 times. It was found that when feed ratios of chitosan increased, d-spacing of clay also increased from 15Å to 18Å, except in the case of chitosan in adipic acid which showed a significant d-spacing of 27Å. This implies that chitosan in adipic acid solution might give favorable condition for intercalation and production of chitosan-clay nanocomposite.

Conclusions

The intercalation of chitosan to Na^+-montmorillonite to form chitosan-clay nanocomposite was successful by using chitosan in mono-carboxylic acid and di-carboxylic acid. The interaction of chitosan and clay was found to be electrostatic

one under the $R\text{-}COO^-\text{-}NH_3^+$ groups of chitosan-dicarboxylate and the negatively charged silicate sites in clay as confirmed by FTIR. The packing structure of clay changed from 12Å to 18Å supporting the formation of chitosan-clay nanocomposite. In the case of chitosan in adipic acid, the intercalating might be accomplished as a double layer of chitosan as evidenced from the significant chitosan content of 25 wt% and a high value of d-spacing of 27Å.

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Figure Captions

Figure 1.   FTIR spectra of the starting Na^+- montmorillonite (a), and nanocomposites in formic acid (b), acetic acid (c), malonic acid (d), succinic acid (e), adipic acid (f), and sebacic acid (g).

Figure 2.   FTIR spectra of the starting Na^+- montmorillonite (a), and nanocomposites with starting chitosan-clay ratios of 0.16:1 (b), 0.4:1 (c), 0.8:1 (d), 1:1 (e), 2:1 (f), 5:1 (g), 7:1 (h), 10:1 (i), 15:1 (j), and 20:1 (k).

Figure 3.   XRD patterns of the starting Na^+- montmorillonite (a) and nanocomposites in formic acid (b), acetic acid (c), malonic acid (d), succinic acid (e), adipic acid (f), and sebacic acid (g).

Figure 4.   TG curves of Na^+- montmorillonite (a), and nanocomposites in formic acid (b), acetic acid (c), malonic acid (d), succinic acid (e), adipic acid (g), sebacic acid (f), and chitosan (h).

Figure 5.   Chitosan-dicarboxylate content found in clay layer of nanocomposites prepared from adipic acid (▲), malonic acid (◇), and acetic acid (■) under the various feed ratios as clarified by TGA.

Figure 6.   d-Spacing of chitosan-clay nanocomposite prepared from adipic acid (▲), malonic acid (◇), and acetic acid (■) under the various feed ratios as clarified by XRD.
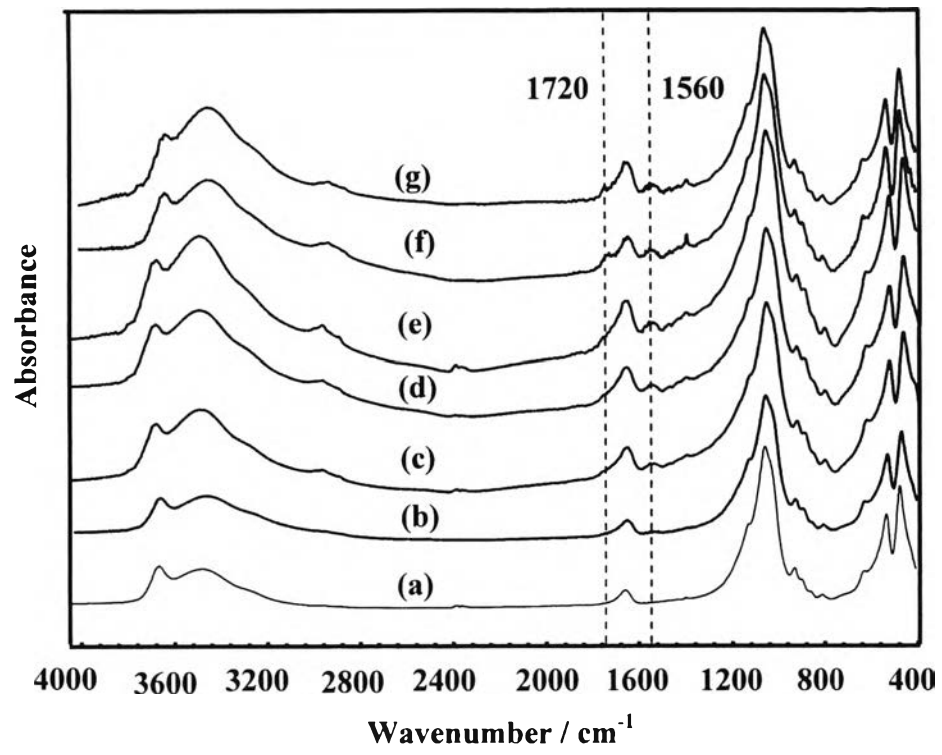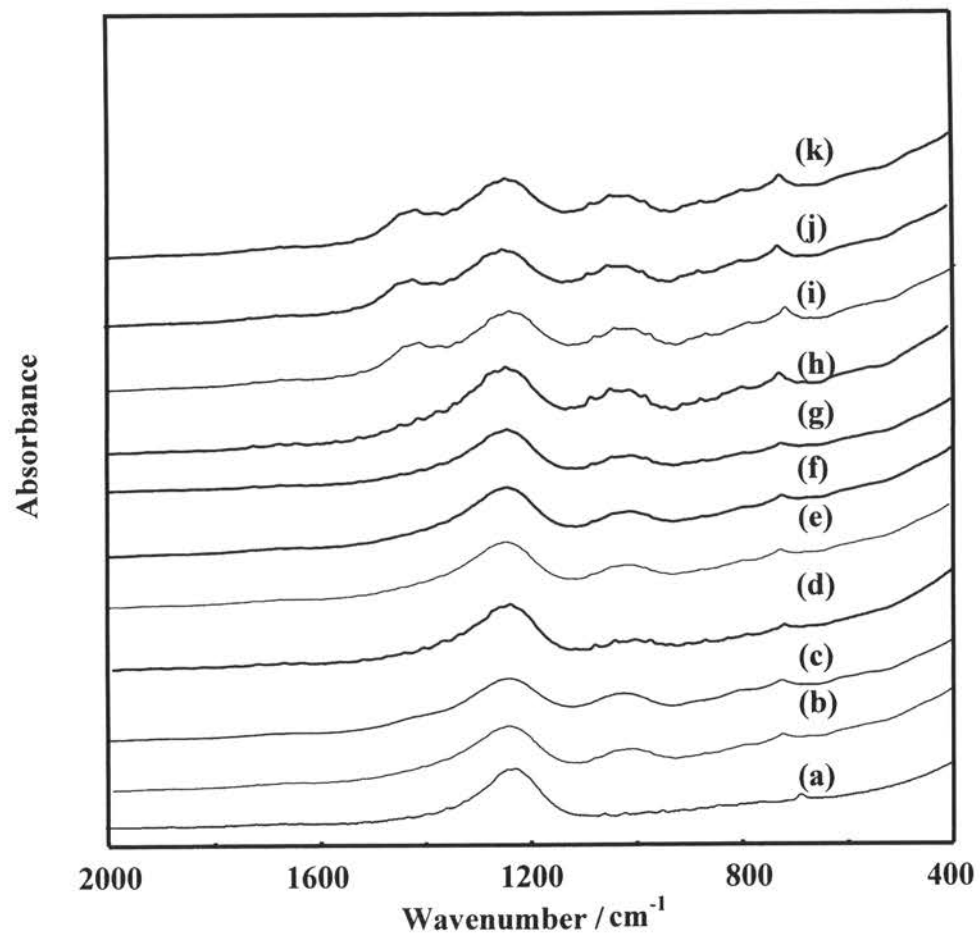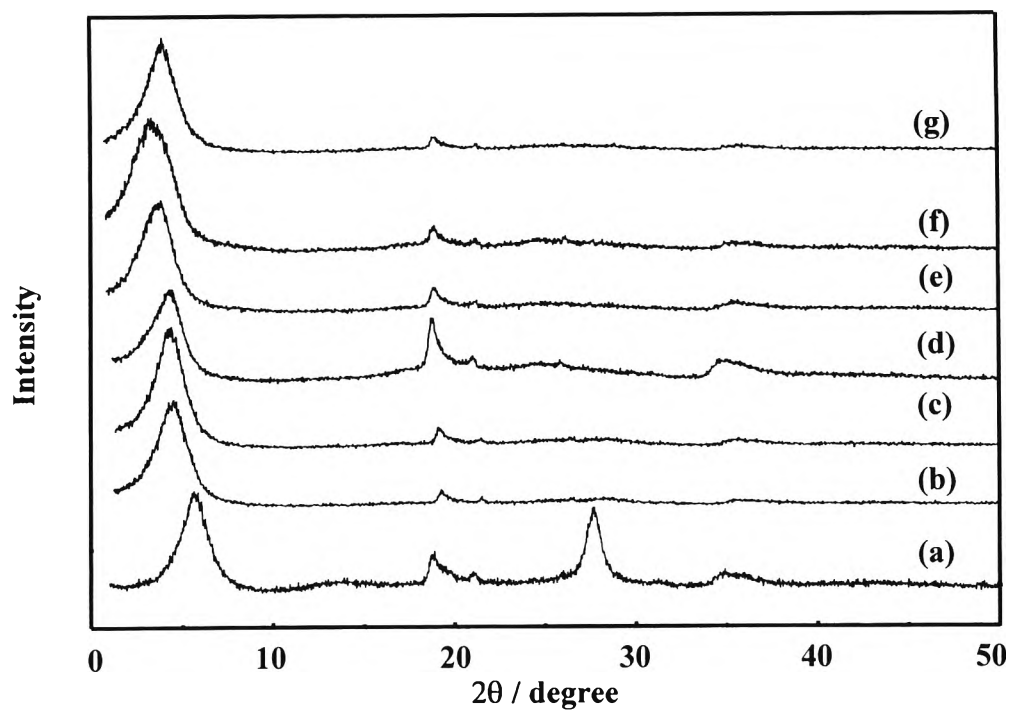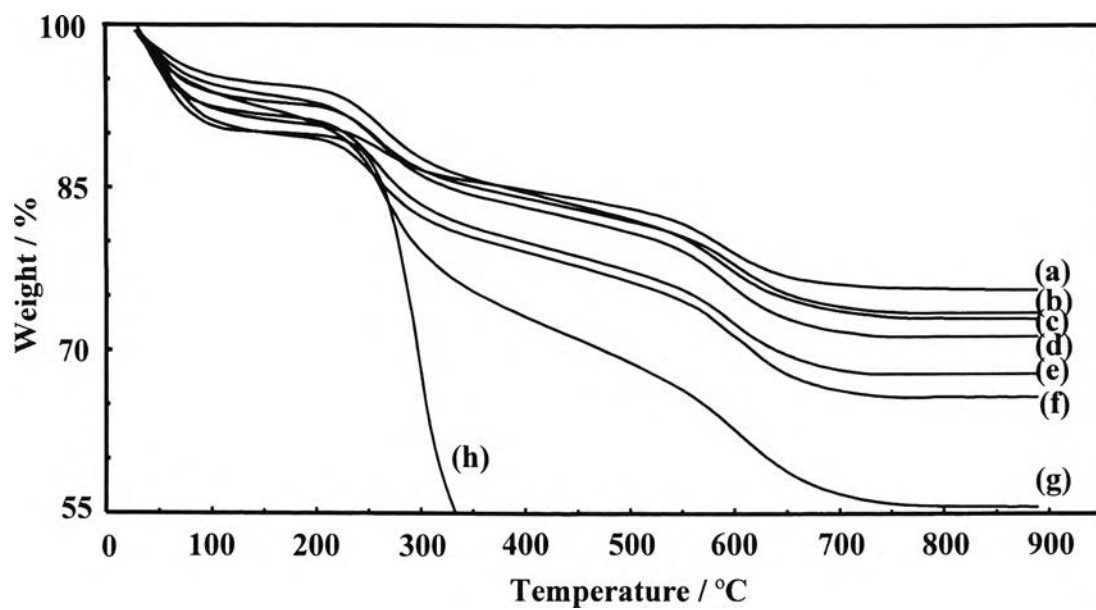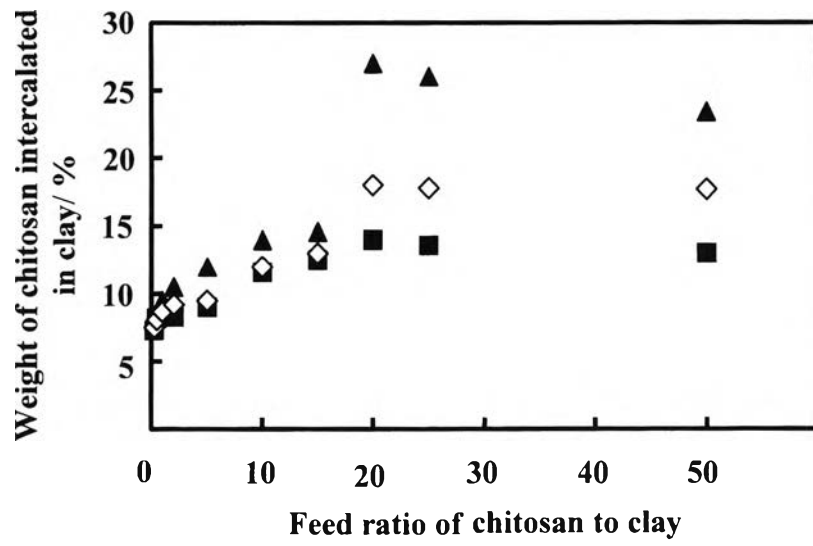
Figure 1.

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