

PREPARATION OF SILICA-CHITOSAN HYBRID FILLERS FROM AGRICULTURAL WASTE BY SOL-GEL TECHNIQUE

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Abstract

Hybrid materials were produced by rice husk ash (RHA) and shrimp shell chitosan (CS) via sol-gel technique. Na_2SiO_3 solution was used as SiO_2 precursor, which was prepared from acidic treatment and thermal treatment of RHA. CS was extracted from shrimp shell waste by demineralization, deproteinization, and deacetylation. Na_2SiO_3 solution was reacted with CS solution to get precipitated SiO_2 -CS hybrid materials. Hybrid material weight ratios (SiO_2 -CS) were 1:1, 2:1, and 3:1. The characteristics of the hybrid materials were characterized using Fourier transform Infra-red spectroscopy (FT-IR), Field Emission Scanning Electron microscopy (FE-SEM), Energy Dispersive X-Ray Analysis EDX, Surface area and pore volume by BET technique, and X-ray diffraction (XRD). The FTIR spectrum of hybrid materials showed the entity of SiO_2 -CS which can also be observed from XRD diffraction patterns and EDX charts. The morphology of hybrid material from FE-SEM analysis exhibited rough and irregular surfaces. The optimum weight ratio of SiO_2 -CS to be used as a filler in polymer composite is 2:1. This ratio gave the material with the surface area, the total pore volume, the average pore diameter, and the average particle size of $441 \text{ m}^2/\text{g}$, $0.60 \text{ cm}^3/\text{g}$, 5 nm and 14 nm , respectively.

Keywords: Rice husk silica, Sodium silicate, Shrimp shell chitosan, Sol-gel, Hybrid materials, Hybrid fillers

Introduction

Rice is not only Thailand's most important crop but also the primary agricultural export. Thailand has for decades been one of the world's largest rice exporters. Rice husk (RH) is a waste product from the rice milling process. It was used in several applications such as adsorbent, biomass feedstock, coating, and filler (Kumar *et al.*, 2013). The rice husk ash (RHA) is a product from RH burning process.

RHA can be converted into soluble sodium silicate (Na_2SiO_3) by reacting with aqueous sodium hydroxide. Sodium silicate can be used as a raw material to produce SiO_2 nanoparticles via sol-gel technique.

Due to its high surface area and silanol groups (Si-OH) on the surface, SiO_2 nanoparticles are popularly used as a filler in composite materials. In

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addition, SiO₂ nanoparticles from RHA has more advantages in terms of its renewable and abundant (Jembere and Fanta, 2017).

In addition, the waste from fishery like shrimp shells, crab shells, and cuttlefish bones are the source of chitin. Chitin is the second widespread biopolymer available in nature. Chitosan (CS) is a carbohydrate polymer consisted of amino groups and hydroxyl groups produced by the deacetylation of chitin. CS can be soluble in acid solution. The advantages of CS are biocompatibility, biodegradability, and anti-bacterial (Hajji *et al.*, 2014). CS from shrimp shells was obtained by following processes, (1) demineralization to remove their calcium carbonate by acid solution (2) deproteinization to remove their protein using alkaline treatment with base solution giving the material that called chitin, and (3) deacetylation to remove acetyl groups from chitin using alkaline treatment with strong base solution (El Knidri *et al.*, 2018).

Preparation of SiO₂-CS hybrid composites by using tetraethoxysilane (TEOS) as a SiO₂ precursor and precipitation by hydrolysis process was reported (Yeh *et al.*, 2007; Smitha *et al.*, 2008). In this study, sodium silicate (Na₂SiO₃) from RHA was used as a SiO₂ precursor. It was precipitated by using CS solution and acetic solution. The goal of this work is to prepare and characterize SiO₂-CS hybrid material from agricultural waste with various ratio between SiO₂ to CS.

Materials and Methods

Materials

RH was obtained from the local rice mill in Nakhon Ratchasima, Thailand. Shrimp shells were obtained from Terd-Tai Seafood Market in Nakhon Ratchasima, Thailand. Hydrochloric acid (HCl), acetic acid, and sodium hydroxide (NaOH) were purchased from ITALMAR (Thailand) Co., Ltd.

Experimental

Preparation of RHA from RH

RH was cleaned by tap water and washed with deionize (DI) water to eliminate any impurities. The washed RH was then oven-dried at 50°C overnight and refluxed with 6 M HCl at 65°C for 3 h. When the reaction was completed, the refluxed RH was washed with DI water several times to remove acid (Moosa and Saddam, 2017).

Preparation of CS Solution from Shrimp Shells

Shrimp shells were rinsed with boiling water several times to eliminate impurities and washed

with DI water, then oven-dried at 80°C overnight. After that, the dried shrimp shells were ground to get shrimp shell powder. The shrimp shell powder was demineralized using 3 M HCl solution to remove calcium carbonate (CaCO₃) at 75°C for 2 h under constant stirring with the speed of 150 rpm. Then, it was washed with DI water and filtered until it was free of acid. The filtered material was oven-dried at 80°C overnight. The obtained material was carried out using 10% NaOH solution at 80°C for 2 h to remove the remaining proteins and other organic materials. After that, it was washed and filtered with DI water until it was neutral. The filtered material was oven-dried at 80°C overnight. The chitin was finally obtained. The deacetylation was used to prepare CS from chitin. The deacetylation was carried out with 50 % NaOH solution at 100°C for 2 h 30 min. After that, it was washed and filtered with DI water until it was neutral. Then, the filtered material was oven-dried at 80°C overnight. Then CS was obtained. The CS solution was prepared by dissolving CS with 2% acetic acid (El Knidri *et al.*, 2018).

Preparation of SiO₂-CS Hybrid Material

SiO₂-CS hybrid material was prepared using Na₂SiO₃ solution and CS solution via sol-gel technique. Na₂SiO₃ solution is a SiO₂ precursor that prepared by dissolving the RHA with 2.5M NaOH (5% w/v). The CS solution was prepared by dissolving the CS with 2% acetic acid (1% w/v). The Na₂SiO₃ solution and CS solution were mixed with ratios of SiO₂-CS (3:1, 2:1, and 1:1). The pH of the mixture was adjusted to 7 by using 2% acetic acid and kept in 24 h to form SiO₂-CS hybrid gel. The hybrid gel was washed several times to eliminate the excess of sodium acetate and oven-dried at 80°C overnight. The obtained material was SiO₂-CS hybrid material.

Characterization

X-ray diffractometry was applied to confirm the amorphous structure of RHA and detect peaks of CS from shrimp shells. X-ray diffractometer (XRD, Bruker D2 PHASER) with Ceramic Cu X-ray source at a 30 kV and 10 mA was used. FTIR spectra of the samples were performed by using Fourier transform infrared spectrometer (FTIR, Bruker Tensor 27) in the frequency range of 400-4,000 cm⁻¹ at a resolution of 4 cm⁻¹. Moreover, the degree of deacetylation (DD) of CS from shrimp shells was calculated using Equation (1):

$$(\%DD) = 100 - [(A_{1655}/A_{3450}) \times (100/1.33)] \quad (1)$$

where A1655 is the amide absorbance at $1,655\text{ cm}^{-1}$ and A3450 is the hydroxyl absorbance at $3,450\text{ cm}^{-1}$ (Anand *et al.*, 2014).

The surface morphology of RHA and CS from shrimp shells were observed using Scanning electron microscope (SEM, JEOL JSM-6010LV). The surface morphology and elements of hybrid materials were observed using Field emission scanning electron microscope (FE-SEM, Zeiss AURIGA FE-SEM/FIB/Energy Dispersive X-Ray Analysis EDX). The surface area, the total pore volume, the average pore volume, and the average particle size of hybrid materials were measured using Surface Area Analyzer, (BET, 3Flex Micromeritics, USA) with a degas temperature at 250°C .

Result and Discussion

X-ray Diffraction (XRD)

The X-ray diffraction patterns of RHA, CS, and hybrid materials were shown in Figure 1. The XRD pattern of RHA showed a broad peak at $2\theta\sim 22^\circ$ and a small sharp peak at $2\theta\sim 26^\circ$ which were attributed to a pattern of amorphous SiO_2 and crystalline SiO_2 (Quartz), respectively (Yuvakkumar *et al.*, 2012; Adams *et al.*, 2014). The XRD pattern of CS showed the diffraction peaks at $2\theta\sim 10^\circ$ and 21° indicating the fingerprints of α -chitosan and γ -chitosan (Ameh *et al.*, 2015). The XRD pattern of hybrid materials at various ratios showed the diffraction peaks at $2\theta\sim 10^\circ$, 21° , 22° , and 28° corresponding to the characteristics of SiO_2 and CS. However, at $2\theta\sim 28^\circ$ the crystalline phase of SiO_2 (Cristobalite) was shown (Ebisike *et al.*, 2018) (Adams *et al.*, 2014).

Fourier Transform Infrared Spectroscopy (FTIR)

The FTIR spectrum of RHA, CS, and hybrid materials were shown in Figure 2. The RHA spectrum showed peaks at the wavenumbers of 462, 798, 1,068, 1,367, and $3,460\text{ cm}^{-1}$. The peak at 462, 798, and $1,068\text{ cm}^{-1}$ were assigned to the bond rocking of the Si-O, symmetric Si-OH bending (silanol), and asymmetric Si-O-Si stretching, respectively (Tuan *et al.*, 2017). The FTIR spectrum of CS showed peaks at wavenumbers of 3476 and $2,925\text{ cm}^{-1}$ assigned to the stretching vibrations of -OH bond and the stretching vibrations of C-H bond. The peaks at 1,658, 1,587, 1,421, and $1,382\text{ cm}^{-1}$ were assigned to C=O stretching of the amide I, N-H bending of amide II, C-H bending, and OH bending, respectively. The peaks at 1,155 and $1,028\text{ cm}^{-1}$ were assigned to asymmetric stretching of C-O-C bridge and C-O stretching (Yasmeen *et al.*,

2016). The degree of deacetylation of CS was calculated by using the absorbance of -OH band and amide I band. %DD of CS was around 65%. All spectrum of hybrid materials showed the same peaks that included the peaks of SiO_2 and the peaks of CS. This indicated that the hybrid materials contained both constituents. The reduction of symmetric Si-OH bending peak of the hybrid materials compared with RHA indicated the interaction between the functional groups of CS and Si-OH (silanol) of RHA.

Field Emission Scanning Electron Microscopy (FE-SEM, EDX) And SEM Analysis

The morphology of the hybrid materials was shown by FE-SEM images in Figure 3. The hybrid material showed an irregular surface indicating higher surface area compared to RHA and CS as shown in Figure 4. In Figure 5, the EDX spectra

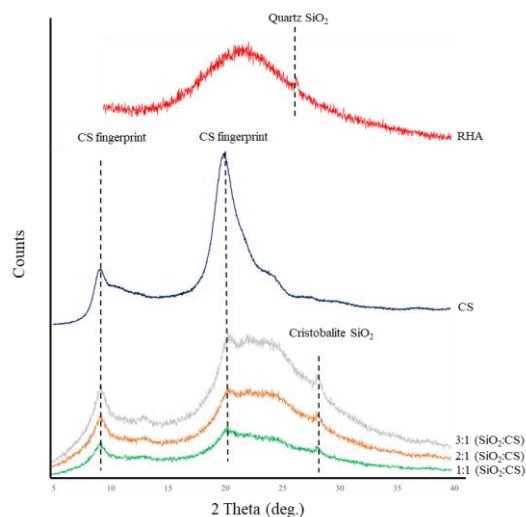


Figure 1. The X-ray diffraction patterns of RHA, CS, and hybrid materials at various ratio

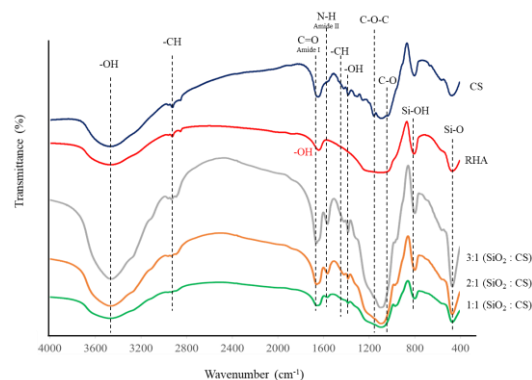


Figure 2. The FTIR spectrums of RHA, CS, and hybrid materials at various ratio

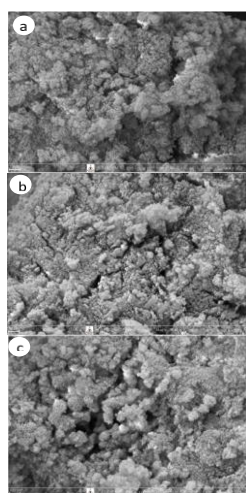


Figure 3. FE-SEM images of the SiO₂-CS hybrid materials (a) 3:1, (b) 2:1 and (c) 1:1 ratio

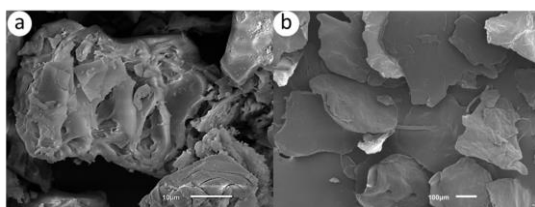


Figure 4. SEM images of (a) RHA and (b) CS

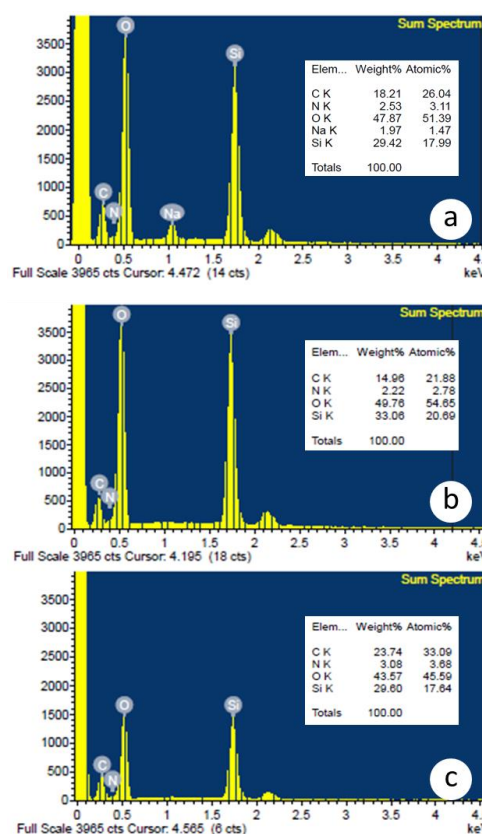


Figure 5. EDX Spectra of the SiO₂-CS hybrid materials (a) 3:1, (b) 2:1, and (c) 1:1 ratio

Table 1. The characteristics of SiO₂-CS hybrid materials

sample	BET Surface Area(m ² /g)	Total Pore Volume (cm ³ /g)	Average Pore Diameter (nm)	Average Particle Size (nm)
SiO ₂ -CS 3:1	265	0.49	7	23
SiO ₂ -CS 2:1	441	0.60	5	14
SiO ₂ -CS 1:1	196	0.27	5	31

showed the elemental composition of hybrid materials. At the ratio of 2:1 (SiO₂-CS), the highest content of Si was also presented by EDX analyzer.

Surface Area and Porosity Analysis

A strong physical contact between filler and polymer matrix was promoted by using a high surface area material as a filler (Conradi, 2013). In this study, the obtained hybrid material showed a high surface area which can be used as a filler in composites. The characteristics of SiO₂-CS hybrid materials were given in Table 1. At the ratio of 2:1 (SiO₂:CS), the highest surface area and total pore volume were obtained. According to the smallest average particle size, this is the suitable ratio to produce the hybrid material to be used as a filler.

The precipitated SiO₂ by sol-gel reaction of Na₂SiO₃ and acid typically has an average size of 30 nm and BET surface area of 5-100 m²/g (Zhang and Cresswell, 2016).

Conclusions

SiO₂-CS hybrid material was successfully prepared from the agricultural waste. The obtained RHA from RH was achieved with high purity. The obtained CS from shrimp shells has the degree of deacetylation about 65%. The optimum ratio between SiO₂ and CS was 2:1 which gave the material with the highest BET surface area and had a potential to use as a filler in composite materials.

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