

CHAPTER VI

PREPARATION OF POROUS HYBRID COMPOSITE FROM CALCIUM SAND

4.1 Abstract

Koh Samed sand, which contains mostly calcium carbonate, was chosen to prepare a porous hybrid composite because it is cheap and non toxic. High molecular weight poly(vinyl alcohol) (PVA) was used as an organic phase, while boric acid was added as a crosslinking agent to improve mechanical properties. The resulting products were characterized by X-ray diffraction (XRD), Fourier transform infrared (FTIR) spectroscopy, Thermogravimetric analysis (TGA), and electron microscopy (SEM) and gas pycnometer. In order to use this hybrid porous material as a sensor to detect nickel ions (Ni^{2+}) in waste water from batteries or nickel alloy manufacturers, 2% (w/w) Dimethylglyoxime (DMG) in ethanol was added as a detector. The formation of the $\text{Ni}(\text{DMG})_2$ complex from nickel (II) ions and DMG had a red-pink complex ion that was visible to the naked-eye. Spectrophotometric measurements were taken to test colorimetric response.

4.2 Introduction

In Thailand, there are many sources of sand as we know that koh-samed is the famous place in Thailand for tourism. Normally, sand's structure is mainly contained with silica while koh-samed's sand is different (Soontaree, 1997). Koh-samed's sand is a raw material which is abundant natural resource. Its particle is a grain, then the pulverize process, which is wasting time and costing too much, is not necessary. Lastly, since koh-samed's sand mainly contains with calcium carbonate, then it's a good choice to bring this sand to use as filler in hybrid porous material; which has high surface area with highly porous, lightweight, hydrophilicity and good mechanical properties. In this project, the preparation of hybrid composite of Koh-samed's sand increases value of original sand. Moreover it is the way to use a new natural resource for future. The final product which is CaCO_3 -PVA hybrid composite was studied on its porous properties and mainly focused on its physical property

which is porous structure, light weight and its application as a heavy metal detector. Morphology and physical properties of calcium carbonate (CaCO_3) based porous composite are, thus, focused. Finally, its properties will be used as a heavy metal (Nickel) detector. These proposed DMG and CaCO_3 -PVA hybrid composite material could be used as naked-eye sensor for nickel in waste water from batteries or nickel alloy manufactures.

4.3 Experimental

A. Materials

Koh-samed's sand was collected from Koh Samed, Rayong. Polyvinyl alcohol (PVA Mw~108,000g/mol and 99.7 mole% hydrolysis) was purchased from Polysciences. Boric acid, Nickel-Standard solution (1000 mg/L Ni) and Ethanol (analytical grade), was purchased from Merck. Acetone was purchased from Lab-Scan. Dimethylglyoxime (DMG) was purchased from Univar. All chemicals were used without further purification, distillation water was used throughout this study.

B. Synthesis of calcium carbonate (CaCO_3) from Samed sand

Samed sand was finely ground by a ball mill. The obtained samed sand powder was separated by a sieving machine to collect particles less than 150 micron, followed by calcination in a furnace from room temperature to 600 °C with a heating rate of 5 °C/ min and held at 600 °C for 5 h. White powder of CaCO_3 sand was kept in a dessicator.

C. Preparation of PVA- CaCO_3 hybrid composite material

Polyvinyl alcohol was dissolved in water at 85 °C for 4 h. with magnetic stirrer (400 rpm), followed by adding calcium carbonate sand. Various amounts of polyvinyl alcohol in water (3, 5, 7, and 9% weight in water) by fixing the optimum content of boric acid which was a crosslinking agent at 1.5 mL of 1M boric acid. Different the weight ratios of poly vinyl alcohol and calcium carbonate sand (75:25, 50:50 and 25:75) were varied. Then the mixture of poly vinyl alcohol and calcium carbonate sand was homogenized for 1 h with magnetic stirrer (400 rpm). Boric acid

solution (1.5 mL, 1M of boric acid) was added into polyvinyl alcohol solution at 85 °C and stirred until homogeneous. After mixing, the obtained highly viscous solution and was added into a plastic mold before placing into a refrigerator at -3 °C for 12 h. This freeze/Thaw process was repeated for 5 cycles, followed by immersing in acetone for solvent exchange for 3 days.

D. Preparation of PVA-CaCO₃ hybrid composite as a nickel sensor

The synthesis produces were similarly to preparation of PVA-CaCO₃ hybrid composite material as mentioned earlier, but the first step, 2 wt% DMG dissolved in ethanol was mixed together with 5 wt% of PVA in water. The volume ratios of water and 2 wt% of DMG in ethanol were varied as follows: (9:1, 8:2, 7:3, 6:4 and 5:5) 1.5 mL.

E. Characterizations

The morphology of the PVA-CaCO₃ hybrid composite was characterized by using scanning electron microscope (Hitachi FE-SEM S4800/Scanning Electron Microscope). The structural information of PVA-CaCO₃ hybrid composite was determined by FTIR (Thermo Nicolet, Nexus 670/Fourier Transform Infrared Spectrophotometer). Koh Samed's sand was characterized by DMAX 2200 HV/X-Ray Diffractometer using XRD in 2θ bragg angle. The porosity of PVA-CaCO₃ hybrid composite material was identified by a gas pycnometer Quantachrome, Ultrapycnometer1000. The reflectance spectrum was obtained by using the fiber-optic spectrophotometer (Ocean optic red tide USB 650), which was connected to a PC.

F. Sensor performance testing

The Ni (II) solutions (0.1, 0.5, 1, 2, 3, 4, 5, 8 and 10 ppm) were prepared by diluting 1000 ppm stock solution with distilled water and adjusting the pH to 9 with 10% ammonium solution. The samples were cut into a disc-shape with the diameter of 2.4 cm and placed in Ni (II) solutions for 2 hrs. After drying in air, the color change of the samples was then observed by UV-spectrophotometer at 547 nm.

4.4 Result and Discussion

4.4.1 Characterizations of Koh Samed's sand

X-ray diffraction was an important tool to inform the composition. Samed sand was characterized by using XRD. The spectrum is shown in figure 4.1, the intense peak was shown at 30° in 2θ scale which can certify it Mineralogical species of calcite were characterized by X-ray powder diffraction employing Bruker Axs diffractometer using monochromated Cu-K α ($\lambda=1.5406 \text{ \AA}$), the result shown that Koh Samed's sand was 99.5% calcium carbonate.

Figure 4.1 shows the XRD pattern of the CaCO_3 from sand. The characteristic peaks at $2\theta = 24.02^\circ, 29.6^\circ, 39.48^\circ, 43.30^\circ, 47.36^\circ, 48.65^\circ, 57.55^\circ, 61.34^\circ$ corresponding to the peaks of CaCO_3 , which are in agreement with those appeared in JCPDS (JCPDS 37-1497) as shown in figure 4.2.

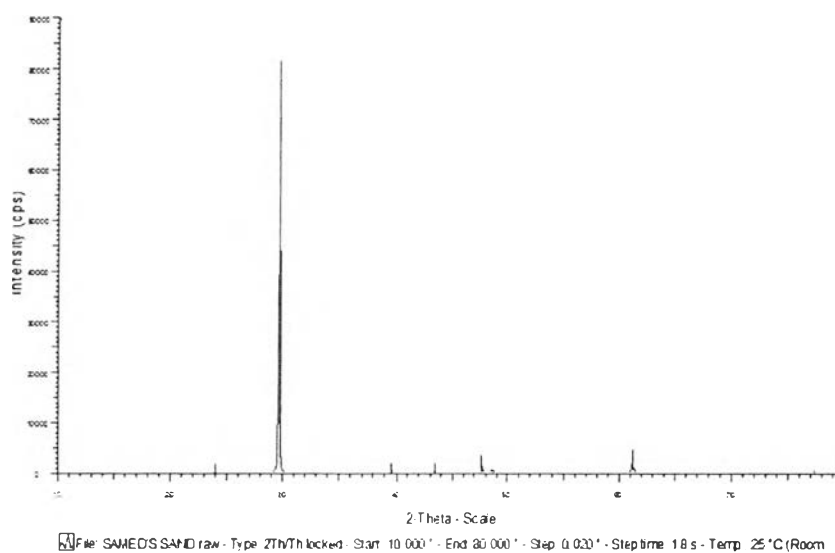


Figure 4.1 XRD spectra of calcium carbonate sand 2θ bragg angle.

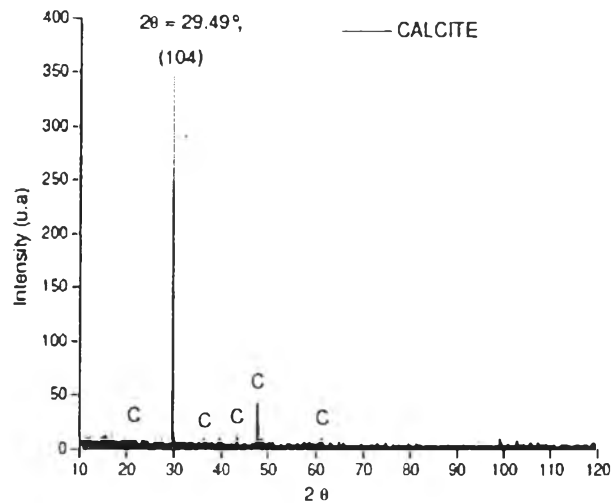


Figure 4.2 X-Ray diffraction patterns of calcite (In agreement with JCPDS, card N°-05-0586).

CaCO_3 powder which was whole from Samed sand was characterized by FT-IR. It was not pass pulverizing process before characterized. The FT-IR spectra of CaCO_3 powder was shown in Fig. 4.3. The characteristic bands at 700, 873, and 1450 cm^{-1} represent characteristics of the C–O asymmetric stretching, out-of plane of C–O, and in-plane bending modes of C–O respectively (Engin *et al.*, 2006).

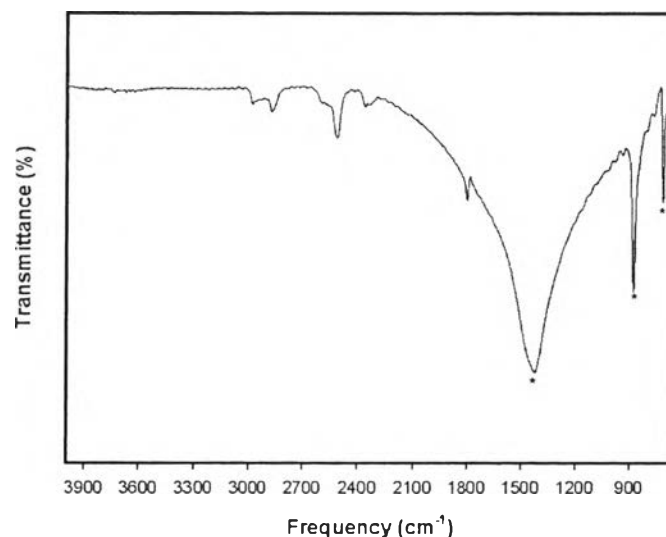


Figure 4.3 FT-IR spectra of CaCO_3 from Samed sand.

4.4.2 Preparation of PVA-CaCO₃ hybrid composite material

The PVA-CaCO₃ hybrid composite material was synthesized from high molecular weight polyvinyl alcohol (Mw~108,000g/mol and 99.7 mole% hydrolysis), calcium carbonate sand and water via sol-gel method. PVA was crosslinked by using 1M boric acid solution.

4.4.2.1 The variation of PVA in water

The content of PVA was varied in to 4 conditions which are 3%, 5%, 7% and 9% in water (by weight). The time that use to dissolve PVA with 200 rpm stirring and heat is shown in table 4.4.

Table 4.4 The preparation of different content of PVA in water.

Content of PVA (g)	Content of water (g)	Percent by weight of PVA in water	Time to dissolve (h)
3	10	3%	4
5	10	5%	4
7	10	7%	5
9	10	9%	12

From the different time that uses to dissolve PVA, 9% of PVA use too long time to dissolve which wasted the time and energy. The polymer which had high molecular weight, it would take a long time to dissolve. The content of PVA was 10 % by weight in water solution, it was regarded as heavy in water, so the high molecular weight of PVA usually use for a few % by weight. The solution of 9% PVA by weight was ignored to use in the synthesis (Lozinsky *et al.*, 1998).

4.4.2.2 The variation of CaCO₃ in matrix

The PVA-CaCO₃ interaction was characterized by using FT-IR to examine the functional groups. The spectrum is shown in figure 4.5.

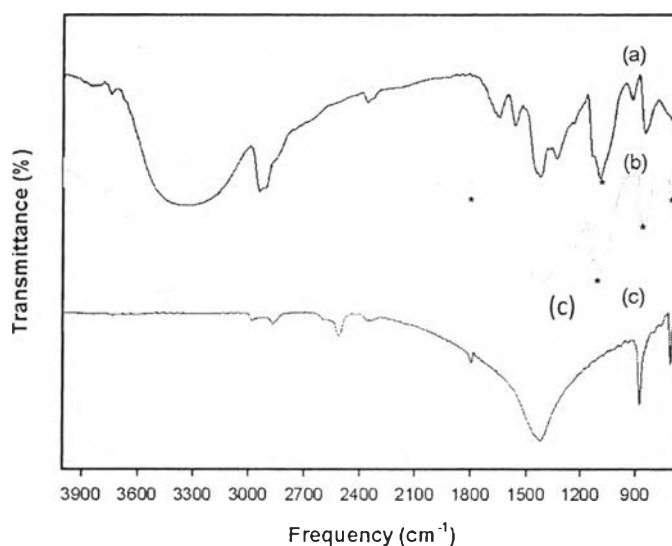


Figure 4.5 The FTIR spectra of pure PVA (a), PVA-CaCO₃ composite (b) and calcium carbonate (c).

The strong adsorptions at 1653, 3438 and 2936, cm⁻¹ are assigned to the stretching vibrations of carbonyl group, methyl groups and OH groups of PVA. The characteristic peak of C–O stretching vibrations of PVA is observed at 1095 cm⁻¹. The weak adsorption at 917 cm⁻¹ corresponded to C–C stretching vibrations of PVA (Iwamoto *et al.*, 1979). From Fig. 4.5(b), pure PVA which experienced the same sequential processes but without adding mineral phase, the new adsorption peak at 713, 857 and 1789 cm⁻¹, represent the peak of CaCO₃ in the hybrid composite can form bonding with CaCO₃ (Manoli *et al.*, 2000). The C–O characteristic peak of PVA was shifted from 1095 cm⁻¹ to 1100 cm⁻¹, indication the bond formation between PVA and CaCO₃ (Choi *et al.*, 2002).

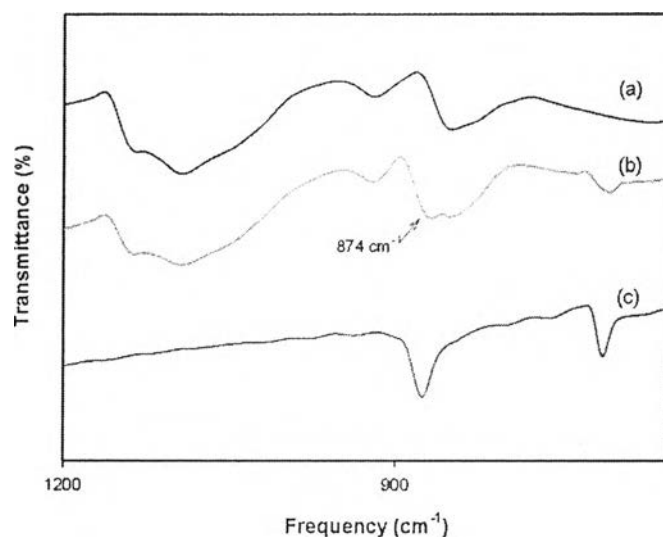


Figure 4.6 The FTIR spectra of pure PVA (a), PVA-CaCO₃ composite (b) and calcium carbonate (c).

Scrutinizing these FTIR spectra give further evidence. The FTIR spectra of pure PVA and the composites in the range of 1200–600 cm⁻¹ are shown in figure 4.6. However, a shift of the C–O characteristic adsorption was observed, 1095 cm⁻¹ for pure PVA and 1100 cm⁻¹ for the composites, confirming the occurrence of molecular interactions between organic and inorganic components in preparation of PVA–CaCO₃ composites. Relevant information about the polymorphs of calcium carbonate could also be drawn from the FTIR spectrum within this range. The adsorption at 874 was used to identify calcite (Choi et al., 2002).

Volumetric shrinkage of the sample can be calculated, using the following equation;

$$\% \text{Shrinkage} = \frac{V_{\text{wet}} - V_{\text{dry}}}{V_{\text{wet}}} \times 100 \quad (1)$$

V_{wet} = Volume of wet sample which is not eliminated water.

V_{dry} = Volume of dried sample which is completely eliminated water.

The volumetric shrinkage of material is an important factor for the synthesized via ambient dry method and affects on the physical properties of the materials. Figure 4.8, 4.9 and 4.10 represent percent shrinkage of the material obtained from various ratios of PVA and CaCO_3 and percent weight of PVA in water in 1.0, 1.5 and 2.0 mL respectively.

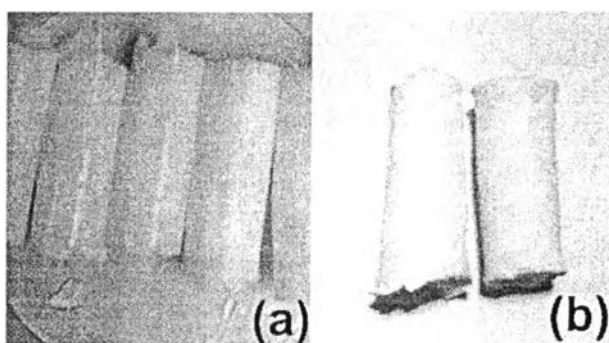


Figure 4.7 Material before (a) and after (b) drying.

The volume shrinkage has measured by calculating, the material before drying and after drying have measured the volume then calculated by the equation 1.

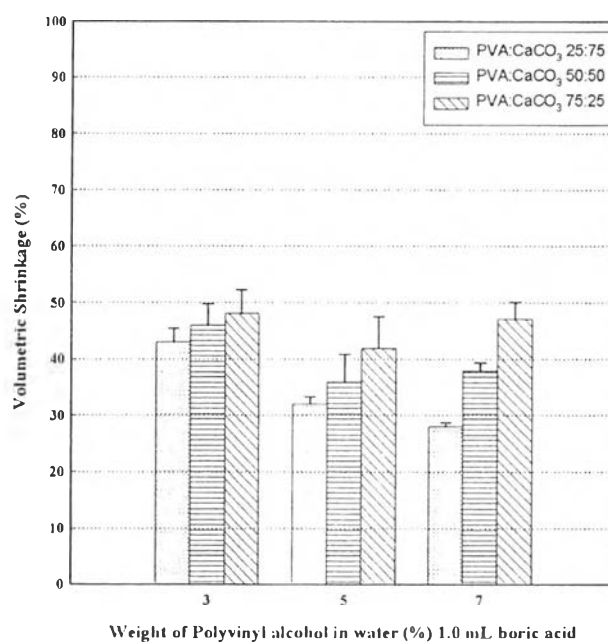


Figure 4.8 Percentage of shrinkage using various ratios of PVA and CaCO_3 and different percentages of PVA in water (with 1.0 mL; 1M boric acid solution).

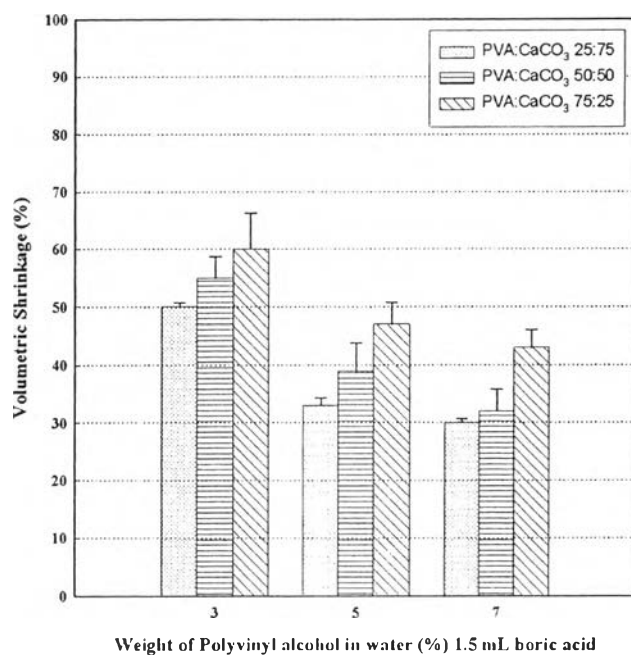


Figure 4.9 Percentage of shrinkage using various ratios of PVA and CaCO₃ and different percentages of PVA in water (with 1.5 mL; 1M boric acid solution).

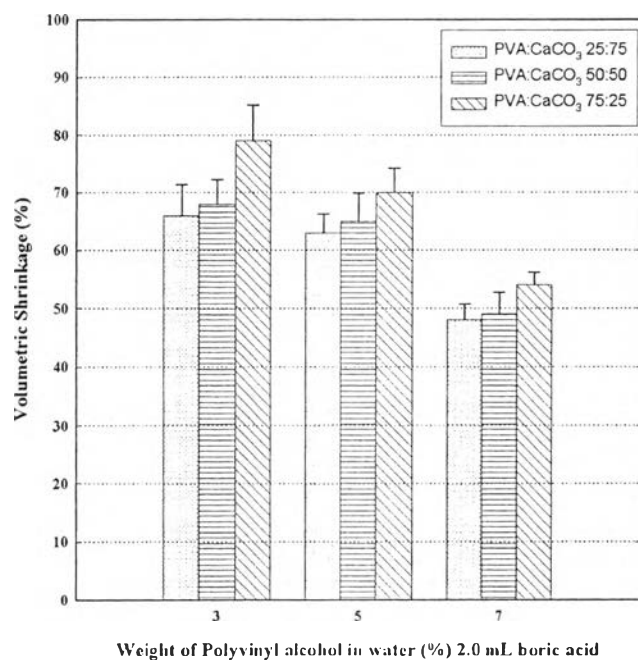


Figure 4.10 Percentage of shrinkage using various ratios of PVA and CaCO₃ and different percentages of PVA in water (with 2.0 mL; 1M boric acid solution).

It was found that PVA which dissolved water led to the shrinkage of material because PVA has high molecular weight and flexible chain, and when the solvent in the material was eliminated via ambient drying, the surface between PVA and water was collapsed and cause the shrinkage of the material. An increase of the PVA content led to a decrease in the volume shrinkage of the material because the lower percentage of PVA in water has more space area after removing water from the material (Safronova *et al.*, 2007 and Krokida *et al.*, 1998). However, 3% PVA in water gave the highest shrinkage when compare with 5 % and 7% wt PVA in water. Moreover the ratio of PVA: CaCO₃ at 75:25 showed the highest shrinkage.

Calcium carbonate has been one of the most commonly used inorganic fillers for thermoplastics; the higher content of CaCO₃ was added to PVA led to the lower shrinkage of material. The volume shrinkage of the composite using a calcium carbonate in different ratio in PVA in water showed the results in Fig. 4.8, 4.9 and 4.10. As can be seen, PVA- CaCO₃ porous composite with higher CaCO₃ has lower volume shrinkage than PVA-CaCO₃ with lower CaCO₃. Calcium carbonate will improve the mechanical properties, such as the shrinkage reducing after mould releasing (Sumita *et al.*, 1983). From FTIR results in figure 4.6 and 4.7 was confirmed that PVA chemically interacts with CaCO₃ (Safronova *et al.*, 2007).

4.4.2.3 The suitable content of Boric acid

The mechanism of PVA–boric acid crosslink is believed to be a didiol (two diol) complex, in which two diol units of polyvinyl alcohol chain with one borate ion to form a crosslink. It involved of the borate ion-aided crosslinking among polyvinyl alcohol molecules and the hydrogen bonding between the didiol complex and polyvinyl alcohol chains (Shibayama *et al.*, 1988).

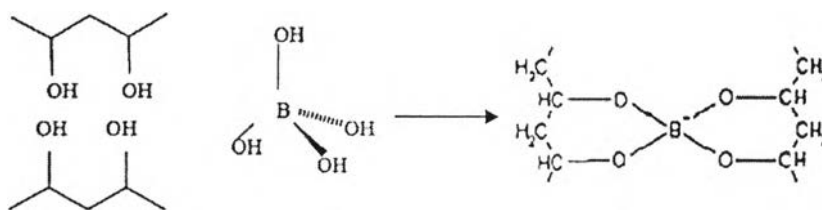


Figure 4.11 The reaction of forming a polymeric gel by boric and PVA (Zain *et al.*, 2011).

PVA that used in the synthesis has $M_w \sim 108,000 \text{ g/mol}$ and 99.7 mole% hydrolysis; the boric content can be calculated from the unit content of hydroxyl group of PVA as shown in table 4.12. The crosslink reaction was occurred by chemical crosslink (Fig 4.11).

Table 4.12 The content of boric acid solution at the volume that would completely react with various content of pure PVA from calculation

%PVA in water (wt)	1M Boric acid solution (mL)
3	1.48
5	2.74
7	3.73

From fig. 4.8, 4.9 and 4.10, they represent percent shrinkage of the material obtained from various ratios of PVA and CaCO_3 and percent weight of PVA in water in 1.0, 1.5 and 2.0 mL respectively. They can be estimated that the optimum shrinkage at different volume of boric acid solution, where shown in table 4.13.

Table 4.13 The content of boric acid solution at the optimum volume for various % PVA

% PVA by weight in water	The optimum volume of 1M Boric acid solution (mL)
3	1.0
5	1.0
7	1.5

From the synthesis, the adding of 2.0 mL boric acid solution made the solution of PVA-CaCO₃ has higher viscosity than adding of 1.5 and 1.0 mL. The relationship of viscosity of the polyvinyl alcohol solution with different boric acid contents was viscosity increased with an increase in boric acid content. This is because the degree of crosslinking is enhanced as the boric acid content is increased, leading to a higher viscosity (Wang *et al.*, 1999).

Moreover, from fig. 4.8, 4.9 and 4.10, which represent percent shrinkage of the material obtained from various ratios of PVA and CaCO₃ and percent weight of PVA in water in 1.0, 1.5 and 2.0 mL respectively. The volume of boric acid solution that used for pure PVA and used for PVA with CaCO₃ was different. The borate ion from boron boric acid was attached to form a crosslink with two diol units of polyvinyl alcohol. The PVA with CaCO₃ was already interacted at diol units so the unoccupied diol units were less than pure PVA without CaCO₃ that leads the less using volume that used in synthesis (Zain *et al.*, 2001). The PVA at 5% and 7% in water use the optimum volume of boric acid solution at 1.0 mL and 1.5 mL respectively. The relationship of PVA and volume of boric acid solution was direct variation to each other and corresponded to the mole ratio (Shibayama *et al.*, 1988).

At 3%, 5% and 7% of PVA in water with 2.0 mL of boric acid solution gave the highest shrinkage. When added a boric acid solution, the water (by product) was created which made the concentration of PVA in water changed from before, similarly to 5% and 7% when added boric acid solution at 2.0 mL. The mixture of

PVA-CaCO₃ which was already gel by boric acid was separated by water. Finally, the product that added 2.0 mL of boric acid solution has high shrinkage and unstable formed.

At 5% and 7% of PVA in water with 1.5 of boric acid solution gave the lower shrinkage for 7% of PVA than 5%, that because the 7% has high concentration; the water (by product) made the concentration slightly changed when compared with 5% and 3% of PVA. Moreover, the higher volume of boric acid solution gave the lower shrinkage of final product, because the higher boric acid crosslinked more than lower volume with PVA. The shrinkage of 7% PVA as final product goes lowest.

At 5% with 1.0 mL of boric acid solution gave the lower shrinkage than 1.5 mL of boric. As the same reason, at 1.5 mL gave water more than 1.0 mL which made the concentration of PVA changed.

From Fig. 4.8,4.9 and 4.10, it can be estimated that the optimum ratio of 7% and 5% PVA-CaCO₃ was occurred by 1.5 and 1.0 mL boric acid solution repectively.

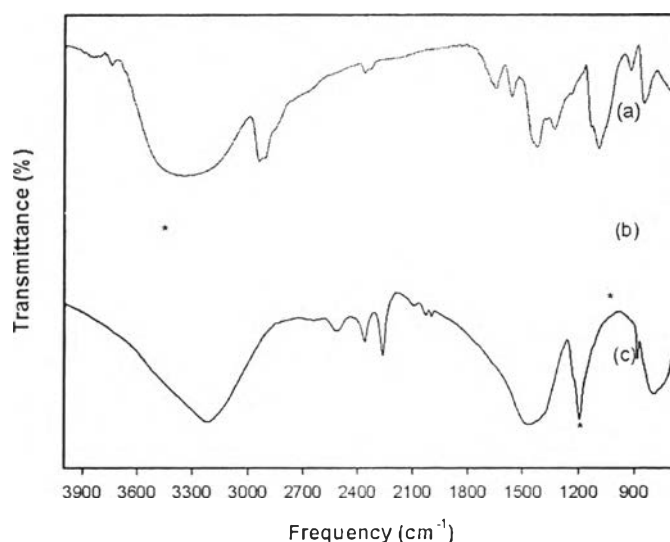


Figure 4.14 The FTIR spectra of pure PVA (a), crosslinked PVA (b) and boric acid (c).

FTIR spectra obtained for boric acid, PVA and PVA crosslinked with boric acid figure 4.14 In case of crosslink PVA, the absorption band at 3400-3500 cm^{-1} apparently disappeared and the new absorption peak at 1030 cm^{-1} was observed representing the stretching vibration of B–O–B bonds (Uslu *et al.*, 2007). This implies the chemical reaction between PVA and H_3BO_3 . Furthermore, the absorption band at 1198 cm^{-1} in the spectrum of boric acid was assigned to the deformation band of B–OH, which disappeared in crosslinked PVA (Yanase *et al.*, 2009).

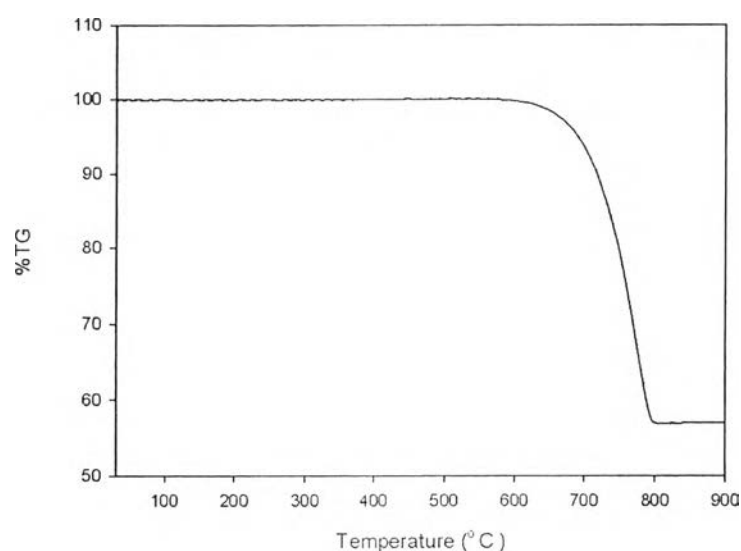


Figure 4.15 TGA thermograms of (a) Samed sand (CaCO_3).

Figure 4.15 presents the thermal properties of the samples obtained in this study. Fig 4.19 is belonging to the samed sand (CaCO_3), showing a step of the weight loss. The step of weight loss, 42 %, at 650° to 750 °C corresponded to the phase formation of CaCO_3 transforming to CaO by freeing CO_2 , as explained in equation (1). When consider at temperature 270-400 °C, there is no weight loss, which indicated decomposition of organic matter was not shown in the sand (Eric *et al.*, 2007).



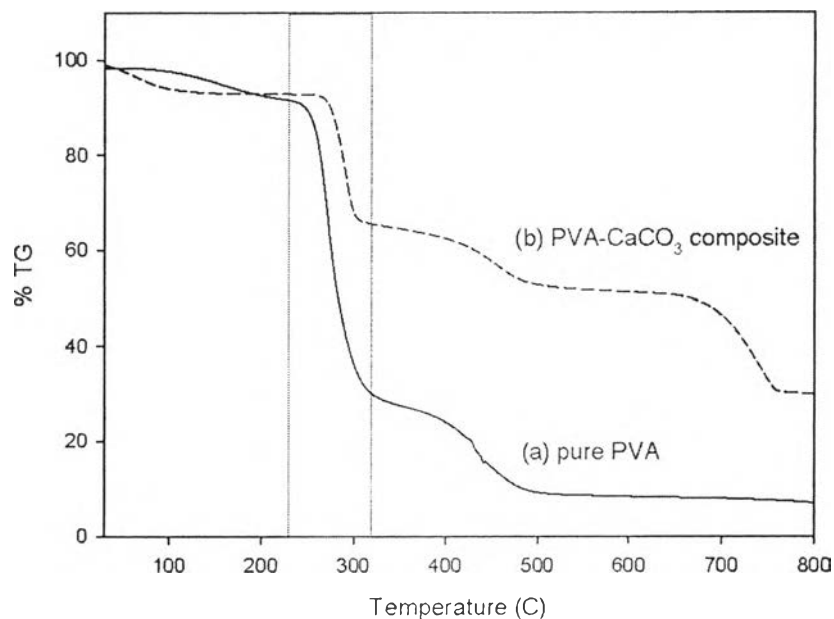


Figure 4.16 TGA thermograms of (a) pure PVA, (b) PVA-CaCO₃ porous composite.

The thermal decomposition of pure PVA and PVA-CaCO₃ porous composite have been studied previously nitrogen gas. Pure PVA can be observed in figure 4.16 (a), at temperature 80-100 °C, the %TG of pure PVA was slightly decreased because of moist in PVA. Furthermore, PVA is an organic phase, it can be degraded at temperature which higher than 80 °C because at high temperature break the bond in PVA structure.

The figure 4.16, curve (a) shows two regions of pure PVA, 235-255 °C and 400-450 °C. The composite material present in these regions have better thermal stability than PVA. In figure 4.16 (b), shows three regions of PVA composite, 255-275 °C, 400-450 °C and 600-700 °C. Figure 4.16 in comparison of pure PVA and PVA composite was observed. The major degradation peak shifted, in general, to higher temperature, that shown in figure 4.16.

TGA thermogram of PVA- CaCO_3 had three-step-degradation. According to Chan *et al.* (2002), the first degradation step at $235^\circ\text{--}255^\circ\text{C}$ is the elimination reaction of the polyvinyl alcohol with 10 %weight loss to give polyenes and water product as shown in figure 17 (a). However, the degradation temperature in the first step is not high enough to break the backbone chain of polyenes.

The second degradation step at $400^\circ\text{--}450^\circ\text{C}$ is chain-scission reaction of polyenes with 10 %weight loss, as shown in the Fig 4.21 b, to low-molecular-weight polyenes and gaseous product. The last transition region at $600^\circ\text{--}700^\circ\text{C}$ is the transformation of calcium carbonate residue to calcium oxide with the weight loss of about 18%, as shown equation 2 (Engin *et al.*, 2006).

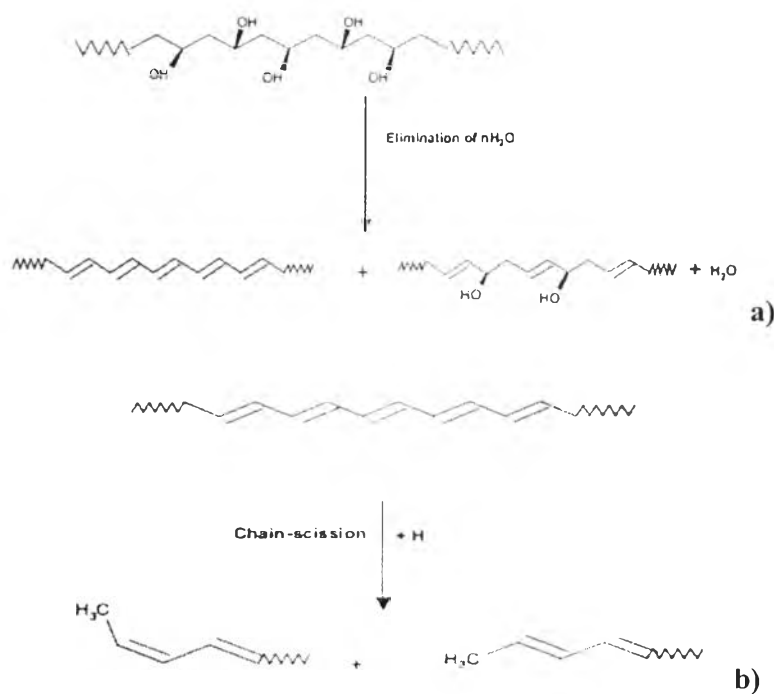


Figure 4.17 Diagram of (a) Elimination reaction of water and (b) Chain-scission reactions of polyenes (Peng *et al.*, 2007).

4.4.3 Material properties

4.4.3.1 The properties results of material in a variation of calcium carbonate sand and % PVA in water from ultracycnometer gas meter.

Finding the surface area to calculate the porosity of porous material has almost done by BET method, But for PVA structure which has mesopore was not applicable in this case (James, 2006). Porosity of the aerogel material was characterized using helium pycnometry. This method provides skeletal volume and density of the determined material. The porosity is calculated using either equation 3, 4 or 5. (Parmentier *et al.*, 2001). The morphology of materials was characterized by SEM and gas pycnometer

$$\frac{1}{\rho} - \frac{1}{\rho_s} = \text{porosity} \quad (3)$$

$$\rho = \text{bulk density}$$

$$\rho_s = \text{skeleton density}$$

$$\text{Porosity} = \frac{\text{Bulk Volume} - \text{Skeletal Volume}}{\text{Bulk Volume}} \times 100 \quad (4)$$

$$\text{Porosity} = \left[1 - \left(\frac{\text{Skeletal Volume}}{\text{Bulk Volume}} \right) \right] \times 100 \quad (5)$$

Sample	5% wt PVA		7% wt PVA	
	(a) PVA : CaCO ₃ (1:1)	(b) PVA : CaCO ₃ (1:3)	(c) PVA : CaCO ₃ (1:1)	(d) PVA : CaCO ₃ (1:3)
Avg Density (g/cc)	0.7235	0.7354	0.9538	0.9865
% porosity	79.32%	77.61%	74.11%	73.59%

Table 4.18 The average density, average volume and % porosity of PVA with different sand contents (using; 1.5 mL of 1.0 M boric acid solution)

different sand contents (using; 1.0 mL of 1.0 M boric acid solution to 5% wt PVA in water and 1.5 mL of 1.0 M boric acid solution to 7% wt PVA in water).

Nevertheless, we found that CaCO₃ was well dispersed in all samples. The size of the porous is in a micrometer scale. In addition, the higher the CaCO₃ content, the higher the density of the composites. The content of PVA and calcium sand are both affected on the porous of material, the calcium sand content corresponded to its density. From the morphology observation, composite (1) PVA-CaCO₃ 50:50 (using; 1.5 mL of 1.0 M boric acid solution) was chosen for further use as a nickel sensor detector.

The bulk volume was measured by Vernier Caliper and the average volume was measured by ultracycrometer gas meter, and then calculated % porosity from above equation equation 2, 3 or 4 (Parmentier *et al.*, 2001).

The porosities of PVA-CaCO₃ porous hybrid material decreased as the PVA content increased because the increasing PVA content in the solution affects to a decrease in the content of the void and the pore, as shown in figure 4.18o, illustrating the morphologies of the porosities of PVA-CaCO₃ (Agda *et al.*, 2009).

Density, also an important physical property of the aerogel material, was measured by ultracycnometer gas meter.

$$\text{Density} = \frac{\text{Weight of material}}{\text{Volume of material}} \quad (6)$$

The densities of PVA-CaCO₃ porous hybrid composite using different percentages of PVA in water are shown, the density of the aerogel material increased with increasing the PVA content in water or decreasing the water amount in the system. In our previous work (Lorjai *et al.*, 2009), water provides voids or pores in the aerogel material, thus, the decrease of water results in the decrease of pores, making the increase in the density. As for different content of calcium carbonate, the density of PVA-CaCO₃ porous hybrid composite was increase when the filler increase (Safronova *et al.*, 2007).

However, the result of 5 wt% PVA in water with CaCO₃ in ratio 1:1 (PVA: CaCO₃) has highest % porosity as confirmed by the SEM micrograph in Fig. 4.13 (a). The Comparing between Fig. 4.13 (a), (b), (c) and (d) showed that calcium carbonate sand has good compatibility and dispersion, from SEM micrographs at the same magnification. The pore size was in micropore scale. The content of PVA and calcium sand are both affected on the porous of material, the calcium sand content corresponded to its thickness. The higher content of calcium sand made thicker pore wall, which decreased the porosity in material (Bai *et al.*, 2010).

In this studied, the highest porous was chosen for use as Nickel sensor. The material in condition of 5 wt% PVA in water with CaCO₃ in ratio 1:1 (PVA: CaCO₃) has highest % porosity with lowest density. The structure of all condition of material was stiff and tough.

4.4.3.2 The properties results of material in a variation of calcium carbonate sand and % PVA in water from SEM

Moreover, figure. 4.19 demonstrated the structural appearance of samples prepared from PVA solutions with different polymer contents. It was seen that with an increase in PVA concentration, both the amount and size of the macropores decrease (Lozinsky *et al.*, 1998).

The porosities of PVA-CaCO₃ porous hybrid composite materials decrease as the PVA content increase because the increasing PVA content in the solution affects to a decrease in the content of the void and the pore, as shown in Fig. 4.19 and 4.20, respectively(Agda *et al.*, 2009).

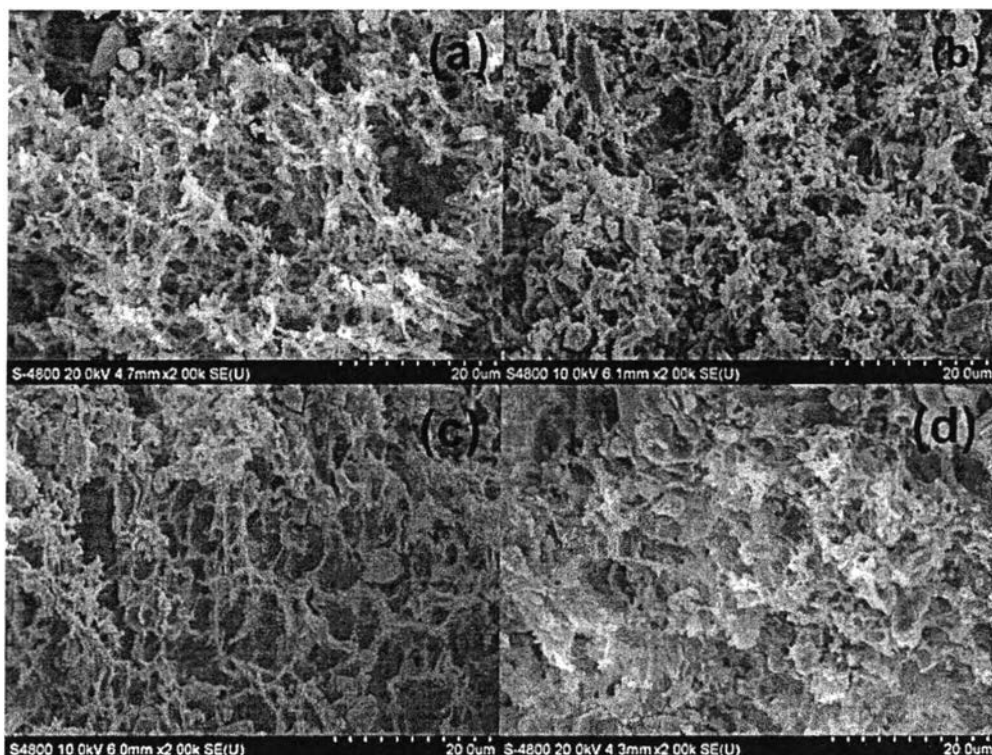


Figure 4.19 SEM micrographs at 2k magnified of (a) 5 wt% PVA in water with CaCO₃ in ratio 50:50, (b) 5 wt% PVA in water with CaCO₃ in ratio 25:75 (c) 7 wt% PVA in water with CaCO₃ in ratio 50:50 (d) 7 wt% PVA in water with CaCO₃ in ratio 25:75.

PVA being water soluble, biodegradable polymer bearing hydrophilic hydroxyl groups, served well as a stabilizer in the present protocol in preventing agglomeration of the particles thus resulting in good compatibility, dispersion, and distribution (Chan *et al.*, 2002).

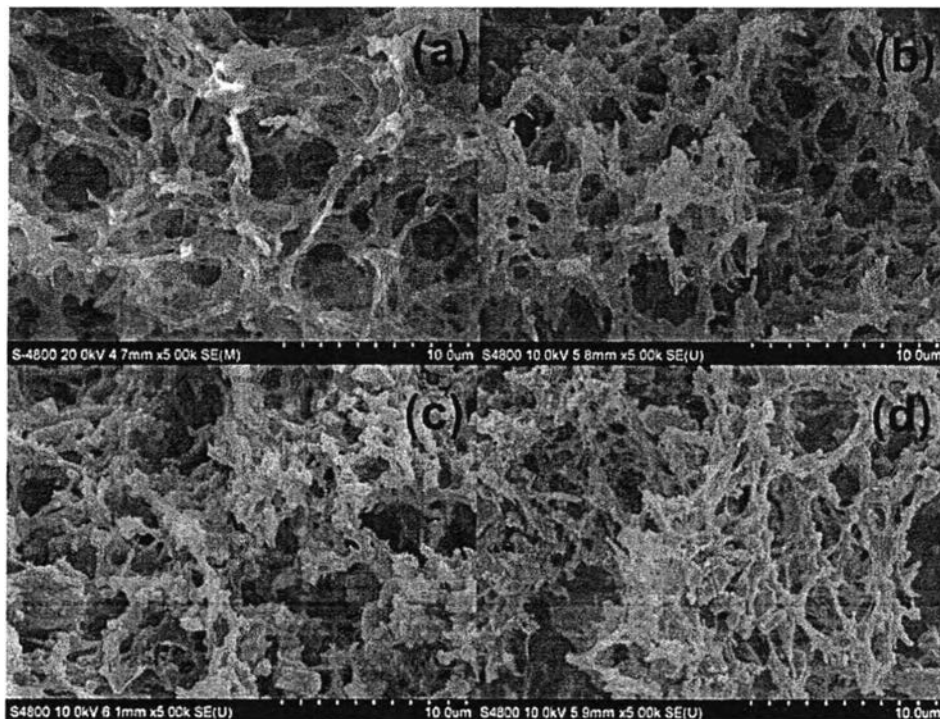


Figure 4.20 SEM micrographs at 5k magnified of (a) 5 wt% PVA in water with CaCO_3 in ratio 50:50, (b) 5 wt% PVA in water with CaCO_3 in ratio 25:75 (c) 7 wt% PVA in water with CaCO_3 in ratio 50:50 (d) 7 wt% PVA in water with CaCO_3 in ratio 25 : 75.

However, the calcium sand was dispersed all together in material. The pore size was in microscale. The content of PVA and calcium sand are both affected on the porous of material, the calcium sand content corresponded to its density. The higher content of calcium sand made higher density (figure 4.19 and 4.20) which decreased the porosity in material. The result of 5 wt% PVA in water with CaCO_3 in ratio 50:50 (PVA: CaCO_3) has higher porosity than 5 wt% PVA in water with CaCO_3 in ratio 25:75 (PVA: CaCO_3) probably due to the content of calcium carbonate sand was varied to 2 different contents at 0.5 and 1.5 g.

The morphology of materials was characterized by SEM and gas pycnometer. Table 4.22 shows the average density, average volume and % porosity of PVA with different sand contents. Nevertheless, we found that CaCO_3 was well dispersed in all samples. The size of the porous is in a micrometer scale. In addition, the higher the CaCO_3 content, the higher the density of the composites. The content of PVA and calcium sand are both affected on the porous of material, the calcium sand content corresponded to its density. From the morphology observation, composite (1) 5% PVA in ratio 1:1 (PVA: CaCO_3) was chosen for further use as a nickel sensor detector.

4.5 Application

In this work, the PVA- CaCO_3 porous composite containing dimethylglyoxime (DMG) could be used as a novel optical sensor for the analysis of nickel (II) ion concentration by soaking into the solution. The optical response of the sensor is based on the well known reaction between nickel and DMG leading to the formation of a red complex of $\text{Ni}(\text{DMG})_2$ with an absorbance peak at 547 nm. DMG was directly mixed with PVA- CaCO_3 porous composite in an ethanol solvent and added to PVA- CaCO_3 composite mixture.

Poly(vinyl alcohol) is a water-soluble material that has been widely used for immobilization of bioactive materials (Ratner et al., 2004 and Mathur et al., 1996), because PVA has many attractive properties (i.e. hydrophilicity, reactivity, film formation, resistance to oxidation, and good mechanical properties) (Demerlis et al., 2003). When PVA is used for the immobilization, the hydrogen bonding ability of its hydroxyl groups, its regular linear structure, and its hydrophilic properties can be maintained (Lozinsky et al., 1997), while its chemical stability and mechanical properties can be improved by physical or chemical crosslinking (Hassan et al., 2000). Therefore, there is great scope for designing better PVA foam carriers for containing DMG and developing new technologies for wastewater bio-sensor.

The highly porous material was chosen for this study. The increasing of porous was responded to the porosity in the material, it helps to increase the surface area of material. The nickel solution can be formed complex with DMG in inside to

the pore of material instead of to be formed only the plain and flat surface. Moreover, the solution of nickel can easily go through into the material because it has the high porosity and hydrophilic property. This formation of a red-pink complex of nickel (II) ions and DMG will show more visible by naked-eye on the materials.

The optical response of the sensor is based on the well known reaction between nickel and DMG leading to the formation of a red complex of $\text{Ni}(\text{DMG})_2$ with an absorbance peak at 547 nm. 2% DMG in ethanol by weight was directly mixed with PVA- CaCO_3 in a water and then crosslinked with boric acid solution.

The content of PVA was fixed at 5% wt in solvent which was water and 2% wt DMG in ethanol in different ratio that shown in table 3.3.4. The mixture was heated at 85 C to dissolve PVA with 200 rpm stirring.

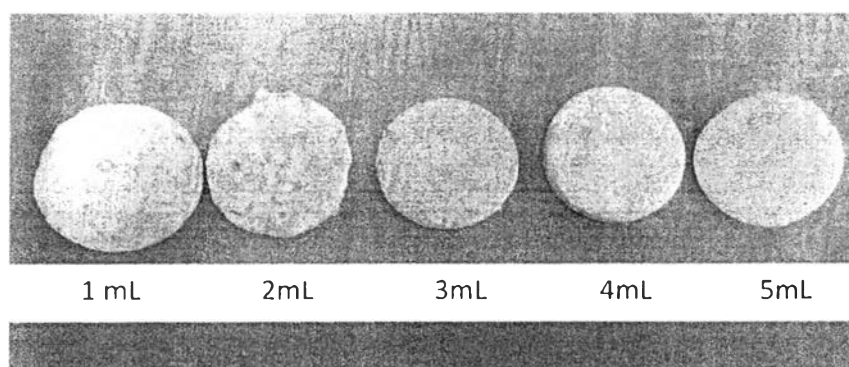


Figure 4.21 The sensor images of different mixture of PVA- CaCO_3 porous composite (2% wt DMG in ethanol at 1 mL, 2 mL, 3 mL, 4 mL and 5 mL as shown in table 4.5).

The morphology of PVA- CaCO_3 porous composite was observed by naked eyed, the condition (5) has uniformity surface with lowest void.

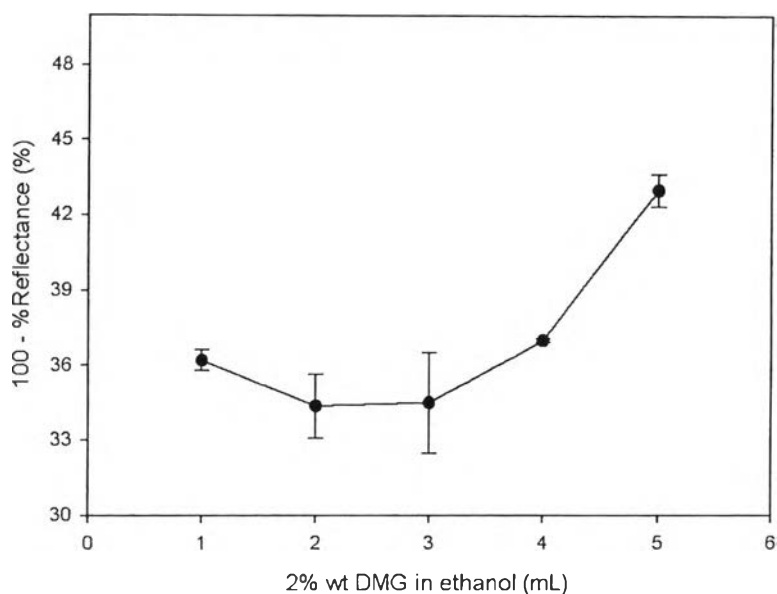


Figure 4.22 The curve of PVA-CaCO₃ porous composite % absorbance that immersed in nickel solutions at 8 ppm for 2 hours.

At condition (5), 2 wt% DMG in ethanol at 5 mL and water 5 mL has highest response when measure with optical microscope. The content of DMG which in material was formed with Ni (II) ions, led to Ni(DMG)₂ which was red-complex. The more adding of adding 2 wt% DMG in ethanol to the hybrid composite, the more redness was visible seen by naked-eye. The condition (5) was chosen for using as sensor.

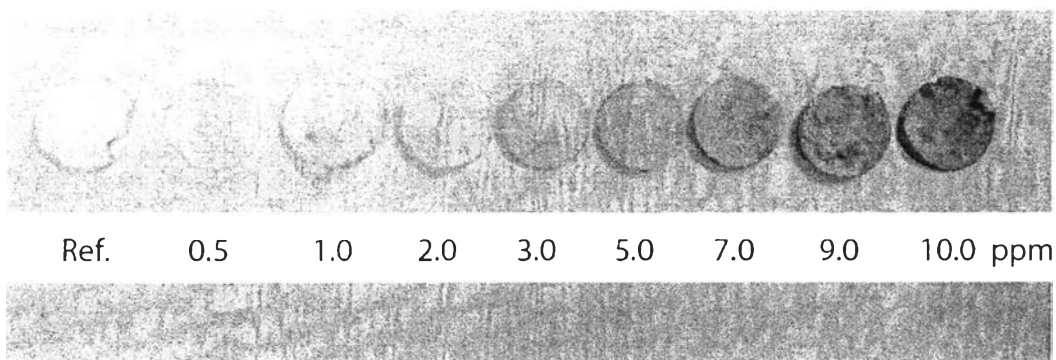


Figure 4.23 The sensor images of PVA-CaCO₃ porous composite that immersed in nickel solutions at concentration of 0.1, 0.5, 1, 2, 3, 5, 7, 9 and 10 ppm for 2 hours.

Although the formation of a red-pink complex of nickel (II) ions and DMG was visible by naked-eye on the materials, spectrophotometric measurements were also performed and are shown in figure 4.23. All PVA-CaCO₃ porous hybrid composite materials were tested for colorimetric response. PVA-CaCO₃ porous hybrid composite materials containing 2% of DMG by weight in ethanol then delivered most uniform fibers with the best sensing property and the least amount of added DMG in porous material. This composition was therefore used in the preparation of the fiber and tested for nickel detection.

However, at concentrations lower than 1 ppm, the color change of sensor and the reflectance spectrum were small as shown in figure 4.24 and did not allow a significant difference to be measured. Therefore, it was concluded that the PVA-CaCO₃ porous hybrid composite materials containing DMG could be used for detecting nickel (II) ions in concentration levels of 1–10 ppm quantitatively by immersion method.

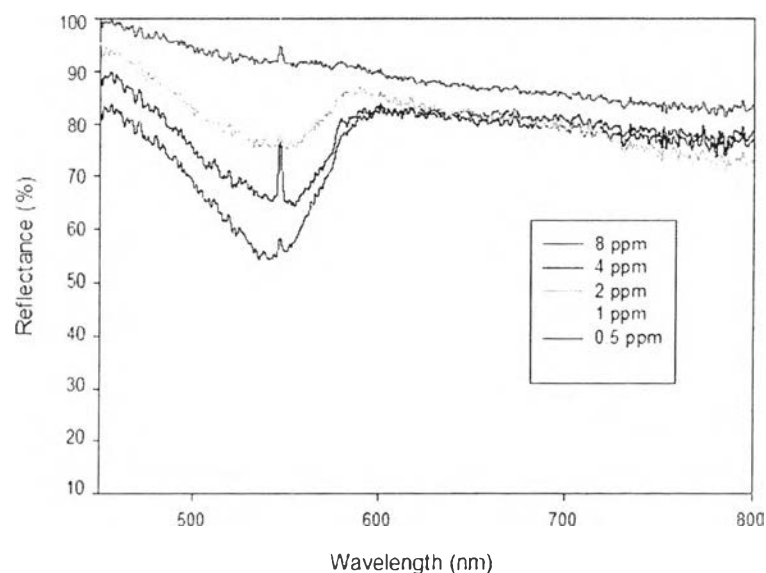


Figure 4.24 The reflectance spectrum of a sensor mat exposed to each nickel concentration of PVA-CaCO₃ porous composite that immersed in nickel solutions at concentration of 0.1, 0.5, 1, 2, 4, and 8 ppm for 2 hours.

The resulting substrate displayed a good color change when exposed to various concentrations of nickel solutions as low as 1–10 ppm of nickel in water. At 0.5 ppm of nickel in water, the material was not obviously changed, but the optical spectrophotometer can detect it with low response.

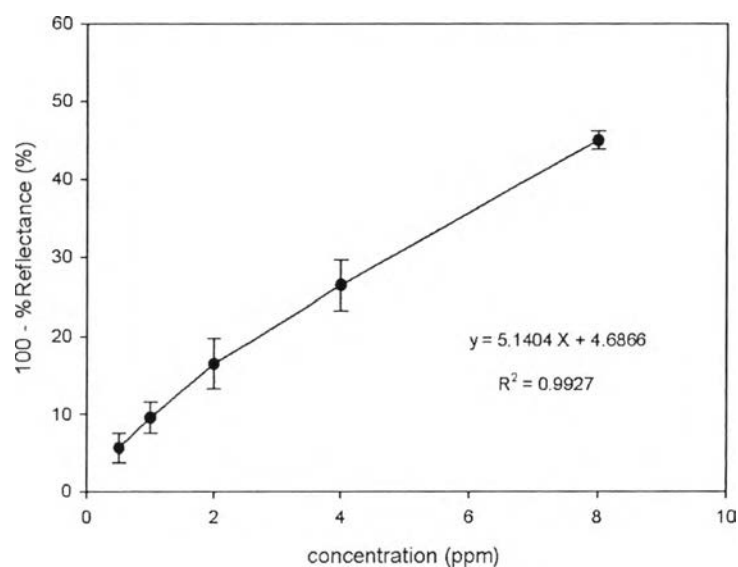


Figure 4.25 The calibration curve of PVA-CaCO₃ porous composite that immersed in nickel solutions at concentration of 0.1, 0.5, 1, 2, 3, 5, 7, 9 and 10 ppm for 2 hours.

A good linear relationship between reflectance signal and nickel concentrations ranging between 1 and 10 ppm was observed with a R^2 value of 0.9927. Therefore, it was concluded that the PVA-CaCO₃ porous composite containing DMG could be used for detecting nickel (II) ions in concentration levels of 1–10 ppm quantitatively by the simple immersion method.

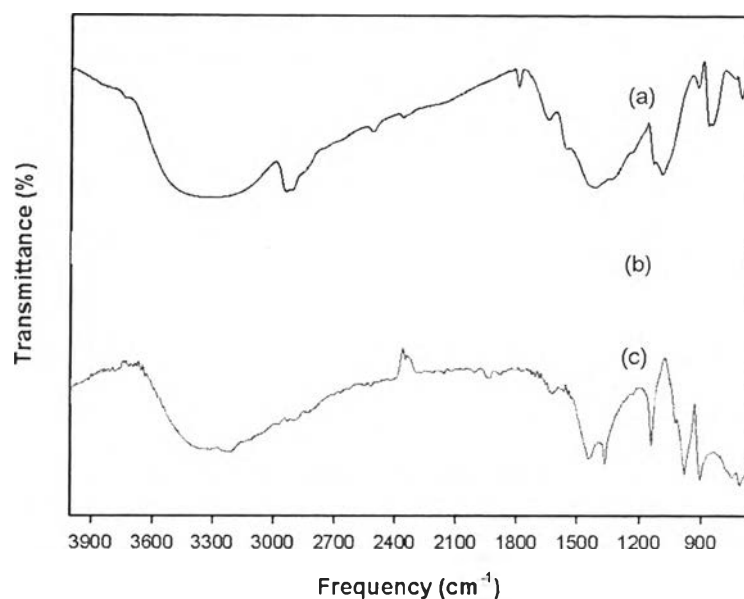


Figure 4.26 The FTIR spectra of PVA-CaCO₃ composite (a), PVA-CaCO₃ composite with DMG (b) and DMG (c).

In the case of DMG figure 4.26 (c), the broad peak at 3205 cm⁻¹ is attributed to the O-H stretching mode and the sharp peak at 979 cm⁻¹ is attributed to the N-O vibration (Ponnuswamy *et al.*, 2002). The peaks positions of DMG and hybrid composite depend with DMG are different (figure 4.26 (b)) suggesting that there are interaction between DMG and hybrid composite. This might be to the strong hydrogen bonding between DMG and the material, leading to the shift of the O-H stretching mode to a lower frequency (Ponnuswamy *et al.*, 2002).

This sensor can be used in the determination of nickel ions concentration in waste water from batteries or nickel alloy manufacturers. The simple dipping method detection makes it easy to be used in the field for example to monitor river contaminations. This developed sensor has shown a good advantage when compared to other analytical techniques which used more time and higher cost.

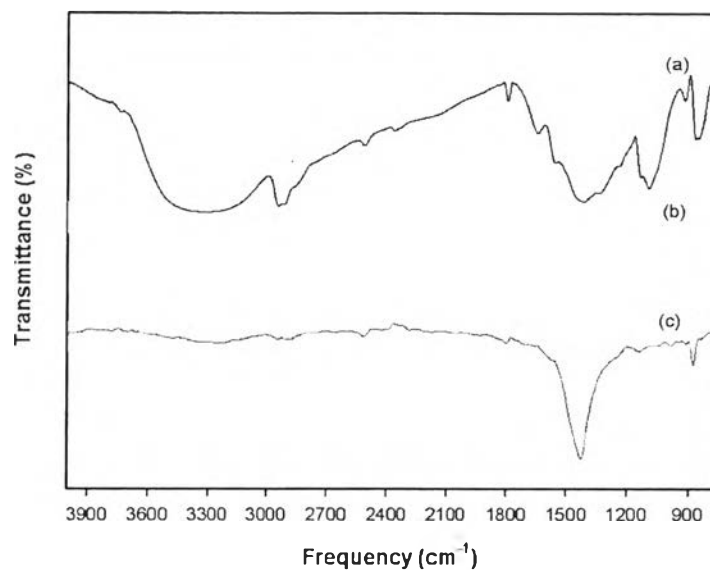


Figure 4.27 The FTIR spectra of PVA-CaCO₃ composite (a), PVA-CaCO₃ composite with DMG (b) and PVA-CaCO₃ composite with DMG immersed with nickel (c).

It can be seen in the spectrum of the PVA-CaCO₃ composite and DMG dipped in the 8 ppm nickel solution that the peak at 3205 cm⁻¹ of DMG is weaker present (figure 4.27 (c)). This is due to the strong hydrogen bonding between DMG and nickel leading to the shift of the O-H stretching mode to a lower frequency (Panja PK *et al.*, 1991). The addition peak at 1572 cm⁻¹ could be attributed to the C=N stretching mode in the Ni(DMG)₂ complex, whereas it does not appear in the DMG or PVA-CaCO₃ composite with DMG spectrum (Ponnuswamy T *et al.*, 2002). The appearance of the unique peak (C-N stretching) in figure 4.28 (c) confirmed that the Ni(DMG)₂ complexes were formed.

Conclusions

The synthesized of PVA-CaCO₃ hybrid material were successfully prepared from calcium carbonate and polyvinyl alcohol, having high porosity and light weight. The optimum ratio of 5 wt% PVA in water and CaCO₃ was 50:50 by using 1.5 mL of 1M boric acid solution as a crosslink agent. FTIR analysis indicated that the interaction between PVA and CaCO₃ was occurred and boric acid was crosslinked with PVA via hydroxyl group. PVA-CaCO₃ porous hybrid material containing dimethylglyoxime (DMG) to use as an optical sensor for nickel (II) was prepared for the first time. All DMG/ PVA-CaCO₃ porous hybrid materials were mixed together at optimum ratio of 2% DMG in ethanol by weight. With the increasing content of DMG, the red-pink complex of nickel (II) ions and DMG showed strong intensity.

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