

CHAPTER IV

SYNTHESIS AND CHARACTERIZATION OF ORGANOCCLAY-COPPER NANOPARTICLES

4.1 Abstract

Copper nanoparticles (CuNP) were synthesized via a chemical method in aqueous solution using ascorbic acid to be a reducing agent and polyvinylpyrrolidone as a dispersant without any inert gas protection. Narrowly distributed CuNPs with an average diameter of about 6 nm was produced and characterized by XRD to confirm the formation of pure CuNPs. Mixing synthesized CuNPs with Bentonite organoclay (OBEN) changed the XRD patterns of OBEN slightly due to adsorption of CuNP onto clay structure. Mixing synthesized CuNPs with Bentonite organoclay provided nanoparticle mixture that would be useful for barrier property and antibacterial activity in polypropylene blown film for prepacked chilled fish packaging.

4.2 Introduction

Copper nanoparticles (CuNP) have exhibited extraordinary properties and have potential applications in several fields such as lubricants, catalysts, thermal transfer nanofluids, electronic materials, optical devices, and antifungal-antibacterial activities. There has also been evaluation to use low-copper loading in food packaging for antibacterial function (Ishitani, 1995, Suppakul *et al.*, 2003). Green chemistry has enormous potential in steering the responsible development of nanotechnology through the design of greener nanoscale materials and the discovery of green nano-manufacturing methods. Ascorbic acid (hydrogen potential of +0.08V) can easily reduce metal ions with standard reduction potentials higher than 0 V, such as Cu^{2+} (Wu, 2007), Ag^+ , Au^{3+} and Pt^{4+} , even without mild heating, but cannot reduce those ions with potentials less than 0 V, such as Fe^{2+} , Co^{2+} , Ni^{2+} . The antioxidant properties of ascorbic acid come from its ability to scavenge free radicals and reactive oxygen molecules, accompanying the donation of electrons to give the semi-dehydroascorbate radical and dehydroascorbic acid (DHA).

Protection of CuNPs with a stabilizer such as surfactant can be given as another stabilization method, and various methods using the stabilizer have been previously reported. The nanoparticles are surrounded with the stabilizer by hydrophilic interaction between the nanoparticles and the stabilizer and/or coordination of functional groups of the stabilizer to metal atoms. However, the stabilizer may not prevent oxidation and aggregation of nanoparticles enough because of their molecular motion (Kobayashi *et al.*, 2009). Polyvinyl pyrrolidone (PVP) was used to help dispersion of colloidal solution and found that the ratio of [PVP]/[Metal ion] played an important role in controlling the size, size distribution and morphology of the nanoparticles (Park *et al.*, 2007, Wu *et al.*, 2006, Zhang *et al.*, 2007). Mechanism of PVP in the preparation of silver and copper nanoparticles was well described in Wang *et al.* (2005) and in Yu *et al.* (2009).

It is common knowledge that microorganisms require low concentrations of copper ions as essential micronutrients and as vital cofactors for processing of metalloproteins and certain enzymes. Higher concentrations of copper (250 ppm) can cause inhibition of growth or even death of microorganisms. The toxic effect of copper on microorganisms occurs by the displacement of essential ions, thereby obstructing functional groups of proteins, inactivating enzymes, producing hydroperoxide free radicals, and altering membrane integrity. Copper compounds have been widely used as algicide, fungicide, molluscicide and acaricide agents in agriculture. Limited information on the possible antimicrobial activity of nano copper particles is available. Copper (0) or copper oxide nanoparticles are cheaper than silver, easily mixed with polymers and relatively stable in terms of both chemical and physical properties.

In this chapter, organoclay-copper nanoparticle mixture was prepared with CuNP loading of 5, 10, 15, and 20 wt%. CuNPs were synthesized via a one-step green route reported by Wu *et al.* Then, the synthesized CuNPs were incorporated into Bentonite organoclay to produce nanoparticles for further mix in polypropylene film in order to modify permeability and antibacterial activity of polypropylene film for prepacked chilled fish packaging. Characterization of nanoparticles was studied by means of transmission electron microscopy (TEM) and X-ray diffraction (XRD)

techniques, and particle size distribution of synthesized copper nanoparticles was also determined.

4.3 Experimental

4.3.1 Materials

Bentonite organoclay (OBEN) was prepared in our laboratory by using sodium activated bentonite (kindly supplied by Thai Nippon Co., Ltd., Thailand) and distearoylethyl hydroxyethylmonium methosulfate and cetearyl alcohol. Polyvinyl-pyrrolidone (PVP, MW 40000 g/mol) and copper (II) nitrate ($\text{Cu(II)NO}_3 \cdot 5\text{H}_2\text{O}$) was purchased from Sigma-Aldrich, Germany. L-ascorbic acid was purchased from Ajax Finechem, Australia.

4.3.2 Synthesis of Copper Nanoparticle (CuNP)

Copper nanoparticles were prepared with a fixed ratio of chemicals in order to produce the same particle size distribution as discussed in Wu *et al.*(2006). 50 ml aqueous solution of 0.4 M L-ascorbic acid and 0.8 M polyvinylpyrrolidone (PVP) were directly mixed with another 50 ml aqueous solution of 0.01 M copper (II) nitrate and 0.8 M PVP under stirring. Then, the mixture was kept at 45 °C without any inert gas protection. After about 1 hour, the initial precursor solution with light blue color changed red colloidal slurry, indicating the formation of Cu nanoparticles. The reaction was kept for 3 hours to complete reduction reaction of copper (II) ion into copper (0) nanoparticles. The colloidal slurry was kept to mix with organoclay in the next step.

4.3.3 Mixing of CuNP into Bentonite Organoclay (OBEN/CuNP)

Bentonite organoclay (OBEN) was dispersed and allowed them to swell in distilled water for 12 hours. Then, the synthesized copper colloidal slurry was added into swollen organoclay slurry with vigorous stirring to allow good distribution between them for 20 min. The weight of CuNP adding into organoclay was calculated to vary nominal contents of 0, 5, 10, 15, and 20 wt%. The abbreviation for OBEN-CuNP mixture is denoted as OBEN-CuNP_x, where x is the amount of copper nanoparticle content (0, 5, 10, 15, and 20 wt%) in the powder mixture.

The OBEN-CuNPx mixture was allowed to sediment for 12 hours. Removal of excess PVP solution was performed by pouring out water above the sediment and adding fresh distilled water into suspended mixtures until clear water was observed above the sediment. The sediment was dried in a vacuum oven at 80 °C for 24 hours, and then grinded by hand to produce fine powder.

4.4.4 Nanoparticle Characterization

Transmission electron microscopy of synthesized copper nanoparticles was performed on JEOL JEM-2100 model and an accelerating voltage of 150 kV. Samples for the TEM imaging were prepared by placing a drop of the colloidal solution on a copper grid. Particle size distribution of synthesized copper nanoparticles was also determined by a particle size analyzer (Malvern Instrument).

Powder X-ray diffraction patterns were measured on a Bruker AXS Model D8 diffractometer with CuK_α radiation operate at 40 kV and 30 mA. The OBEN/CuNP powder was observed on the 2θ range of 2-80 degree with a scan speed of 2 degree/min and scan step of 0.01 degree.

4.4 Results and Discussion

4.4.1 Characterization of Copper Nanoparticles (CuNP) by TEM

Fig.4.1 shows TEM images of synthesized copper nanoparticles (CuNP) in a typical experiment with different scale bars. It is seen that the synthesized CuNP consisting of nearly spherical and small sized particles in nanoscale range. Coated layer of PVP could not be observed from the TEM images. PVP was used to stabilize and control the copper nanoclusters growth. It is believed that PVP can coordinate to the particles surface via O–Cu coordination bond and wrap around the particles with its long and soft polyvinyl chain to stop their growth and aggregation toward bulk particles.

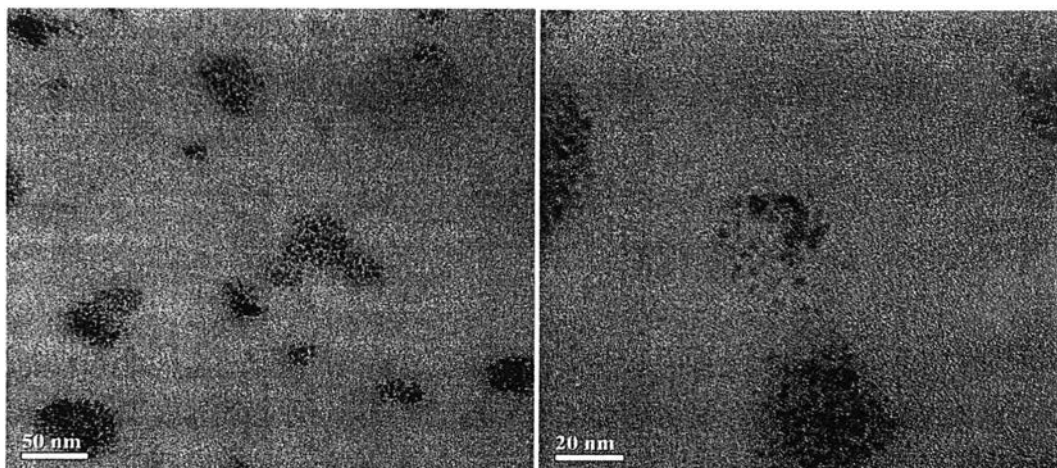


Figure 4.1 TEM images of synthesized copper nanoparticles.

In this research, the CuNP were synthesized with the optimized [PVP]/[Cu²⁺] ratio as described in Wu *et al.* (2006) where they reported that about 92.9% of the total particles were in the range of 1.3–4.7 nm, and 78.2% of the total were in the range of 2.2–3.7 nm, indicating a nearly monodisperse distribution. They stated that PVP was verified as an ideal candidate for stabilizing and controlling the copper nanoclusters growth. Compared to Wu *et al.* (2006), the average CuNP size determined from TEM images is about 2.5–5.0 nm which agglomeration of CuNP was observed. Since the CuNP are much denser than water (density of copper is 8.94 g/cm³), their colloidal particles can sediment very fast in aqueous medium. The particle size distribution of CuNP were also determined by a particle size analyzer and found that the average particle diameter was 6.579 nm as presented in Fig.4.2 and Table 4.1. However, it is worth to note that the histograms of particle size distribution were not stable implying fast sedimentation of CuNP in medium (water) during the test.

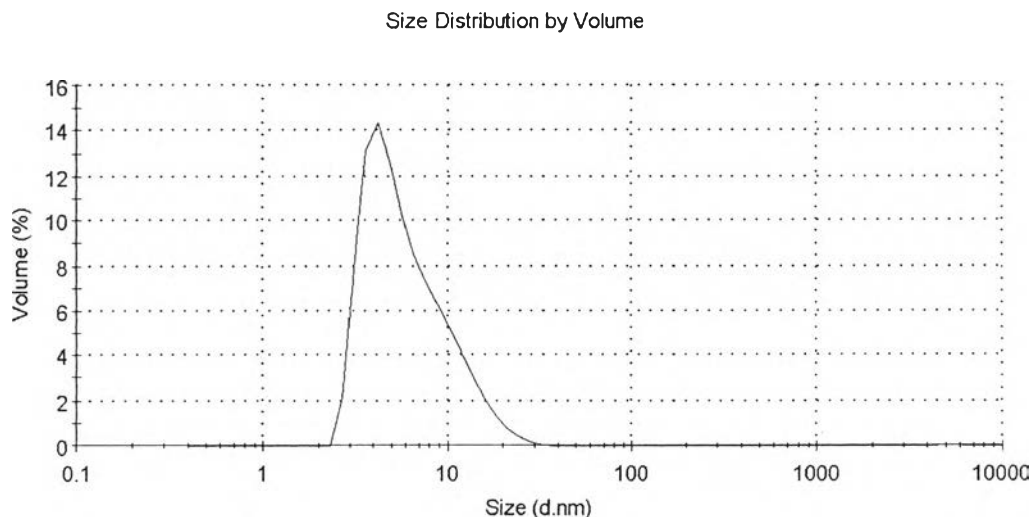


Figure 4.2 Particle size distribution of synthesized copper nanoparticles.

Table 4.1 Particle size distribution (by volume) of synthesized copper nanoparticles

	Diameter (nm)	Volume (%)	Width (nm)
Peak 1	6.579	99.9	3.893
Peak 2	5362	0.1	674.4

4.4.2 X-ray Diffraction Patterns of Organoclay-Copper Nanoparticles (OBEN-CuNP)

Fig.4.3 shows the XRD patterns of OBEN and OBEN-CuNPx at 2θ between 2-80 degrees. In all OBEN-CuNPx samples, there are three main characteristic diffraction peaks of copper at $2\theta = 43.2, 50.4$ and 74.0 , corresponding to (111), (200) and (220) crystal planes respectively. This confirms the formation of pure fcc copper nanoparticles similarly to those reported in Wu *et al.* XRD patterns of copper oxides occur at different 2θ . Zhang *et al.* (2007) reported the XRD pattern of cuprous oxide (Cu_2O) nanoparticles to be at $36.4, 42.3,$ and 61.5 corresponding to (111), (200), (220) crystal planes respectively. Ruparelia *et al.* (2008) prepared cupric oxide (CuO) which the XRD patterns were $38.3, 48.8,$ and 67.98 corresponding to (111), (200) and (220) crystal planes respectively. From the XRD

patterns, it indicates the efficiency of PVP to stabilize the growth of the copper nanoparticles during the reduction reaction of Cu^{2+} by ascorbic acid.

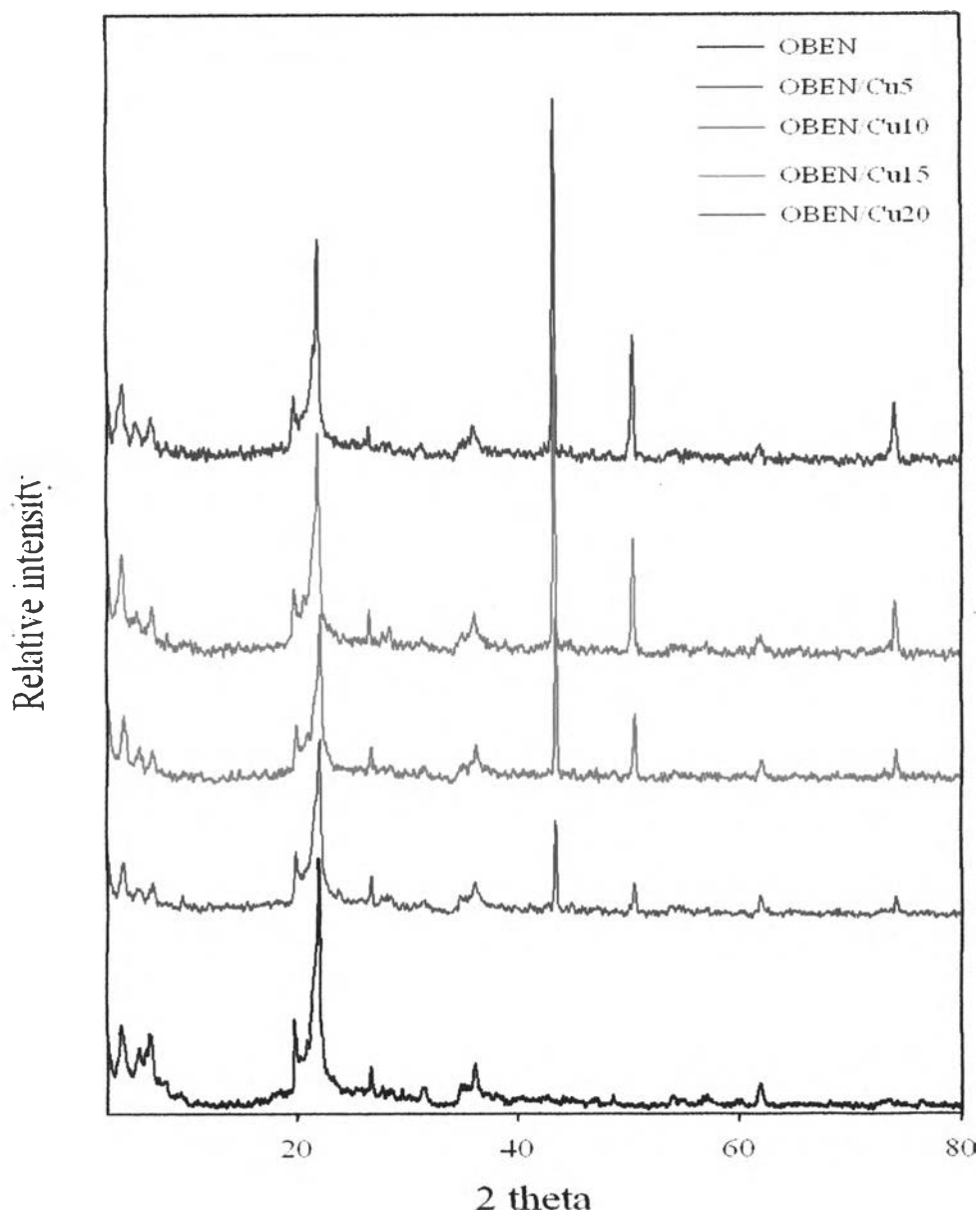


Figure 4.1 XRD patterns of OBEN and OBEN-CuNP_x powder. (x = copper nanoparticle content in wt% adding into OBEN-CuNP mixture).

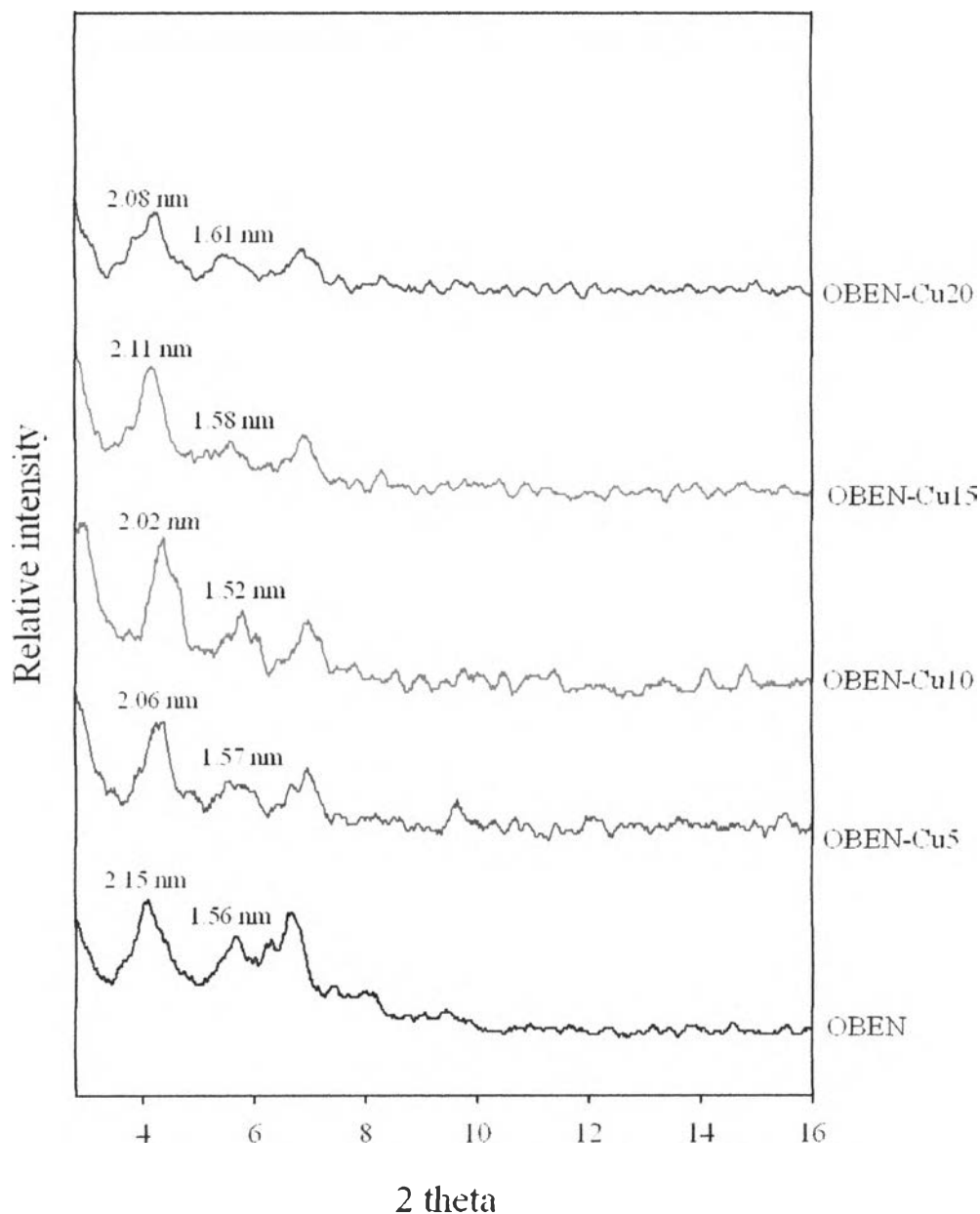


Figure 4.1 XRD patterns of OBEN and OBEN-CuNPx-ray at 2θ between 2-16 degree. (x = copper nanoparticle content in wt% adding into OBEN-CuNP mixture).

Fig.4.4 shows the XRD patterns of OBEN and OBEN-CuNPx at 2θ of 2-16 degree. It is seen that the OBEN has the characteristic peaks at $2\theta = 5.67^\circ$ and 4.09° which corresponding to d-spacing of 1.56 and 2.15 nm, respectively. The d-spacing of 2.15 nm indicates that the ammonium ions are intercalated between the

silicate layers thus expanding the basal spacing to be higher than the d-spacing of 1.51 nm of the pristine Bentonite clay. In XRD of all OBEN-CuNP_x, it is observed that the d-spacing of 2.15 nm are slightly decreased. The reduction in d-spacing of OBEN would be attributed with the adsorption of CuNP onto the clay structures. Zhirong *et al.* (Zhirong *et al.*, 2011) found the XRD patterns of the Cu(II)-loaded Na-bentonite clay samples showing a decreased shift in the position of the d_{001} peak from 14.29 to 12.48 and 12.23 \AA and a slight decreased shift in the position of the d_{020} peak from 4.49 to 4.48 and 4.47 \AA . They purposed that the reduction in the basal spacing of this feature resulting from a decrease in the number of water layers in the interlayer space as a consequence of the Cu(II) adsorption on the structure of clay minerals. They used FTIR results to argue that the Cu(II) cations replaced the original metal ions in the interlayer or located into hexagonal cavities of Si–O sheet in the Cu(II)-loaded Na-bentonite samples. Construction modification of tetrahedral sheets due to the presence of Cu(II) cations either in hexagonal holes and/or in the previously vacant octahedral sites induced changes in the Si–O vibration modes.

4.5 Conclusions

Copper nanoparticles were synthesized via a chemical method in aqueous solution using ascorbic acid to be a reducing agent and polyvinylpyrrolidone as a dispersant without any inert gas protection. From TEM images, it is seen that the CuNPs were nearly spherical with small size in nanoscale range, however, coated layer of PVP could not be observed. Narrowly distributed copper nanoparticles with an average diameter of about 6 nm was obtained and characterized with XRD to confirm the formation of pure copper nanoparticles. Mixing synthesized copper nanoparticles with Bentonite organoclay changed the XRD patterns of OBEN slightly due to adsorption of CuNP onto clay structure.

4.6 References

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