



## CHAPTER IV RESULTS AND DISCUSSION

### 4.1 Ag/Cu Zeolite-A Preparation Appearance

Metal loaded zeolite was prepared by varying the concentration of Ag<sup>+</sup> solution as follow in the table 1.

**Table 4.1** Concentration of metal ions

Ratio of Ag <sup>+</sup> :Cu <sup>2+</sup>	Concentration (ppm)	
	AgNO <sub>3</sub>	Cu(NO <sub>3</sub> ) <sub>2</sub>
Valfor zeolite-A	0	0
Ag/zeolite	20000	0
Cu/zeolite	0	7200
0.5:1	3600	7200
1:1	7200	7200
2:1	14800	7200

After 1 hour of stir, the zeolite was washed with DI water and dried at 70 °c. The blue zeolite was obtained as a final product of this process.

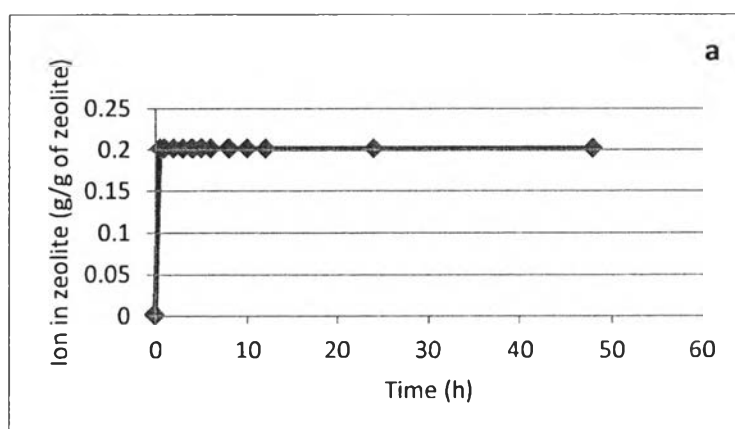
## 4.2 Ion Exchange Study

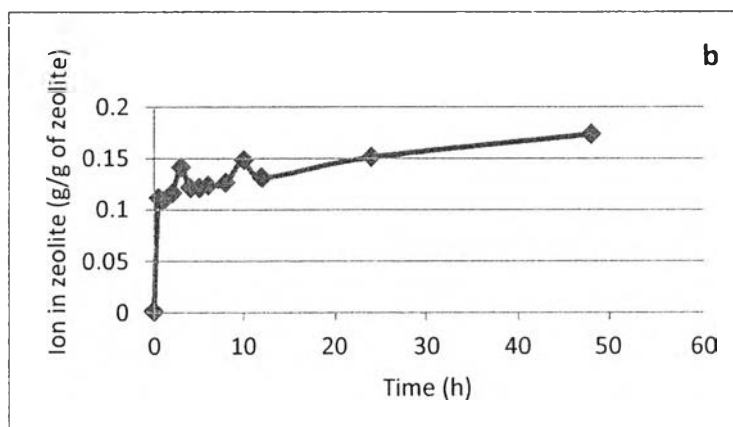
The ion exchange behavior of zeolite was studied in order to optimize the exchange time and concentration of metal ion. The objective of optimization is to maximize the product (zeolite) with low cost.

### 4.2.1 Optimum Ion Exchange Time Study

The optimum ion exchange time was studied by stirring the solution of  $\text{AgNO}_3$  and  $\text{CuSO}_4$  at concentration 8000 ppm for 48 hours and the solution was collected every hour within 2 days. The concentration of metal ion that can impregnate into zeolite can be calculated by using Atomic Adsorption Spectroscopy (Spectra 300, Varian).

The result (figure 1a) showed that  $\text{Ag}^+$  was exchanged with  $\text{Na}^+$  in zeolite readily when stirring was started and reached plateau region within 1 hour. As for  $\text{Cu}^{2+}$  (figure 1b), the exchange process is slower than the process of  $\text{Ag}^+$ . However, the high amount of  $\text{Cu}^{2+}$  was able to exchange within 1 hour and slowly increase after that. The  $\text{Cu}^{2+}$  concentration in zeolite reached the plateau region in 10 hours after stirring. Furthermore, some important criteria of production are maximization of product and lowest costs (Tunjo Perić and Zoran Babić, 2008). From the result, the optimum time that both  $\text{Ag}^+$  and  $\text{Cu}^{2+}$  could impregnate into zeolite-A at highest rate and high concentration was 1 hour of mixing.





**Figure 4.1** graph between a)  $\text{Ag}^+$  ion concentration, (b)  $\text{Cu}^{2+}$  ion concentration impregnated into zeolite-A and exchange time up to 48 hours.

#### 4.2.2 Ion Exchange Equilibrium Isotherm Study

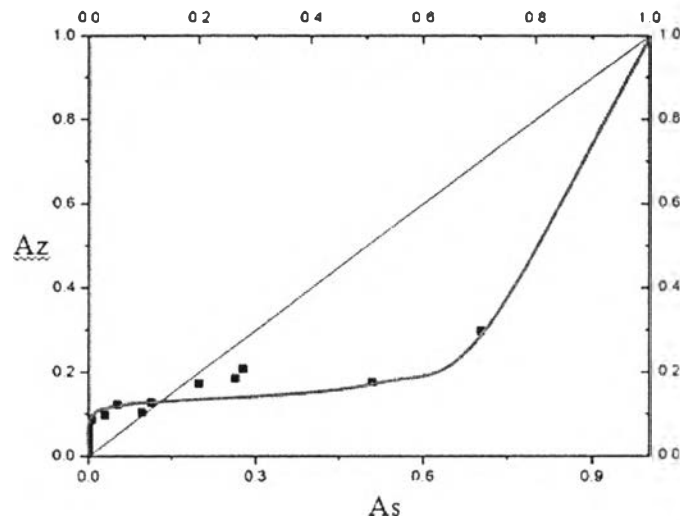
Equilibrium distribution of Cu-Na pair between zeolite-A and solution phase were investigated at 25 °C. The concentration of solution is varied. The initial and final concentration of ion was measured by using atomic adsorption spectroscopy. Ion exchange equilibrium isotherms were plotted in terms of the equivalent fraction of the ion in solution ( $A_s$ ) and ion in the zeolite ( $A_z$ ).  $A_s$  and  $A_z$  were calculated from the equation below.

$$A_s = \frac{c}{c_0} \quad \text{and} \quad A_z = \frac{c_0 - c}{CEC}$$

$C$  = concentration of ion in the solution.

$C_0$  = concentration of ion in the solution at the beginning

CEC = Cation exchange capacity of zeolite (5.30 meq/g)



**Figure 4.2** ion exchange isotherm of  $\text{Cu}^{2+}$ - $\text{Na}^+$  pair.

From the isotherm of  $\text{Cu}^{2+}$ , the line is above the diagonal line only at the low concentration of  $\text{Cu}^{2+}$  that mean  $\text{Cu}^{2+}$  can exchange with  $\text{Na}^+$  in zeolite-A completely at low concentration. The maximum value of  $\text{Cu}^{2+}$  that can impregnate is at  $A_z =$  and  $A_s =$  this point is at the 7200 ppm of  $\text{Cu}^{2+}$ . If the concentration of  $\text{Cu}^{2+}$  goes beyond this point, it will cause a partial exchange. From both isotherms,  $\text{Ag}^+$  has a better selectivity and high capacity of exchange to zeolite-A compared with  $\text{Cu}^{2+}$ .

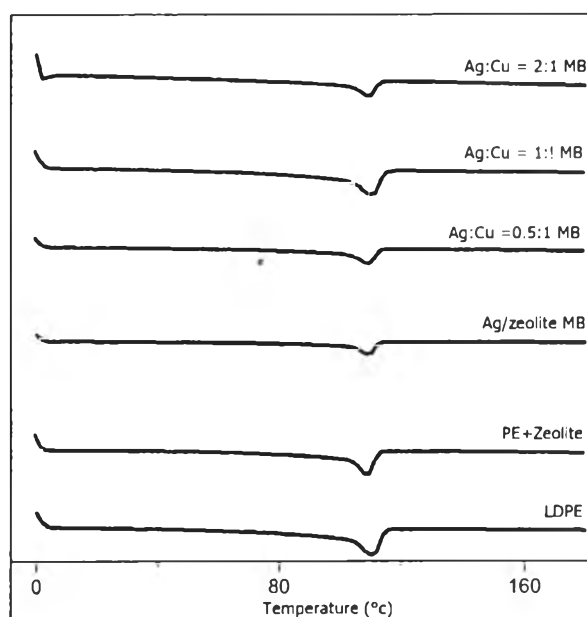
### 4.3 Master Batch Preparation

The aim of master batch preparation is adding as high as possible amount of filler into plastic. So, the 50% of each formula of metal/zeolite was added into the LDPE (50/50). After extruded and cut into cylinder plastic pellet, the master batch that mixed with zeolite containing  $\text{Cu}^{2+}$  was a blue color and turned into dark blue and green when the Ag content in zeolite increased. The color of master batch turned into dark brown color when Ag/zeolite was compounded.

## 4.4 Master Batch Characterization

### 4.4.1 Crystallinity Change of Master Batch

From the DSC thermogram, LDPE and its master batch have the same melting point, around 108.00 – 111.00 °C. The similarity in melting point showed that zeolite will not deter the thermal properties of plastic after compound them together. However, the crystallinity of LDPE was reduced due to the addition of filler into plastic in which it can observe by the reduction of the area of melting peak compared with the melting peak of non-filled LDPE (figure 12). The crystallinity of master batch was around 50% to 80% as follow in table 3. The lowest crystallinity was the master batch that has a untreated zeolite as a filler.



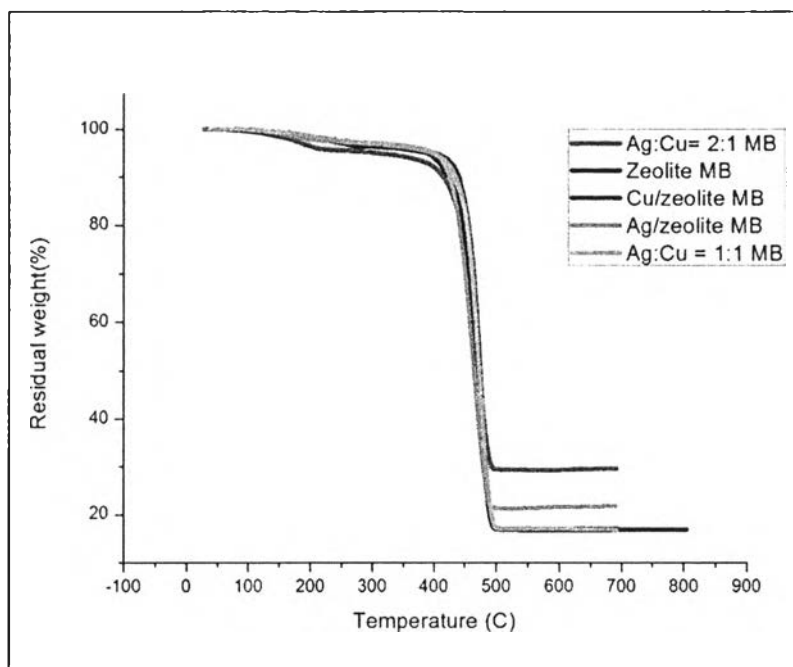
**Figure 4.3** DSC thermogram of LDPE and LDPE master batch.

**Table 4.2** Thermal properties of LDPE and LDPE's master batch

Master batch	Onset (°C)	Endset (°C)	peak (°C)	Enthalpy (J/g)	Crystallinity (%)
LDPE	101.42	114.09	109.81	112.03	100
LDPE+zeolite	102.02±0.31	112.92±0.64	109.51±0.67	54.52±6.23	48.67±5.57
LDPE+Ag/zeolite	103.19±0.96	115.35±1.63	110.97±1.85	74.23±15.27	66.07±14.06
Ag:Cu = 0.5:1	104.12±2.08	114.78±1.24	110.79±1.24	67.45±13.88	60.21±12.39
Ag:Cu = 1:1	102.13±2.11	115.52±1.56	111.26±1.34	87.96±1.31	78.51±1.17
Ag:Cu = 2:1	103.95±1.38	114.72±2.01	110.66±1.63	65.42±5.53	58.39±4.93

#### 4.4.2 Moisture Content and Weight of Filler in Master Batch Study

The thermal behavior in the range of 30 °C to 700 °C was investigated by TGA. The thermogram gave the slowly loss of the sample weight at 100 °C due to the sublimation of water in the master batch. Around 450 °C all master batches was starting to degrade and degradation process finished around 470 °C This show that filler added into the plastic had no any effect on thermal properties of LDPE . After the degradation process weight of sample have lossed about 60% which is a polymer content. The final residue was a weight of zeolite which was around 20% to 30% of overall weight of master batch.



**Figure 4.4** TGA thermogram of master batches.

**Table 4.3** Thermal properties of master batches

Master batches	Water content (%)	Filler content (%)	Degradation temperature (°C)
LDPE+zeolite	3.75±1.44	19.20±2.24	467.69±2.00
LDPE+Ag/zeolite	3.29±1.32	24.66±2.09	459.67±3.12
LDPE+Cu/zeolite	3.92±0.24	14.46±2.26	471.00±1.00
Ag:Cu = 0.5:1	4.55±0.12	14.46±2.26	471.44±1.00
Ag:Cu = 1:1	3.43±0.38	18.80±1.82	467.49±4.44
Ag:Cu = 2:1	4.71±0.51	34.14±2.01	464.15±1.11

#### 4.4.3 Metal Composition in Zeolite Study by XRF

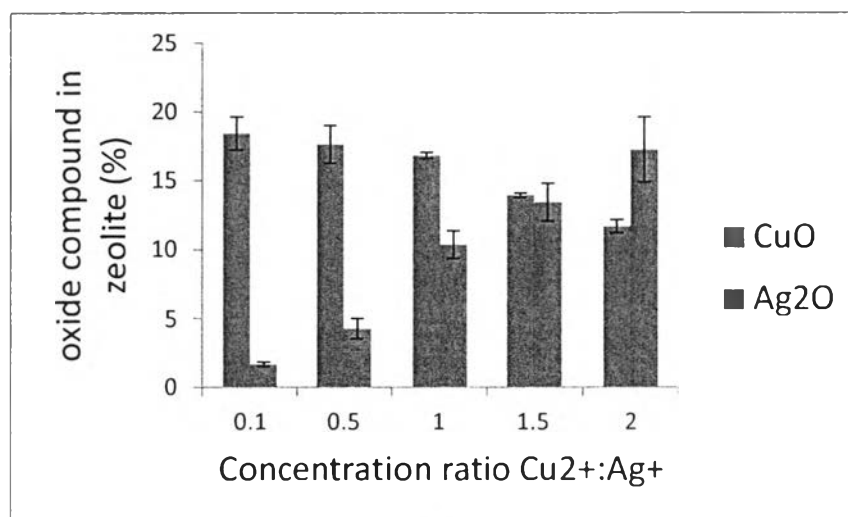
The composition of zeolite was investigated by X-ray fluorescence spectroscopy technique. The sample used in this study was firstly exchanged with  $\text{Cu}(\text{NO}_3)_2$  and  $\text{AgNO}_3$  in the concentration as follow in the table 4.

**Table 4.4** Concentration of  $\text{Ag}^+$  and  $\text{Cu}^{2+}$  used to exchange with Na in zeolite for XRF investigation

Sample	Concentration (ppm)	
	$\text{Ag}^+$	$\text{Cu}^{2+}$
Ag:Cu = 0.1:1	720	7200
Ag:Cu = 0.5:1	3600	7200
Ag:Cu = 1:1	7200	7200
Ag:Cu = 1.5:1	10800	7200
Ag:Cu = 2:1	14400	7200

The result was as follow in the table 5. It showed the percentage of  $\text{SiO}_4$  and  $\text{Al}_2\text{O}_3$  of the zeolite. The ratio of Si/Al calculation was 1.77 which is a characteristic of zeolite-A. Furthermore, the result showed the increase of  $\text{Cu}^{2+}$  and  $\text{Ag}^+$  quantity and the reduce of  $\text{Na}^+$ , a mobile ion when the zeolite was exchange Na with  $\text{Cu}^{2+}$  and  $\text{Ag}^+$ . The graph in figure 5 showed the reduction of  $\text{Cu}^{2+}$  in zeolite when the concentration of  $\text{Ag}^+$  increase. This also supported the conclusion from ion exchange equilibrium study, that zeolite has higher selectivity toward  $\text{Ag}^+$  than toward  $\text{Cu}^{2+}$ .





**Figure 4.5** Quantity of Cu and Ag in zeolite obtained from XRF data.

The composition in masterbatch was also investigated from XRF. The master batch was compressed into a film and cut into a circular shape (5 cm in diameter) in order to fit the XRF pan.

#### 4.5 Preliminary Antibacterial Activity Test

Antibacterial activity of master batches was investigated using two methods. The first method is the minimal inhibition concentration (MIC) test to measure the lowest concentration of zeolite that can inhibit the growth of bacteria. The second method is bacteria reduction. This method is to test the ability of master batches to inhibit bacterial growth.

#### 4.5.1 Minimal Inhibition Concentration Test(MIC)

This test was carried on for each ratio of zeolite and the result showed in the table 4.5 as follow.

**Table 4.5** The minimal inhibition concentration(MIC) test of all zeolite-A.

Sample	Strain	Concentration of zeolite( $\mu\text{g/ml}$ )				
		4000	2000	1000	500	250
Zeolite-A*	S. aureus	-	-	-	-	-
	E.coli	-	-	-	-	-
Ag/zeolite	S.aureus	+	-	-	-	-
	E.coli	+	+	-	-	-
Cu/zeolite	S.aureus	-	-	-	-	-
	E.coli	-	-	-	-	-
Ag:Cu=0.5:1/zeolite	S.aureus	-	-	-	-	-
	E.coli	-	-	-	-	-
Ag:Cu=1:1/zeolite	S.aureus	-	-	-	-	-
	E.coli	-	-	-	-	-
Ag:Cu=2:1/zeolite	S.aureus	+	-	-	-	-
	E.coli	+	+	-	-	-

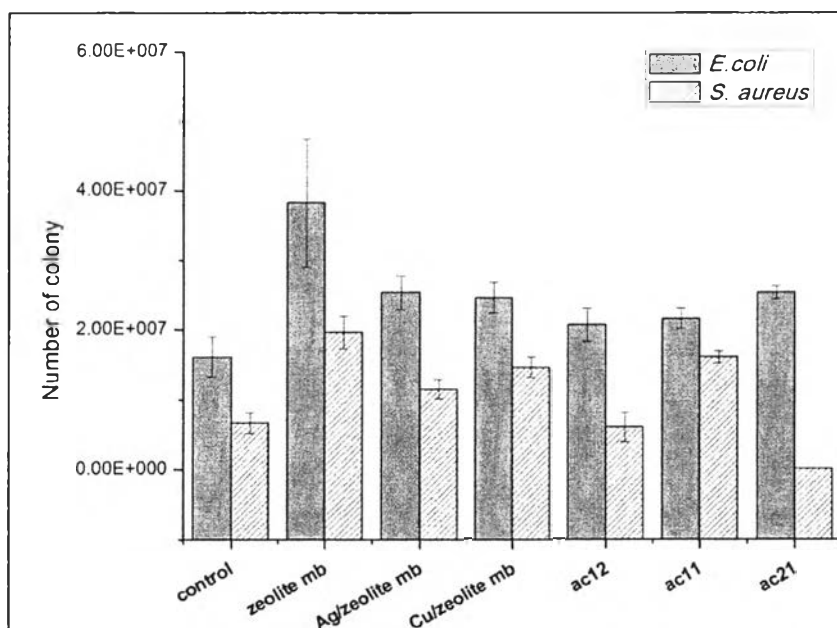
- = There is the colony of bacteria growth in the plate

+ = There is no colony of bacteria growth in the plate

Table 4.5 showed the MIC on two samples which are Ag/zeolite and zeolite at Ag:Cu = 2:1 at 4000  $\mu\text{g/ml}$  for *S.aureus* and 2000  $\mu\text{g/ml}$  for *E.coli*. The cu/zeolite showed no antibacterial activity because  $\text{Cu}^{2+}$  cannot release or release not enough concentration from the zeolite.

#### 4.5.2 Bacterial Reduction Test

Figure 5 showed the reduction of colony number in Ag:Cu = 2:1 master batches only. This is because the metal ion from this master batch can release from the film to inhibit the growth of bacteria. As for other master batches, the metal ion cannot release from the film, this is because some metal ion in the zeolite was reduced to be metal oxide during the production process. The color change of plastic after extrude can support this hypothesis. The metal oxide was so stable and not release to be a free metal ion which is an antibacterial active.



**Figure 4.6** Number of bacteria colony when shaking with master batches for 24 hour.