EMULSION COPOLYMERIZATION OF STYRENE-CO-MALEIC ACID AND INCORPORATION OF CU_2O INTO ITS MATRIX

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ABSTRACT
Incorporation of inorganic materials into polymer matrix using emulsion polymerization technique provides many advantages. In our work, we synthesized poly(styrene-co-maleic acid) with Cu_2O incorporation into the polymer matrix. The process was optimized by varying monomers weight ratio and Cu_2O weight percentage. The products were characterized by Fourier Transform Infra Red spectroccopy and Particle Size Analyzer. FTIR result showed that Cu was attached to carboxylic group indicated by the shift of C=O band. From particle size analysis, the variation of Cu2O % weight did not show any significant difference, but for 15%wt of Cu_2O, the particle distribution was dispersed more uniformly.

Keywords: copolymer, emulsion copolymerization, Cu_2O.

INTRODUCTION
Incorporation of inorganic materials into polymer matrix by polymerization has been done in many research (Mahdavian a et al., 2015). Many tipes of inorganic particles, such as calcium carbonate, titanium dioxide, and silica were used in the research. By using polymerization technique, the agglomeration can be avoided and the mechanical properties can be improved.

Many polymerization technique has been done to achieve the purpose such as free radical polymerization, suspension polymerization, emulsion polymerization etc. Emulsion polymerization provides advantages such as high molecular weight colloidal polymer, more environmentally friendly and safe process (Yamak, 2013). Besides, narrow particle size distribution can be obtained from this type of polymerization (Rivas, 2000).

Shao-Hai et al has made styrene-maleic acid via free radical copolymerization and encapsulated Pigment Red 122 into it. The result showed that with increasing molar content of maleic acid, the particle size decreased first and then increased. Otherwise, the stability of dispersion was increased first and then decreased.

Deb et al studied that the metal complex clusters fairly uniformly distributed in the polymer beads with local concentrations of metal higher than stoichiometric amounts , they investigated the crosslinked styrene-maleic acid copolymer complexes of some transition metals and their adsorption behavior. The copolymerization of styrene-maleic acid was carried out suspension polymerization.

In our study, we incorporated Cu_2O into poly(styrene-co-maleic acid) via emulsion polymerization. The effect of monomer ratio, Cu_2O percent weight on structure and particle size distribution were investigated.

METHODOLOGY
Materials that carried out for this study were Maleic Acid and Sodium Dodecyl Sulfate (SDS) were purchased from Merck. a,a'-Azobisisobutyronitrile (AIBN) as initiator was purchased from Aldrich. Styrene monomer was purchased from PT. Brataco. Distilled water was used in this study. Cu_2O was supplied from PT. Sigma Utama, Cibinong, Indonesia.

Polystyrene-co-maleic acid-Cu copolymer was synthesized by emulsion polymerization. The reaction was carried out in 300 ml three-neck flask equipped with a magnetic stirrer, silicon oil bath, a condensor, and a thermometer). Styrene, AIBN, and Cu_2O were prepared as oil phase solution. Styrene and AIBN was stirred at 600 rpm until well mixed then Cu_2O was added to the solution. The water phase solution was prepared by stirring the SDS, maleic acid, and distilled water. Then, oil phase solution was added to water phase solution and mixed well for 30 minutes. Deoxygenation was performed by nitrogen gas flushing for 5 minutes at atmospheric pressure. The reaction temperature was elevated until it reach 75°C. Then reaction was carried out for 3 hours. The product consisted of three layers, the viscid white forth at the top, the green solution at the middle and yellow precipitate in paste form at the bottom. The paste was separated from the solution and then dried in oven for 72 hours at 40°C, crushed, and then characterized by Fourier Transform InfraRed Spectrophotometer (FTIR) and Particle Size Analyzer (PSA).

IR spectra of the copolymers were recorded with a FTIR spectrum analyzer (IR Prestige-21, Shimadzu) with ATR 800 method. The average diameter of the particle was measured by Particle Size Analyzer (Nanoplus, 660 nm).

RESULTS AND DISCUSSIONS
The synthesis of polystyrene-co-maleic-acid)-Cu copolymer has been investigated with variation of monomer weight ratio and weight percent (wt.%) of Cu_2O. Table 1 and 2 showed the formulations of these variations.

Copolymerization reaction between styrene and maleic acid is supposed as below:

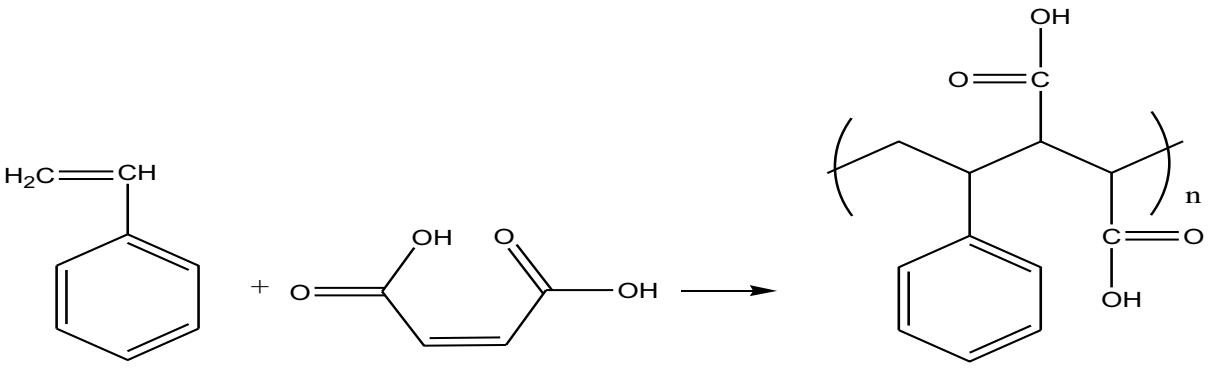

FIGURE-1. The proposed reaction of styrene and maleic acid to form copolymer poly(styrene-co-maleic acid)

TABLE-1. Monomer weight ratio variation

Code	Monomer weight ratio (w/w)		AIBN (ml)	SDS (g)	Aquadest (ml)	Cu_2O (wt.%)
	Styrene	Maleic Acid				
PE 1	1	1	1	1,4	250	0
PE 2	1	1				5
PE 3	2	1				
PE 4	3	1				
PE 5	4	1				

TABLE-2. Cu_2O weight percent variation

Code	Monomer weight ratio (w/w)		AIBN (ml)	SDS (g)	Aquadest (ml)	Cu_2O (wt.%)
	Styrene	Maleic Acid				
PE 1	1	1	1	1,4	250	0
PE 2						5
PE 6						15

1. FTIR result

The IR spectrum is used to confirm the formation of this copolymer. Figure 2 and 3 shows the spectra of variation used in this research.

Based on FTIR spectra, it can be seen that all the copolymers showed the characteristic stretching vibration of –CH at 3500-3300 cm^{-1}, stretching vibration of C=O at 1687– 1705 cm^{-1}, stretching vibration of C-OH from carboxylic acid at 1261-1381 cm^{-1}, C=C aromatic ring at 1506-1595 cm^{-1}.

We also investigated the weight percentage (wt.%) of copper (Cu) to know the optimal Cu adsorbed into the polymer matrix. Table 2 shows Cu_2O weight percentage variation used in our research.

Based on FTIR spectrum, it can be seen that all the copolymers in this variation showed the characteristic stretching vibration of CH aromatic stretching at 3500-3300 cm^{-1}, C=C aromatic stretching vibration at 1577-1625 cm^{-1}, stretching vibration of C=O at 1699–1705 cm^{-1}, C-OH at 1257-1382 cm^{-1}. The IR Spectra for Cu_2O at 15%wt showed the shift of C=O band to lower wave number. Intensity reduction of the carboxylate peak indicated acid consumption from carboxylic and showed that metal carboxylates were formed. From FTIR spectra, it was suggested the Cu attachment to the carboxylic group.

2. Particle Size Analysis

Table 3 showed mean particle diameter for each variation. There were no significant difference in particle size for each variation, but the 15%wt weight of Cu_2O showed smaller particle diameter than the 5%wt. This phenomenon was supposed as that amount of Cu_2O that entrapped into polymer matrix was same for all of monomer ratio and % weight of Cu_2O. Or in other word, the amount of styrene and Cu2O %weight did not give much significant effect on the particle size of this composite.

TABLE-3. Mean diameter of poly(styrene-co-maleic acid)-Cu_2O particle with varied %weight of Cu_2O

Code	Styrene (mol)	Maleic acid (mol)	% weight Cu2O	Mean diameter (d) μm
PE 2	1	1	5	1,8
PE 4	3	1	5	1,7
PE 6	1	1	15	1,1

Figure 5 and 6 describes the volume distribution for 5%wt and 15% wt of Cu in monomer ratio 1:1. The more Cu_2O percent weight showed narrower particle volume distribution. This result indicated that with 15%wt

of Cu_2O, the particle distribution was dispersed more uniformly in aqueous media than that of 5%wt (6).

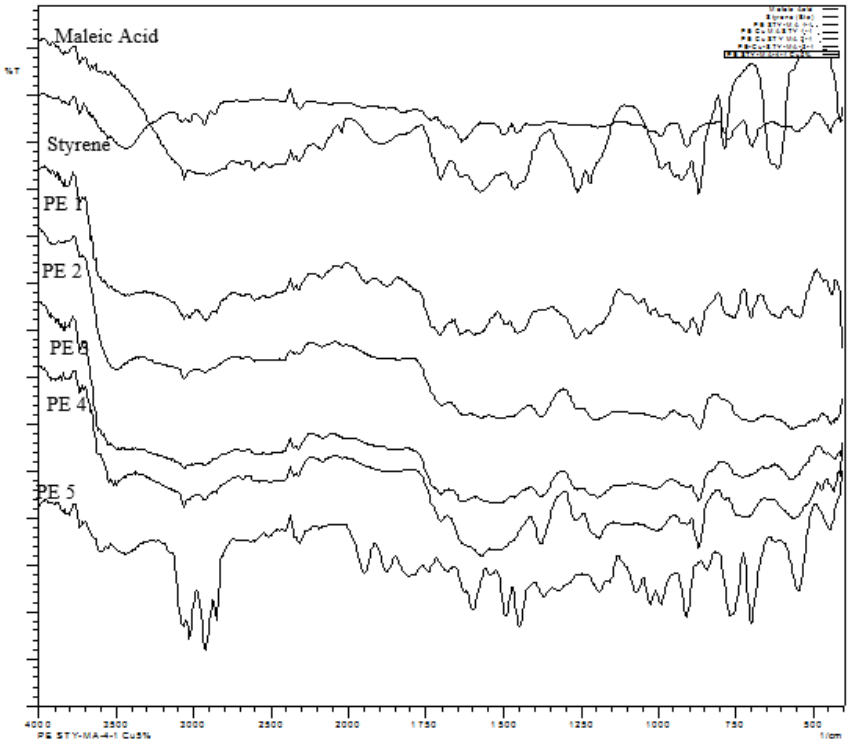

FIGURE-2. FTIR spectra of Poly(styrene-co-maleic acid)-Cu with monomer weight ratio variation.

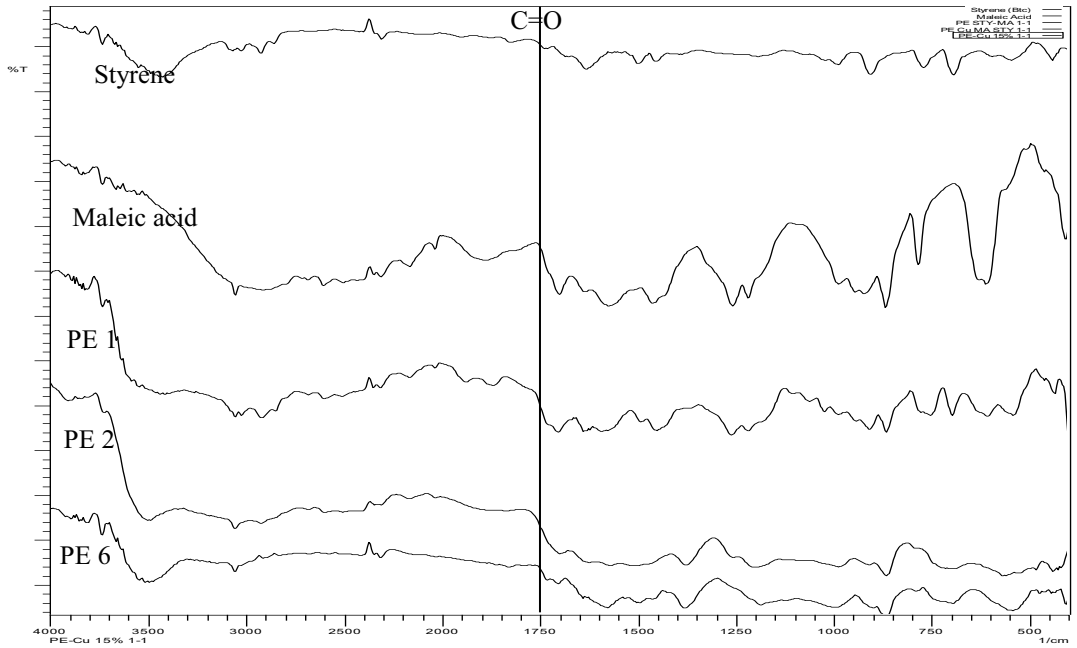

FIGURE-3. FTIR spectra of Poly(styrene-co-maleic acid)-Cu with Cu_2Oweight percent variation

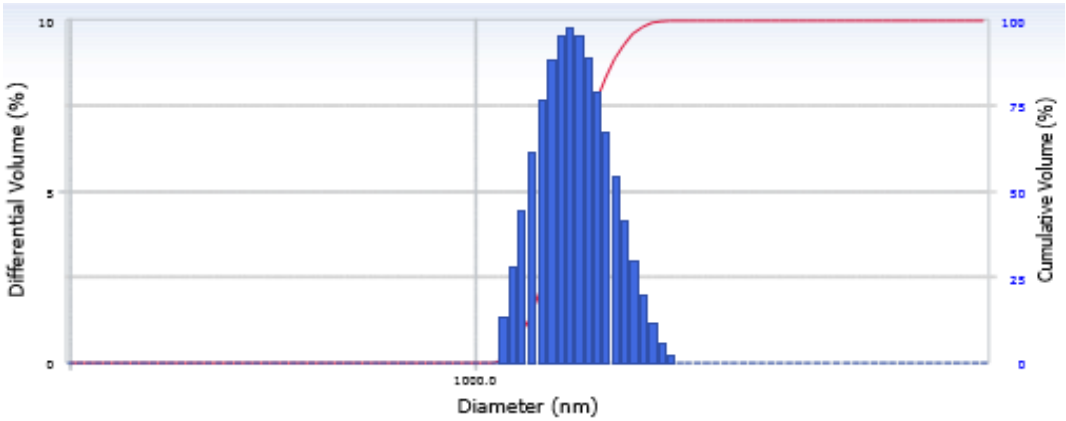

FIGURE-4. Volume distribution Poly(Sty-co-MA) 1:1 Cu 5%

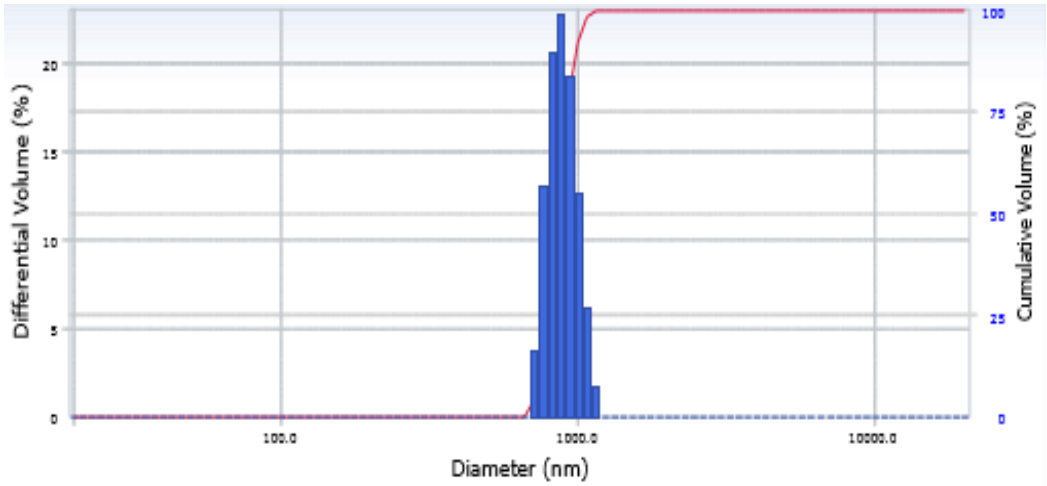

FIGURE-5. Volume disribution Sty-Ma 1:1 Cu 15%

CONCLUSIONS

The copolymer poly (styrene-co-maleic acid)-Cu was synthesized via emulsion copolymerization. From FTIR spectra, it was confirmed that the Cu was attached to carboxylic group indicated by the shift of C=O band. From particle size analysis, the amount of styrene and Cu2O %weight did not give much significant effect on the particle size of this composite. For 15%wt of Cu2O, the particle distribution was dispersed more uniformly in aqueous media than that 5%wt.

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