



## POLYMERIZATION OF VINYL ACETATE AND ACRYLIC ACID MONOMERS USING AZOBISISOBUTYRONITRILE (AIBN) INITIATOR AS POLYMERIC BIOCIDES

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### ABSTRAK

**POLIMERISASI MONOMER VINIL ASETAT DENGAN ASAM AKRILAT MENGGUNAKAN INISIATOR AZOBISISOBUTILRONITRIL (AIBN) SEBAGAI BIOSIDA POLIMER.** Telah dipelajari Polimerisasi vinil asetat dan asam akrilat dengan Cu sebagai kopolimer biosida (PVAc/AA-Cu) dalam pelapisan material kelautan. Pendekatan proses yang akan digunakan adalah kopolimer untuk pembuatan biosida sebagai *antifouling*. Proses polimerisasi asam akrilat dengan vinil asetat menggunakan AIBN sebagai inisiator telah berhasil dilakukan. Karakterisasi produk dilakukan dengan menggunakan analisa FT-IR (*Fourier transform infra red*) untuk menentukan struktur molekul polimer. Selain itu, menggunakan AAS (*Atomic absorption spectroscopy*) untuk menentukan konsentrasi Cu yang terperangkap ke dalam biosida polimer (PVAc/AA-Cu). Selanjutnya, analisa TEM (*Transmission Electron Microscope*) untuk mengidentifikasi morfologi, ukuran dan bentuk dari produk polimer.

**Kata kunci:** Polimerisasi, Kopolimer, Biosida, Inisiator, Antifouling.

### ABSTRACT

**POLYMERIZATION OF VINYL ACETATE AND ACRYLIC ACID MONOMERS USING AZOBISISOBUTYRONITRILE (AIBN) INITIATOR AS POLYMERIC BIOCIDES.** Polymerization of vinyl acetate/acrylic acid with Cu (PVAc/AA-Cu) copolymer as biocide in marine coating was studied. The proposed approach of the copolymer will be used as a biocide for antifouling. Polymerization process of acrylic acid with vinyl acetate using AIBN as an initiator has been done. Characterization of the products was conducted using Fourier transform infra red (FT-IR) to determine the structure of polymer molecules. Moreover, atomic absorption spectroscopy (AAS) was also used to determine the concentration of Cu, which was entrapped into the polymeric biocide (PVAc/AA-Cu). On the other hands, transmission electron microscope (TEM) was conducted to identify morphology, size and shape of the products.

**Keywords:** Polymerization, Copolymer, Biocide, Initiator, Antifouling

### INTRODUCTION

Polymer microspheres have extensive applications in the fields of bioseparation, immunoassay, drug delivery, imaging, etc. [1]. Polymerization materials of homogeneous composition were fundamentally important for application development. Certain industrial processes use monomers that offer vary different reactivity to produce polymeric material [2]. The use of

vinyl acetate in suspension copolymerization for medicinal applications influenced drug concentration [3]. Vinyl acetate monomers (VAc) were polar and reactive, however, they difficult to be polymerized with less polar and more reactive monomers. Addition polymerization needs initiator to generate free radicals lead to the propagation of the polymer chain during radical

mechanism. The initiator can be either water or oil soluble [4]. Polymerization of hydrophilic with hydrophobic monomers produce product that has amphiphilic properties. Hydrophilic and hydrophobic properties of polymer will influence their temperature responsive [5].

Polymeric biocide is one of the important material in marine coating because marine bio-fouling of metal surface in contact with seawater is the main cause of several technical problems and economic loss in industry. Marine bio-fouling is defined as the accumulation of unwanted organism on hard surface and found growing on permanently submerged surface such as hulls and other submerged parts of ships including oil rigs, barges and other object in seawater. The growth of unwanted organism interferes with the efficient work of the surfaces such as reducing the flowing of fluids through the pipelines, reducing the heat transfer equipment in the heat exchanger system, ship's speed and defect of the support legs of oil rigs [6]. Polymers containing quaternary phosphonium or quaternary ammonium groups and preparation of biocidal materials were investigated by several researchers for various purposes. On the other hands, complexation of anionic polyelectrolytes with quaternary ammonium surfactants [7] and/or  $\text{Cu}^{2+}$  cations [8] has been exploited for the preparation of thickening agents or hybrid organic/ $\text{Cu}^{2+}$  nanoparticles. Thus, the biocidal action can be produced from quaternary phosphonium salts [9] and/or combined with copper (II) ions [10].

In the present study, the preparation and development of polyvinyl acetate-co-acrylic acid-Cu (PVAc/AA-Cu) as biocidal polymer were investigated. The characterization of the biocidal polymer such as, according to molecule structure, diameter size, shape and entrapped Cu content was determined using a Fourier transform infrared (FT-IR) spectroscopy, Transmission electron microscopy (TEM), and an Atomic absorption spectroscopy (AAS) respectively.

## EXPERIMENTAL METHODS

### Materials

Acrylic acid (AA,  $\geq 99\%$ ) monomer was purchased from Merck KGaA. Vinyl acetate (VAc,  $\geq 99\%$ ) monomer was purchased from Sigma Aldrich, Germany and stored at  $2 - 8^\circ\text{C}$ . Azobisisobutyronitrile (AIBN) which used as initiator for polymerization process was purchased from Sigma Aldrich, USA and stored at  $2-8^\circ\text{C}$ .  $\text{Cu}_2\text{O}$  was obtained from PT. Sigma Utama, Indonesia. Methanol was purchased from Merck KGaA and  $\text{CuSO}_4$  ( $\geq 99\%$ ) was purchased from Sigma Aldrich, Japan. Distilled water was produced using GFL (Gesellschaft für Labor Technik mbH D-30938 Burgwedel, Typ 2012). All of the materials

mentioned above were employed directly without any purification

### Methods

#### Preparation of Polyvinyl Acetate-co-acrylic Acid-Cu (PVAc/AA-Cu)

Acrylic acid monomer (34.31 ml, 1 mol), vinyl acetate (46.09 ml, 1 mol) and AIBN (0.2 ml, 1% wt) were placed into the three-neck flask (reactor) equipped with a magnetic stirrer, a thermometer and a condenser. Methanol (80,4 ml) as solvent was put into the reactor and then -stirred for 5 minutes. Then, 10 wt.% of source of copper ( $\text{Cu}_2\text{O}$  or  $\text{CuSO}_4$ ) was added into the reactor. Deoxygenation was performed by nitrogen gas flushing for 5 minutes at atmospheric pressure. Furthermore, reaction mixture was stirred at 600 rpm and heated until  $75^\circ\text{C}$  for 3 hours. In this study we investigated effect of reaction time (3 and 5 hours) and, sources of Cu as shown in (Table 1). The obtained PVAc/AA-Cu was analyzed by FT-IR spectroscopy, Transmission electron microscopy (TEM) and atomic absorption spectroscopy (AAS).

**Table 1.** Formulation of PVAc/AA-Cu

Samples	Source of Cu content (wt %)		Reaction time (hours)
	$\text{Cu}_2\text{O}$	$\text{CuSO}_4$	
PVAc/AA-Cu 4	-	1	5
PVAc/AA-Cu 5	1	-	5
PVAc/AA-Cu 6	-	1	3

#### Transmission Electron Microscopy (TEM)

Transmission electron microscope was used to provide information about size and shape (morphology) of polyacrylic acid-co-vinyl acetate (PAA/VAc). TEM was also used to identify incorporated Cu into polymer structure. TEM analysis was performed on a JEOL (JEM-1400) electron microscope, operating at an accelerating voltage of 100 kV. The sample was prepared in solution and then dropped in copper grids coated with 200 mesh strong carbon.

#### Fourier Transform Infra-Red (FT-IR) Spectroscopy

Infrared spectroscopy is a technique based on the vibration of the atoms in a molecule. An infrared spectrum is commonly obtained by passing infrared radiation through a sample and determination fraction of the incident radiation is absorbed at a particular energy. Chemical structure of the obtained copolymer was observed by FT-IR spectroscopy using IR Prestige-21 Shimadzu.

#### Atomic Absorption Spectrophotometry (AAS)

Atomic Absorption Spectrophotometry (AAS) was conducted to determine the Cu content in the

copolymer and measure at 820 nm using APHA Standard Methods 3111 B-2012. AAS has basic principle to aspirate the metallic element in its solution in the form of an aerosol into a high temperature flame.

## RESULTS AND DISCUSSION

### FT-IR Spectroscopy

Synthesis of polyvinyl acetate-co-acrylic acid-Cu (PVAc/AA-Cu) has been carried out and characterized using FT-IR, AAS, TEM and NMR. FT-IR spectroscopy is informative measurement for studying the functional group attached of polymer. Figure 1(A) shows the infrared spectra of PVAc/AA-Cu. The peaks in the 1690  $\text{cm}^{-1}$  region was attributed to C=C stretching vibration, and its intensity was greatly enhanced after functionalization compared with Figure 1 (B) and (C). The bands at 1760  $\text{cm}^{-1}$  and 2975  $\text{cm}^{-1}$  were assigned to C=O stretching and C-H stretching vibration of the carboxylic group from monomers, respectively. The carboxylic groups had the ability to form coordination bonds with the metal ions. The interactions of the copolymers with the metal ions were caused by short distance coordinating interactions. There were two bands at 3325  $\text{cm}^{-1}$  and 970  $\text{cm}^{-1}$  related to the -OH and C-C groups in acrylic acid. Moreover, peaks at 1100  $\text{cm}^{-1}$  was indicated C-O bonding in vinyl acetate. There was a little change in the structure after additional of Cu and the structure was dominated by PVAc/AA. It can be noted that all of spectra of the prepared samples have absorption of -OH stretching located at 3325 to 3410  $\text{cm}^{-1}$ . The phenomenon was clearly observed in the sample containing 10 wt % Cu, the absence of the peak at 1180  $\text{cm}^{-1}$  and 1240  $\text{cm}^{-1}$  were due to the loss of the hydrogen bonding between O-H and C-O groups as a result of the formation of the Cu complex [11].

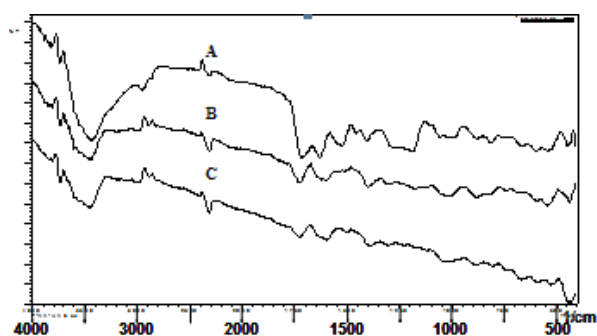


Figure 1. FTIR spectra of polyvinyl acetate-co-acrylic acid-Cu (PVAc/AA-Cu): (A) PVAc/AA-Cu 4; (B) PVAc/AA-Cu 5 and (C) PVAc/AA-Cu 6

### Atomic Absorption Spectrophotometry (AAS)

The results of AAS analysis of Copper (Cu) ion entrapped into PVAc/AA-Cu is shown in Table 2. From

Table 2. Copper (Cu) content of polyvinyl acetate-co-acrylic acid-Cu.

Samples	Source of Cu content (% wt)		Cu content on solution (mg/kg)
	Cu <sub>2</sub> O	CuSO <sub>4</sub>	
PVAc/AA-Cu 4		1	122.36
PVAc/AA-Cu 5	1	-	2134.44
PVAc/AA-Cu 6	-	1	157.52

AAS analysis, the copper ion concentration is the highest in sample PVAc/AA-Cu 5 and the lowest in sample PVAc/AA-Cu 4. The copper ion concentration as 2134.44 mg/kg was resulted by PVAc/AA-Cu using Cu<sub>2</sub>O as the source of copper.

### Transmission Electron Microscope (TEM)

The transmission electron micrographs of polyvinyl acetate-co-acrylic acid-Cu (PVAc/AA-Cu) with variation sources of Cu content can be seen in Figure 2A. According to Figure 2A, the surface morphology of PVAc/AA-Cu appears to be uneven, rough and some black spot with the average diameter of 20 - 100 nm. The black spot is predicted as entrapped Cu in PVAc/AA. The morphology and shape of the polymer depend on temperature based on the formation by hydrogen bonding [12]. The average diameter of the PVAc/AA-Cu 5 is about 100-200 nm, that increased remarkably compared with PVAc/AA-Cu 4 or PVAc/AA-Cu 6. It is indicated that the PVAc/AA-Cu 5 has core-shell structure in polymer [13]. The image of PVAc/AA-Cu 6 (Figure 2C) shows irregularly shaped particles and

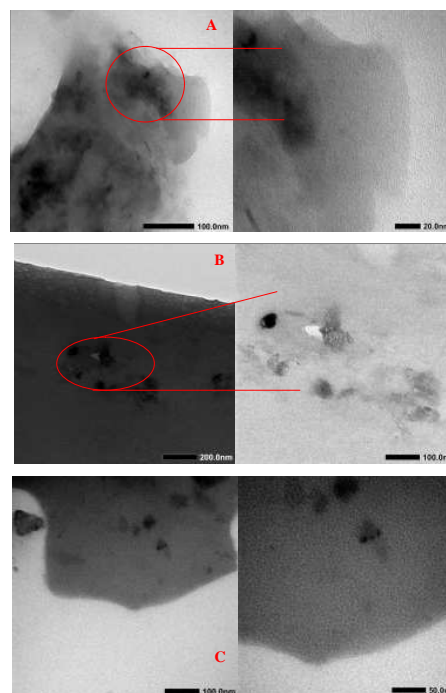


Figure 2. TEM micrographs of polyvinyl acetate-co-acrylic acid-Cu: (A) PVAc/AA-Cu 4; (B) PVAc/AA-Cu 5 and (C) PVAc/AA-Cu 6

almost the same of morphology in Figure 2A. TEM analysis suggests that PVAc/AA-Cu 5 has highest entrapped of Cu content compared with PVAc/AA-Cu 4 or PVAc/AA-Cu 6.

## CONCLUSION

Cu ion entrapped into polyvinyl acetate-co-acrylic acid (PVAc/AA) that known as PVAc/AA-Cu has been successfully prepared by copolymerization process. FTIR analysis shown that the peak at  $1180\text{ cm}^{-1}$  and  $1240\text{ cm}^{-1}$  disappear due to the loss of the hydrogen bonding between O-H and C-O groups as a result of the formation of the Cu complex. The highest entrapped Cu in the polymer was 2134.44 mg/kg using  $\text{Cu}_2\text{O}$  as source.

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