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Synthesis and Characterization of Poly (Acrylamide-co-Acrylic Acid)-grafted-Poly (Styrene-co-Methyl Methacrylate) Microgels by Emulsion Polymerization

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Abstract – *Microgels in this study was prepared by semibatch emulsion polymerization using acrylic acid (AAc), acrylamide (AAm), methyl methacrylate (MMA) and styrene (St). All of monomers that have been used in this research are less toxic. Microgels particle size is affected by changes in temperature. The prepared microgels have been characterized using Scanning electron microscope (SEM) and Fourier Transform Infrared (FTIR). SEM images showed the morphology of microgels and FTIR was used to determine the chemical structure and confirmed the crosslinking of microgels. Microgels formed by emulsion polymerization are distributed well in the whole product.* ***Copyright © 2015 Penerbit Akademia Baru - All rights reserved.***

Keywords: Microgels; Emulsion polymerization, Hydrogel, Copolymer

1.0 INTRODUCTION

Microgels is known as gel which has micron sized in diameter and have three-dimensional cross-linked structures [1]. Microgels which have hydrophilic groups become good thickening agents because of, which are capable to form non-Newtonian fluids and can improve rheological properties [2]. To improve the qualities of cross-link reaction rate, film appearance, mechanical properties of the film and rheology of compositions microgels can be mixed with coatings. Microgels are cross-linked polymer networks of colloidal size can be immersed in a liquid. It also can reversibly swell and deswell in response to changes in external stimuli, which include temperature, pH, ionic strength, solvent composition, and presence of adsorbing and nonadsorbing polymers or surfactants [3]. Furthermore, microgels can be applied for enhanced drug delivery, catalysis, pollution control and enzyme immobilization. Microgels preparation which based on particle formation can be classified into three such as homogeneous nucleation, emulsification and complexation. Homogeneous nucleation is refers to synthesize of microgels particles from initially homogeneous solution. Emulsification refers to the methods where aqueous pregel solution form in brine phase or oil. Microgels also can produce by mixing two types of monomer water soluble which form complex in water [4].

Standard emulsion polymerisation usually used to prepare microgels although other methods of synthesis are available. Preparation of microgels using the emulsion polymerisation is a complex process that is affected by the used monomers, surfactants and initiator and also by the polymerisation itself. [5] The latex particles originate either from micelles hydrophobic monomers and surfactant concentrations above the critical micelle concentration (CMC). Polymerization of oil-in-water and water-in-oil monomer emulsion allows the production of smaller particles. Usually, type of emulsion polymerization is oil in water emulsion where in a continuous phase of water, droplets of monomer (oil) are emulsified with surfactants. Water-soluble polymers can also act as emulsifiers or stabilizers for example certain polyvinyl alcohols and hydroxyethyl celluloses. Microgels formed in an emulsion with a sufficient amount of crosslinker, behave like a macroscopic spherical gel and have a similar internal structure. From previous study, N-isopropylacrylamide (NIPAM) usually used to produce emulsion microgels. However, it is an expensive monomer. Since NIPAM and acrylamide have many similar properties as a significance of similar chemical composition, acrylamide is chosen in this study where it can reduce production cost [6].

Surfactants have been used in this study due to its strong effect in reducing the surface tension between the water and the air. Due to the presence of surfactants, commercial emulsion polymerization can be run smoothly and quite rapidly with many water-insoluble monomers. The appropriate surfactant selection is an important consideration. Anionic and non-ionic are the most effective and widely used surfactant in emulsion polymerization [7]. Anionic surfactants prevent coagulation by electrostatic repulsions originated from the anionic charges adsorbed on the polymer particles and their associated double layers. For non-ionic surfactants, it can prevent coagulation by spatial or steric stabilization. The purpose of this study is to synthesize emulsion microgels using hydrophobic and hydrophilic monomers in the presence of crosslinker and surfactant. Besides that, the chemical structure and particle morphology of emulsion microgels have been characterized in this study.

2.0 METHODOLOGY

2.1 Materials

Acrylamide (AAm, 99%), methyl methacrylate (MMA, 99%), acrylic acid (AAc, 99%), and styrene (St, 99%) were used as monomers. N,N'-methylenebisacrylamide (MBA, 99%) was used as crosslinker. Sodium dodecyl sulfate (SDS, 99%), sorbitan monooleate (span 80), and octylphenol ethylene oxide (triton X-100) were used as surfactants. Potassium persulphate (KPS, 99%) was used as initiator. All of the materials were used without further purification.

2.1.1 Pre-emulsified Monomer

Pre-emulsified monomer was prepared by mixing the monomers (AAm, AAc, St, MMA) and cross-linker (MBA) with the surfactants (SDS, triton X-100 and span 80) and deionized water in a 500 ml beaker. The 0.5 ppm of SDS, 1.5 ppm of span 80, 0.5 ppm of triton X-100, and 50 ppm of AAm were dissolved in 87 ppm of deionized water. The stirring speed was set to 500 rpm. The process was carried out at 30 ^{o}C, and hot plate was used for this purposes. After 15 minutes of mixing, the hot plate was turn off and 17.5 wt.% of MMA, 26.5 wt.% of St, 3.5 wt.% of AAc, and 1.5 ppm of MBA were added to the mixture under stirring. At room temperature, when the color of the mixture was changed from hazy to whitish, the stirring speed was increased to 900 rpm, and the mixing was continued for another 30 minutes . The obtained pre-emulsified monomer was filled into 500 ml graduated dropping funnel for the next step.

2.1.2 Synthesis Polymer Microgels (Poly(Acrylamide-co-Acrylic Acid)-grafted-Poly (Styrene-co-Methyl Methacrylate))

First, initiator was added to reactor in order to generate free radicals semi-batch emulsion polymerization. 116 ppm of deionized water was poured into a 2000 ml jacketed glass reactor with five neck lid equipped by a thermocouple, a four blades stainless steel impeller, and a nitrogen inlet [9]. Next, 0.6 ppm of SDS has been added into the reactor. The reactor content was heated to 80 ºC under 100 ml/min nitrogen flow and 350 rpm stirring. Once the reactor temperature reached 80 ºC, 5.5 ppm of KPS solution (9.1% in water) was added to the reactor and the free radical were created after a few minutes. After that, 6.06 ppm of KPS solution (0.99% in water) and the prepared monomer were fed continuously to the reactor. The monomer was added drop wisely by a graduated funnel, and the KPS solution was added one drop in every 5 minute using 25 ml burette. The reaction temperature was controlled at 80–82 ºC. The microgels were stirring at a speed of 450 rpm to ensure completed conversion after the feeding was completed for 24 hours. The obtained microgels emulsion was cooled down to room temperature.

2.2 Characterization

2.2.1 Fourier Transform Infrared (FTIR)

The FTIR spectra of polymer emulsion microgels and pre-emulsified monomer were recorded with a Perkin Elmer Spectrum 2000 using CAF2 disks. The 16 scans were taken, and the resolution in wave number was 4 cm^{-1}.

Table 1: Formulation of rHDPE/EVA/ESP composites

Composite code	rHDPE (phr)	EVA (phr)	ESP (phr)	ESP_{APTES} (phr)
rHDPE/EVA/ESP0	50	50	-	-
rHDPE/EVA/ESP5	50	50	5	-
rHDPE/EVA/ESP10	50	50	10	-
rHDPE/EVA/ESP15	50	50	15	-
rHDPE/EVA/ESP20	50	50	20	-
rHDPE/EVA/ESP25	50	50	25	-
rHDPE/EVA/$ESP5_{APTES}$	50	50	-	5*
rHDPE/EVA/$ESP10_{APTES}$	50	50	-	10*
rHDPE/EVA/$ESP15_{APTES}$	50	50	-	15*
rHDPE/EVA/$ESP20_{APTES}$	50	50	-	20*
rHDPE/EVA/$ESP25_{APTES}$	50	50	-	25*

*3-aminopropyltriethoxysilane (APTES) was added at 6wt% of eggshell powder

2.2.2 Scanning Electron Microscope (SEM)

Morphology study by SEM was considered the microstructures and particle morphology of synthesized microgels. Particle morphology of polymer microgels was observed in a Hitachi TM3000 SEM at an accelerating voltage of 15 kV.

3.0 RESULTS AND DISCUSSION

3.1 FTIR Analysis

FTIR spectra of pre-emulsified monomer and polymer microgels are given in Figure 1. Both spectra showed a broad absorption band at 3700-3000 cm^{-1} corresponding to OH and NH groups. The peak at 1675 cm^{-1} represents carbonyl group (C=O) of AAm and shifted to 1671 cm^{-1} upon polymerization [38]. The peak at 1630 cm^{-1} is assigned to C=O stretching of carboxylate and can be seen from the shoulder peak upon polymerization. The peaks at 1600 cm^{-1} in both spectra are assigned to NH_2 scissors of amides (AAm). The peak at 1492 cm^{-1} is corresponding to C-C of aromatic ring modes. Furthermore, the peaks at 1433 cm^{-1} in both spectra are assigned to C-N stretching vibration of amides. The medium intensity bands at 1361 cm^{-1} and 1283 cm^{-1} are assigned to CH_2 wagging vibration from MBA monomer and polymer, respectively. The peak at 1200 cm^{-1} is assigned to C-C-O stretching vibrations of ester group which disappear upon polymerization. The disappearance of C-C-C stretching peaks at 1330-1160 cm^{-1} is an evidence of the grafting and cross-linking in polymer microgels [10].

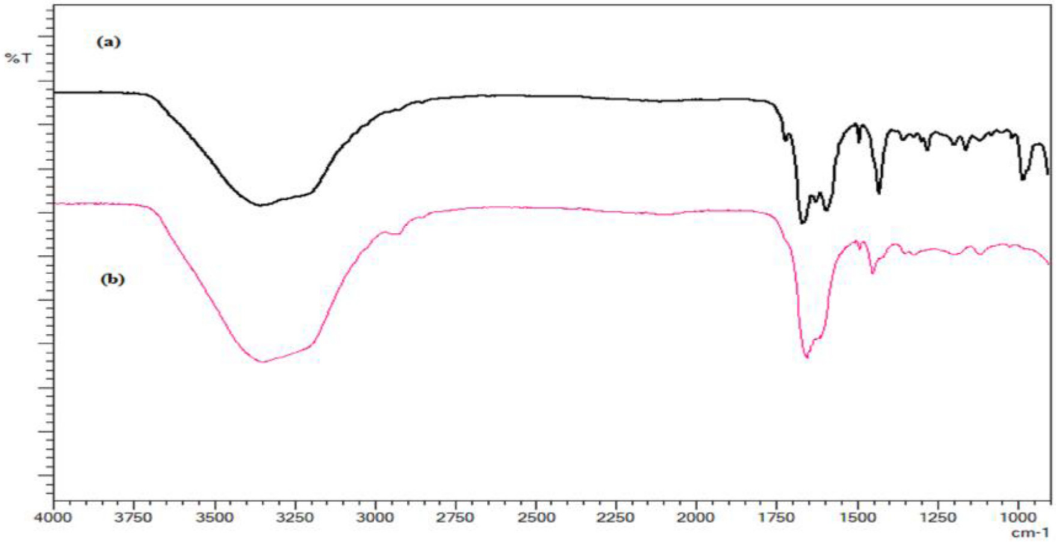
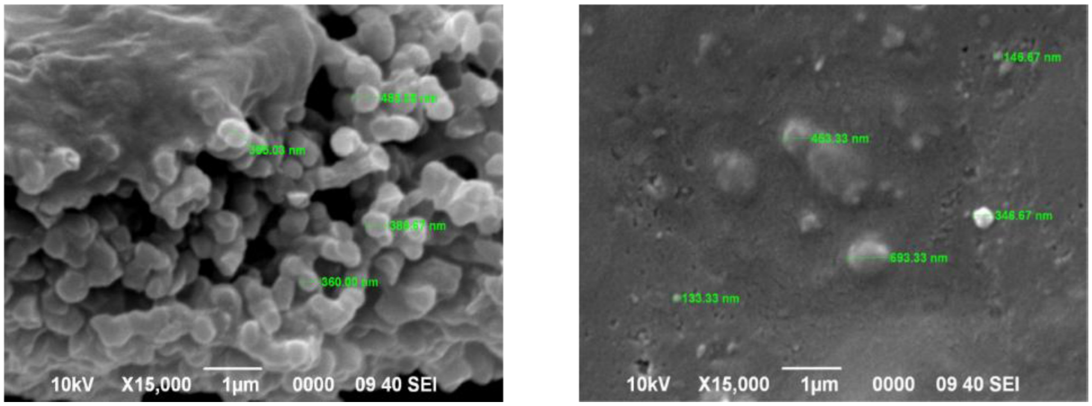


Figure 1: FTIR spectra of (a) pre-emulsified monomer and (b) polymer microgels

3.2 Scanning Electron Microscope (SEM)

Two or more families of polymers which include in composite particles are incompatible and that will phase separate through nucleation and growth [11]. The particles in this study are consists of poly(AAm-co-AAc), which uniformly cross-link with MBA and grafted to poly(St-co-MMA). The resulting particle morphology cannot simply describe as a core–shell type. This is due to interchange of thermodynamics as well as kinetics parameters during the polymerization process. Therefore, spherical shape like structure was formed during the transition morphologies (morphologies in between the limits of complete phase separation).

The structure of polymer emulsion microgels system containing a certain amount of water during film-forming process was revealed by SEM in Figure 2 (a). While Figure 2 (b) shows morphology of microgels after dried it in oven. By using SEM, these particles were identified as polymerized monomer droplets and as aggregates of microgels. The accumulation is expected because microgels may collide with each other and residual groups of particles may react with radical centers of neighboring particles thus bonding them covalently together. This reaction is called interparticle crosslinking [12].



(a) (b)

Figure 2: (a) and (b) SEM images of spherical particles

4.0 CONCLUSION

Microgels emulsion which based on water was polymerized using hydrophilic monomers (acrylamide and acrylic acid) and hydrophobic monomers (styrene and methyl methacrylate) by semi batch emulsion polymerization in the presence of KPS initiator and three types of surfactant which are SDS, Triton-X and Span-80. The resulting particles are small sizes, monodisperse, narrow size distribution and spherical morphologies. Characterization of emulsion microgels by FTIR spectra suggests that the disappearance of C-C-C and C-C-O stretching is due to grafting and crosslinking. Accordingly, SEM observation reveals that the morphology of polymer microgels particles is spherical shape and formed in micron size.

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