

EFFECT OF REACTION TEMPERATURES ON SYNTHESIS OF  
POLY(ACRYLAMIDE-*co*-ACRYLIC ACID) GRAFTED POLY(STYRENE-*co*-  
METHYL METHACRYLATE) MICROGELS

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Thanks **ALLAH** for everything.

Dedicated to the special person in my life,  
my beloved parent,

*Ahmad Rifa'i bin Selamat and Siti Asma binti A Kadir,*

my siblings,

*Latifah Adawiyah and her family*

*Aina Mardziah*

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## ABSTRACT

Poly(acrylamide-*co*-acrylic acid) grafted poly(styrene-*co*-methyl methacrylate) was synthesized through simultaneous crosslinking and graft copolymerization in the presence of N,N'-methylenebisacrylamide crosslinker and potassium persulphate initiator. The main objective of this research was to produce a polymer microgel using emulsion polymerization process. Three different reaction temperatures, 60, 70 and 80 °C were used for the polymerization process. The chemical structure and the morphology of the polymer microgel were characterized using an attenuated total reflectance-Fourier transform infrared (ATR-FTIR) and scanning electron microscopy (SEM), respectively. Total solid content, water absorption and gel content were also analyzed. ATR-FTIR spectra of pre-polymerization sample and microgel showed the appearance of a new peak in the range of 2800 - 2950 cm<sup>-1</sup> and also a peak loss in the range of 970 - 1000 cm<sup>-1</sup> after the polymerization process. SEM showed the surface formation of spherical microgel of around 100 to 600 nanometers. The total solid content (49.50 ± 1.43 %), water absorption (135.13 ± 1.90 %) and gel content (50.79 ± 1.23 %) at temperature 70 °C were higher which showed better colloidal properties compared to emulsion microgel at the temperature of 60 and 80 °C. Microgel produced at 60 °C polymerization temperature was used to coat two types of substrate, stainless steel and polymethyl methacrylate (plexiglass), however the coating was cracked and detached from the substrate after it dried. This microgel is suggested to be used as a coating for future study.

## ABSTRAK

Poli(akrilamida-*ko*-akrilik asid) tercantum poli(stirena-*ko*-metil metakrilat) telah disintesis melalui paut-silang serentak dan ko-pempolimeran cantum dengan kehadiran paut silang N,N'-metilenabisakrilamida dan pemula kalium persulfat. Objektif utama kajian ini adalah untuk menghasilkan mikrogel melalui pempolimeran emulsi. Tiga suhu tindak balas yang berbeza, 60, 70 dan 80 °C telah digunakan untuk proses pempolimeran. Struktur kimia dan morfologi polimer mikrogel telah dicirikan masing-masing menggunakan pantulan keseluruhan dikecilkan-inframerah transformasi Fourier (ATR-FTIR) dan mikroskop elektron imbasan (SEM). Jumlah kandungan pepejal, penyerapan air dan kandungan gel juga telah dianalisa. Selepas proses pempolimeran, ATR-FTIR spektrum untuk sampel pra-pempolimeran dan mikrogel menunjukkan kemunculan puncak baru pada julat 2800 hingga 2950  $\text{cm}^{-1}$  dan juga kehilangan puncak yang lama pada julat 970 hingga 1000  $\text{cm}^{-1}$ . SEM menunjukkan permukaan mikrogel ini berbentuk sfera dan saiznya sekitar 100 hingga 600 nanometer. Jumlah kandungan pepejal ( $49.50 \pm 1.43\%$ ), penyerapan air ( $135.13 \pm 1.90\%$ ), kandungan gel ( $50.79 \pm 1.23\%$ ) pada suhu 70 °C adalah lebih tinggi menunjukkan sifat koloid yang lebih baik berbanding dengan emulsi mikrogel pada suhu 60 dan 80 °C. Mikrogel yang dihasilkan pada suhu pempolimeran 60 °C telah digunakan sebagai salutan ke atas dua jenis substrat iaitu keluli tahan karat dan polimetil metakrilat (kaca pleksi), bagaimana pun salutan itu retak dan tertanggal daripada substrat selepas mikrogel kering. Mikrogel ini dicadangkan boleh digunakan sebagai salutan untuk kajian akan datang.

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**LIST OF ABBREVIATIONS**

°C	-	Degree Celcius
2-EHA	-	2-Ethylhexyl acrylate
AAm	-	Acrylamide
AAc	-	Acrylic acid
ABS	-	Acrylonitrile butadiene styrene
AIBN	-	2,2-Azobisisobutyronitrile
ASTM	-	American Standard of Testing and Method
ATR	-	Attenuated Total Reflectance
BA	-	Butyl acrylate
DSC	-	Differential scanning calorimetry
FRP	-	Free radical polymerization
FTIR	-	Fourier Transform Infrared Spectroscopy
g	-	Grams
KPS	-	Potassium persulfate
kV	-	Kilovolt
MBA	-	N,N-methylenebisacrylamide
MA	-	Methacrylic acid
MMA	-	Methyl methacrylate
MW	-	Molecular weight
NIPAM	-	N-isopropylacrylamide
PAAc	-	Poly(acrylic acid)
PAAm	-	Poly(acrylamide)
PEGDA	-	Poly(ethylene glycol) diacrylate
PEO	-	Poly(ethylene oxide)
PNIPAM	-	Poly(N-isopropyl acrylamide)
pph	-	Part per hundred
rpm	-	Rotations per minute

SDS	-	Sodium dodecyl sulfate
SEM	-	Scanning Electron Microscopy
Span 80	-	Sorbitan monooleate
SS	-	Stainless steel
St	-	Styrene
Triton X-100	-	Octylphenol ethylene oxide
TSC	-	Total solid content
T <sub>g</sub>	-	Glass transition temperature

## CHAPTER 1

### INTRODUCTION

#### 1.1 Research Background

The microgels were assumed as parts of synthetic rubber and the synthesis of polybutadiene can be used to produce microgel (Funke and Okay, 1998). Alberto *et al.*, (2011) defined microgel as a colloidal dispersion of gel particles which have few criteria such as the particle size range of microgel should be 10 to 1000 nanometer, that size is normal for colloidal particles. Microgels can be dispersed in a solvent and swollen by the solvent. Microgels can be described as micrometer-sized particles which contain cross-linked polymer network swollen by solvent (Seiffert, 2013). They can be described as three-dimensional network structures, can absorb and retain significant amount of water (Rosiak and Yoshii, 1999).

Recently, various industries are interested in microgels due to their potential applications. Furthermore, there are so many great research with various aspects of microgel preparation, characteristics and applications (Thorne *et al.*, 2011). Microgel can be prepared by several methods such as emulsion polymerization (Machotová and Šňupárek, 2009), dispersion polymerization (Hong *et al.*, 2013) and suspension polymerization (Zhu *et al.*, 2005).

Microgels can be synthesized from monomers by using the emulsion polymerization method where it can yield particles of spherical shape and narrow size distributions due to microgel properties (Machotová *et al.*, 2008). The polymer particles frequently coagulate during polymerization especially when the amount of crosslinker is large in emulsion crosslinking polymerization (Tobita *et al.*, 2000).

Emulsion polymerization can be produced either in batch or semi batch; semi-batch gives an advantage in this process where it involves a constant flow of monomers and the other raw materials over a set amount of time. Compared to the whole amount of monomer that goes in the batch, the constant flow of monomer enters the system very slowly. The slow addition of monomer and predictable amount of heat control helps to control the best batch temperature. The heating system can accurately track the set point of the batch with constant addition where it can reduce fluctuation and deviation. Since the monomer is constantly added, the reaction is not starved of monomer and there is no potential for uneven distribution of monomers into the polymer backbone (Arnold, 2015).

Microgels can be applied in many fields such as catalyst (Ajmal *et al.*, 2015), oil recovery, biomaterials (Basu *et al.*, 2010), drug delivery wastewater treatment (Nur *et al.*, 2009) printing and coatings (Kausar *et al.*, 2008). Normally coatings are used based on these reasons which are for decoration, protection or some functional purpose. Adhesion is an important part to most coating (Zeno *et al.*, 2007). Previously, the study for microgel coating have been done by few researchers, for example Latnikova *et al.*, (2012) have prepared self-healing coatings from two component water based of epoxy coating which are a suspension of epoxy prepolymer in water solution and a solution of the polyamine mixture in water using interfacial emulsion polymerization method.

## 1.2 Problem Statement

Pelton and Hoare (2010) reported that macrogel is being formed with the polyacrylamide solution and it also cannot be formed in water by homogeneous polymerization. The polymerization was carried out using hydrophobic and hydrophilic monomers to avoid the formation of macrogels in the existence of water and oil soluble surfactant.

Semi-batch is the most widely used emulsion polymerization process due to its versatility and advantages over a batch process. Unlike batch polymerization, semi-batch is highly reproducible, offers operational flexibility, and control over the size and morphology of particles produced. Semi-batch is characterized by the controlled addition of monomer, surfactant, initiator, or water to a reaction vessel throughout the reaction.

Previously, toxic chemicals have been used in the coating industry, they developed efficient paints using organotin compounds for example tributyltin (TBT) and triphenyltin (TPT). Maréchal and Hellio (2009) stated that both chemicals were highly toxic for many aquatic organisms and have been proven to contaminate the food chain and harm the environment. To overcome the issues of toxic coating, the monomers have been chosen if they are less toxic.

Besides that, before this expensive monomer is used for example tributylsilyl methacrylate (TBSM) (Hong *et al.*, 2013), so conventional monomer was suggested to synthesize microgels, which can be used for widen application and also can reduce cost. The monomer can be introduced as either a pre-emulsion (monomer in water stabilized by surfactants) or as a neat monomer feed (monomer only) (van Herk, 2005).



Four main monomers were used in this study which are acrylamide, acrylic acid, methyl methacrylate and styrene where these monomers are less toxic and not so expensive. Besides that, the dispersion medium of emulsion polymerization is water, so it provides low-cost, nonflammable, harmless and no odor systems. The technological process of this polymerization has relative simplicity. Since the viscosity of latex does not depend on the molecular weight, so it can produce high molecular weight polymer at a high reaction rates. Emulsions with low viscosity to solutions of polymers can be achieved due to the producing of high solids content (Yamak, 2013).

Poly(acrylamide-co-Acrylic Acid) grafted Poly(styrene-co-Methyl Methacrylate) microgels with certain properties such as high crosslinking degree, stable, spherical morphologies and small particles expected to produce in this research. Besides that, hydrophobic and hydrophilic monomers have been combined to produce the microgel. To get the best performance on microgel, few variables should be studied such as total solid content, crosslinking degree and water absorbency. Since the process of polymerization is exothermic, the effect of temperature was analyzed.

### **1.3 Objective of Study**

The main objective of this project is to develop polymer microgel poly(Acrylamide-co-Acrylic Acid) grafted poly(Styrene-co-Methyl Methacrylate) using emulsion polymerization. Therefore, the objectives of this study are:

- i. To synthesize a polymer microgel from hydrophobic monomer (acrylamide and acrylic acid) and hydrophilic monomer (styrene and methyl methacrylate) using a semi batch emulsion polymerization method.

- ii. To evaluate the effect of reaction temperatures on the physical properties, coating adhesion, surface morphology and swelling behavior of polymer microgels.

#### 1.4 Scope of Study

The scopes of this study are listed below:

- i. Preparation of emulsion polymer from hydrophilic monomer (Acrylamide, Acrylic Acid) and hydrophobic monomer (Styrene, Methyl Methacrylate) with an assistance of *N,N'*-methylenebisacrylamide (MBA) and potassium persulphate (KPS) functionalized as crosslinker and initiator, respectively.
- ii. Three different temperatures which are 60, 70 and 80 °C were used to study the effect of reaction temperature during polymerization on the reaction of time.
- iii. Evaluation of few properties such as percentage of total solid content, gel content and water absorption of emulsion microgels.
- iv. Characterization and morphology study of the synthesized microgels using:
  - a) Attenuated Total Reflectance Fourier-Transform Infrared Spectroscopy (ATR-FTIR).
  - b) Scanning Electron Microscopy (SEM).

## **1.5 Significance of Study**

From this research, a polymer microgel with hydrophobic and hydrophilic properties was formed which has the potential to be applied in biofouling application. The reaction parameters studied assist the optimum synthesis of the microgel. The changes in reaction temperature give different effect on few properties such as for total solid content, gel content, water absorption and also for the surface morphology. The results obtained from this study can be applied in a big scale or industry based on optimum temperature which can produce an emulsion microgel of good quality.

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