Journal of Chemical Process and Material Technology
http://publikasiilmiah.unwahas.ac.id Purnavita et.al., vol(1), 10-17, 2022

Polymerization of Poly Methyl Methacrylate Using Emulsion Method and H_2O_2 as Initiator

Sari Purnavita[1*], Cyrilla Oktaviananda[2], Sri Sutanti[3], Herman Yoseph Sriyana[4], Antonius Prihanto[5]
[1,2,3,4,5] Program Studi D3 Teknik Kimia, Politeknik Katolik Mangunwijaya
**Corresponding Author: cyrillaoktaviananda.28@gmail.com*

Abstract

Polymethyl Methacrylate is a synthetic polymer prepared by free radical addition and polymerization. By emulsion polymerization, polymethyl methacrylate can be applied as paints, adhesives, and coatings. The amount of polymer produced from a reaction will be influenced by the type of initiator according to the characteristics of the monomer and the amount of initiator added. Therefore, research is needed to study the effect of the number of initiators (H_2O_2) on the amount of polymer formed. The independent variables in this study were H_2O_2 by 1%, 2%, 3%, and 4%. This research procedure was carried out in a two-stage process. The first stage is the process of separating the inhibitor contained in the methyl methacrylate monomer by adding a 1 N concentration of NaOH solution while stirring until evenly distributed, then put into a separating funnel to separate pure methyl methacrylate from the inhibitor dissolved in alkaline solution. The second stage is the polymerization reaction process using the emulsion method. Dissolve polyvinyl alcohol in hot water at 70°C, put the polyvinyl alcohol solution into a three-neck flask equipped with a stirrer and a hot plate heater, add the initiator to 60°C, then add methyl methacrylate monomer while stirring and heating at room temperature 100°C for 1 hour. . The resulting product is a thick poly methyl methacrylate emulsion, and milky white. The results showed that the more initiators were added, the higher the viscosity and the higher the solids content.

Keywords: Initiator; Methyl Methacrylate, Emulsion

INTRODUCTION

Polymethyl methacrylate is clear, colorless transparent plastic with a higher softening point, better impact strength, and better wearability. It is available in molding and extrusion compositions, syrups, cast sheets, rods, and tubes. Perhaps the outstanding property of poly methyl methacrylate is its optical clarity and lack of color (Billmeyer, 1994).

PMMA (IUPAC name: poly [1-(methoxycarbonyl)-1-methyl ethylene]) is a synthetic polymer prepared by the free radical addition and polymerization of methyl methacrylate ($C_5H_2O_8$) to poly methyl methacrylate ($(C_5O_2H_8)_n$ (Zafar, 2020). Polymethyl

Methacrylate (PMMA) is a versatile transparent thermoplastic polymer. It has fairly good impact resistance and excellent bio-compatibility (Saurabh *et al*., 2012).

Some of the uses of PMMA in daily life are as a resin (a polymer capable of forming a film layer) in the coating industry, and as a replacement for glass, such as car rear windows and airplane windows. In addition, it is also used in industries such as automotive, monitor, electrical filling, optical equipment, and machinery. PMMA can also be used as a template in the manufacture of porous membranes (Ady and Viandari, 2016). PMMA can be used as an adhesive (Partuti *et al*., 2016).

By emulsion polymerization, a variety of synthetic materials like paints, toners, adhesives, coatings, etc. are being commercially produced by various industries (Saurabh *et al*., 2012). The polymerization reaction of methyl methacrylate monomer to form PMMA polymer proceeds in a chain with the steps of initiation, propagation, and termination (Wahyuni and Dewi, 2003).

The monomer is a mobile liquid with a characteristic sweet-smelling odor and with the following properties: boiling point (760 mmHg) 100,5^{o}C, and density 0,936-0,94 Mg/cm^3 (Brydson, 1966). Solubility of methyl methacrylate in water (30^{o}C) 1,5%. A hydrophilic monomer is a monomer with a water solubility of more than 1%, and methyl methacrylate is a typical hydrophilic monomer. The addition of chemical inhibitors to the monomer aims to prevent self-polymerization during storage (Brydson, 1966).

The initiation stage is the stage of free radical formation that comes from the breakdown of the chain at the initiator and the bond between the free radicals and the methyl methacrylate monomer. Propagation is a chain growth stage, namely the reaction between chains containing free radicals originating from the initiation stage will bind to the methyl methacrylate monomer so that the chain will increase in length. The termination reaction is a combination of disproportionation. PMMA terminates entirely by disproportionation at polymerization temperatures above 60^{o}C (Billmeyer, 1994).

Polymer emulsions are not emulsions but rather dispersions of high molecular weight solid materials in a non-solvent, liquid medium. These formulations are called emulsions because they are produced using a heterogeneous polymerization in the presence of a water-soluble initiator and an emulsifier. In emulsion polymerization, the diffusion of heat can easily be controlled and the rate of polymerization and the degree of polymerization can be manipulated to achieve the desired results. Emulsion polymerization, where the particles are less than 1 μ. Various additives are used in emulsion polymerization: emulsifiers, initiators, protective colloids, water mediums, and plasticizers (Schick and Fowkes, 1974).

The initiators commonly used in emulsion polymerization are soluble in water. We shall devote our attention principally to systems in which ammonium persulfate, hydrogen peroxide, cumene hydroperoxide, t-butyl hydroperoxide, and azobisisobutyronitrile are used as the initiator. These initiators have different reaction temperatures. The choice of initiator must be adjusted to the PMMA polymerization reaction temperature. Hydrogen peroxide is an initiator that can react at a temperatures of 40-60^oC so it is suitable for polymerization at a temperature of 60-100 ^oC. The radicals in the oxidation-reduction system, are frequently used to accelerate polymerization at low temperatures (Schick and Fowkes, 1974). The initiator is a source of free radicals. In the polymerization process, a free radical is any atom or group that has one or more unpaired electrons. Without the initiator, the initial stages of polymerization cannot occur. The initiator is not a catalyst because a certain amount of the initiator is consumed in a chemical reaction. Commonly used initiators are redox initiators such as H_2O_2 (Suswanti, 2008). The main advantage of redox initiators over thermal initiators is that the production of radicals can occur over a wider temperature range and results in higher molecular weights. Additionally, the redox initiator requires only a lower activation energy for decomposition, which is about 10 Kcal/mol. Another advantage of the redox initiator in the initiation process is that the reaction rate is not greatly affected by temperature so polymerization can be carried at temperatures between 20-70^oC (Kuswantiningsih, 2010).

Emulsions do not show a significant increase in viscosity until the solids content reaches approximately 50%, which makes them much more desirable for many applications. Dispersions of solid polymers can be prepared by fine drops of monomers to produce a polymeric emulsion. The best method for achieving stable polymer dispersion is to produce the emulsion using the emulsion polymerization method, and for that reason, emulsion polymerization is critical commercially. Since water is the most common dispersing medium, it is convenient to classify monomers according to whether they are hydrophilic or hydrophobic. A hydrophilic monomer like methyl methacrylate is polymerized both in the water phase and in the micelle so that the emulsifier exists not only on the surface but also in the interior of particles. This means that the emulsifier is not as effective in stabilizing the particles, and consequently, the addition of a protective colloid is required (Schick and Fowkes, 1974).

In general, protective colloids (mainly water-soluble polymers) have been used to stabilize emulsion particles. Synthetic or semi-synthetic polymers, such as polyvinyl alcohol and hydroxyl methyl cellulose, are employed as protective colloids. When a protective colloid is added to an emulsion, the particles are stabilized by its adsorption or by the increased viscosity of the system (Schick and Fowkes, 1974).

The factors that affect the characteristics of emulsion polymerization are molecular size and shape, molecular weight, molecular weight distribution, solid content, and viscosity. In emulsion polymerization, particle size analysis and particle size distribution are critical. This is related to the kinetic theory concerning particle formation, the particle growth, and particle interactions when related to polymerization reaction conditions. In the industry, particle size and distribution are related to such things as paint properties and stabilization of emulsion polymers. Generally, the stabilization of an emulsion or dispersion system will decrease with increasing particle size and distribution. The particle size distribution is influenced by the amount of initiator and surfactant used in the polymerization technique. Generally, higher molecular weight polymers are stronger but difficult to manufacture. The degree of polymerization and molecular weight are the most important characteristics of macromolecular compounds. Both of these indicate how many monomer units make up a polymer chain. Emulsion polymers resulting from the emulsion polymerization process involving two liquid phases and producing a solid phase dispersed in a liquid medium can have uniform particle sizes. The particle size distribution of polymers can be divided into polydisperse and monodispersed (Suswanti, 2008). The process of making a poly (methyl methacrylate) with the emulsion method is also influenced by the concentration of reactants, stirring speed, and temperature (Gunawan *et al.,* 2003. The particle size of the beads is determined by the shape and size of the reactor, type, and rate of agitation and protective colloids present. Polymerization can be carried out rapidly, usually in less than an hour (Brydson, 1966). The total solids content is important to see the amount of polymers formed because these solids are polymer solids formed. Emulsions with high polymer solids content will have good quality, especially adhesion.

Several studies that have been carried out by previous researchers are about the polymerization of MMA with the emulsion method with the result that there is an initiator effect on particle size (Krishan and Magaritova, 1961). The polymerization of methyl methacrylate has been carried out by (Laelani, 2007) and (Kurniahati, 2007). Badr (2018) studied monodispersed poly (methyl methacrylate) (PMMA) nanoparticles that were synthesized by combined dispersion and emulsion polymerization, using aqueous alcohol (methanol/water) as the dispersion medium. The influence of the dispersion medium ratio, stabilizer concentration, and initiator type and concentration on the colloidal stability, particle size, size distribution, and % conversion, was investigated

(Badr *et al*., 2018). Saurabh (2012) studied the synthesis and kinetic study of PMMA carried out in a batch emulsion polymerization reactor using Potassium Persulphate (KPS) as initiator Sodium Oleate as surfactant and distilled water as medium (Saurabh *et al*., 2012).

In this paper the synthesis of poly methyl methacrylate in batch emulsion using H_2O_2 as initiator and comparison concentration initiator to the characterization of PMMA.

EXPERIMENTAL SECTION

Provide sufficient detail to allow the work to be reproduced, which may include Materials, Instrumentation, and Procedure (ASTM, 2014).

Materials

The materials used are monomer (methyl methacrylate), initiator (H_2O_2), protective colloid (PVA), and water medium.

Instrumentation

A three neck, beaker glass, thermometer, hot plate, magnetic stirrer, and reflux.

Procedure

1) Monomer purification

Methyl methacrylate will polymerize readily and the effect may be observed with uninhibited samples of monomers during storage. In commercial practice, the monomer is supplied with up to 0-10% of an inhibitor such as hydroquinone which is removed before polymerization, by washing with an alkaline solution (NaOH) 2,5N (Brydson, 1966).

2) Emulsion polymerization

One part of methyl methacrylate was agitated with two parts of PVA solution and H_2O_2 was employed as an initiator. The reaction temperature is 100^{o}C. Polymerization was complete in about an hour (Brydson, 1966).

3) Analysis procedure

a) Viscosity

PMMA emulsion viscosity is tested using the ford viscosity cup number 4 (ASTM, 2014).

b) Solids content (%)

PMMA emulsion is heated at 100^{o}C. The total solids content is a measure of the amount of material remaining after all the water has been evaporated.

RESULTS AND DISCUSSION

a. Effect of Initiator Concentration on Total Solids Content

The effect of initiator concentration on total solids content and viscosity of poly methyl methacrylate is shown in the figure 1.

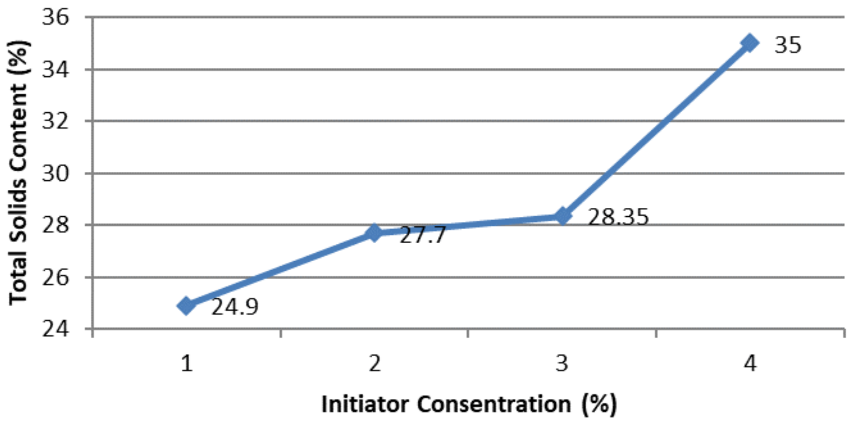

Figure 1. Effect of initiator concentration on total solids content (%)

Based on Figure 1, the addition of the number of initiators affects the solids content of the poly methyl methacrylate (PMMA) emulsion and the initiator concentration of 4% gives the highest solids content of 35%. The solids content in the PMMA emulsion indicate the number of polymer particles formed, so that the more initiators, the faster the addition polymerization reaction of PMMA formation, the number of polymer particles formed is also increasing. According to research by Lela S. Laelani and Umi K. (Kuswatiningsih, 2010), the concentration of the initiator affects the polymer produced. In the polymerization of methyl methacrylate, there is a tendency to increase the conversion percentage as the concentration of the initiator used increases. This is due to the increasing number of free radicals produced so that the polymerization rate increases. According to SNI, the minimum solids content is 40%. The results obtained in this study are still below the SNI but only a difference of 5%. The total solids content is important to see the amount of polymer formed because these solids are polymer solids formed. Emulsions with high polymer solids content will have good quality, especially adhesion. The highest solids content obtained in this study was 35% and almost the same as the results of research by Budianto and Sarwono (2008), which was 37%.

b. Effect of Initiator Concentration on Viscosity (Cp) of Poly Methyl Methacrylate

Effect of Initiator Concentration on Viscosity (Cp) is shown in the Figure 2.

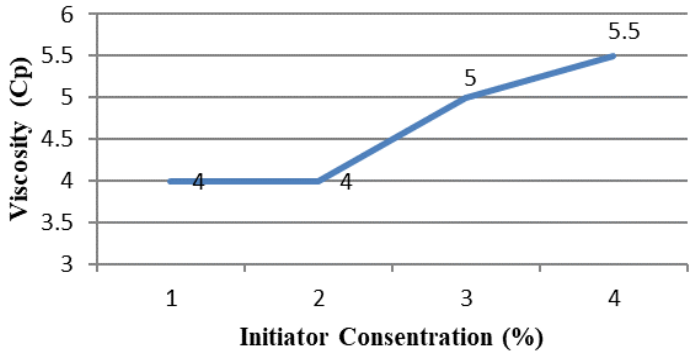

Figure 2. Effect of Initiator Concentration on Viscosity (Cp)

Based on Figure 2, the addition of the number of initiators has an effect on the viscosity of the polymer formed, the initiator concentration of 4% gives the highest viscosity result, namely 5.5 Cp. The results of this study were compared with those (Supri and Siregar, 2004) where the viscosity obtained was between 7.5 and 10.

The more initiators are added, the faster the rate of free radical formation and in the end will accelerate the polymerization reaction. The more initiators, the more polymer particles are formed. With the increasing number of polymer particles formed, the number of PMMA polymers formed is also increasing, so that the viscosity of the emulsion will increase.

According to (Supri and Siregar, 2004) in the early stages of adding monomer and initiation catalyst into the reactor, the monomer granules were dispersed in a continuous phase of water, but at a temperature of 70°C, the color of the mixture in the reactor became bluish and whiter.

CONCLUSION

1. The addition of the initiator affects the solids content of the poly methyl methacrylate (PMMA) emulsion. The initiator concentration of 4% gives the highest solids content of 35%.

2. The addition of the number of initiators has an effect on the viscosity of the polymer formed. The initiator concentration of 4% gives the highest viscosity of 5.5 Cp.

ACKNOWLEDGEMENTS

The authors would like to express the highest appreciation to Prodi D3 Teknik Kimia Politeknik Katolik Mangunwijaya for their support in this study.

REFERENCES

Billmeyer, F. W. 1994. *Textbook of Polymer Science*. Third Edit. John Wiley and Sons, New York.

Brydson, J. A. 1966. *Plastics Materials*. London Newnes-Butterworths, London.

Gunawan, I., Darwinto, T., Sudaryanto, dan Handayani, A. 2003. Sintesis dan Karakterisasi Microsphere Berbasis Poli Metil Meta Akrilat (PMMA). *J. Sains dan Teknol. Indones.*, 4 (4): 1–7.

Kurniahati, U. 2007. Studi Polimerisasi Core Metil Metakrilat: Pengaruh Konsentrasi Inisiator Ammonium Persulfat (APS) Dan Surfaktan Sodium Lauril Sulfat (SLS) Terhadap Ukuran Dan Distribusi Ukuran Partikel. *Universitas Indonesia.*

Kuswantiningsih, T.2010.Polimerisasi Bulk Metil Metakrilat: Pengaruh Perbandingan Jenis Dan Variasi Komposisi Initiator Redoks Terhadap Persen Konversi Dan Berat Molekul.*Universitas Indonesia.*

Krishan, T., and Magaritova, M. 1961.A Study of Emulsion Polimerization. *U.S..S.R*, 52: 139–145.

Laelani, S. 2007. Pengaruh Konsentrasi Surfaktan Sodium Lauril Sulfat Dan Inisiator Redoks Terhadap Ukuran Dan Distribusi Ukuran Partikel Pada Homopolimerisasi Metil Metakrilat. *Universitas Indonesia*.

Partuti, T., Dwiyanti, Y., Fitrullah, M., and Trenggono, A. 2016. Pengaruh Pelarut Mek/Toluena Terhadap Peel/Shear Strength Perekat Hasil Grafting Neoprena dan MMA', *J. Integr. Proses*, 6 (1): 39–44.

Saurabh, Upadhyaya, S., Dohare, R. K., Agarwal, M., and Gupta, A. 2012. Kinetic Study of PMMA Synthesis by batch Emulsion Polymerization, *Oriental Journal of Chemistry*, 28 (1): 565–570.

Schick, M. J., and Fowkes, F. M. 1974. *Emulsions and Emulsion Technology. II. Lissant, K. J. (Ed.)'*, Marcel Dekker Inc, New York and Basel.

Supri, and Siregar, A. H. 2004. Sistensis Dan Karakterisasi Homopolimer Emulsi Poli (Metilmetakrilat) Dengan Variasi Konsentrasi Surfaktan Dan Zat Pengalih Rantai. *Universitas Sumatera Utara.*

Suswanti, I. 2008. Polimerisasi Core-Shell Metil Metakrilat - Butil Akrilat: Pengaruh Variasi Pengikat Silang Glisidil Metakrilat Dan Teknik Polimerisasi Terhadap Ukuran Partikel Dan Indeksi Polidispersitas. *Universitas Indonesia.*

Wahyuni, D., and Dewi, S. R. 2003. Penelitian Pembuatan Poli Metil Metakrilat (PMMA)', *J. Teknol. Dirgant.*, 2 (1): 22–32.

Zafar, M. S. 2020.Prosthodontic Applications of Polymethyl Mathacrylate (PMMA): Un Update', *Polymers (Basel).*, 12 (2299).