Purification Process of Poly Methyl Methacrylate Products Made with Suspension Polymerization Techniques

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Abstract. Poly Methyl Methacrylate (PMMA) is a commodity polymer produced from Methyl Methacrylate (MMA) monomer. This applied in various industries such as automotive and in the manufacture of artificial joints. Suspension polymerization techniques are able to produce polymer powders in micron size, uniform molecular weight and desired particle size distribution. This research was initiated by conducting polymerization process by heating Polyvinyl Alcohol (PVA, dispersant)/aqua dest (H₂O) mixture accompanied by nitrogen gas purging and stirring, then MMA and Benzoyl Peroxide (BPO, initiator) was added. The results of the polymerization process produce PMMA products in the form of powders which are suspected to still contain MMA, BPO, and PVA so that the washing process is required for PMMA products. Therefore, PMMA products resulting from the polymerization process are washed with water solvent with stirring, then the results of washing PMMA products are filtered and dried. The results of final PMMA products in the form of white powder which are then analyzed using Fourier Transform Infrared Spectroscopy (FTIR) analysis showed that product there is still a residual MMA. Scanning Electron Microscopy (SEM) analysis which results produce spheres of varying size and average particle size of 64.45 µm. Particle Size Analyzer result presents the average size of 62.05 µm.

1. Introduction

Poly Methyl Methacrylate (PMMA) is a synthetic polymer made from the monomer methyl methacrylate. This material was discovered in the early 1930s, and its application was introduced by Otto Rohm, in 1934. In general, PMMA is used in optical, automotive, and medical applications in the manufacture of artificial joints, dental prostheses and contact lenses [1]. Two important properties that differentiate it from other polymers are the optically clear and colourless properties (having a light transmittance of 92%), and their extremely hard surface. That's what it's good for medical applications; such as breathing apparatus, urological accessories, blood handling components, and catheter accessories [2].

These micron-sized granular polymer products can be prepared by a variety of techniques, the most popular of which are suspension or emulsion polymerization. The suspension polymerization
technique is able to produce small powders with the desired control over molecular weight and particle size [3]. In the suspension polymerization technique, MMA monomers that are mutually soluble with the initiator (Benzyol Peroxide, BPO) are mixed and dispersed into a mixture of Polyvinyl alcohol (PVA, as a dispersant) and water. For this reason, PMMA products may still contain Polyvinyl alcohol, Benzyol peroxide and Methyl methacrylate; as an impurity [4]. The residual monomer causes a pungent odour, and the presence of Benzyol peroxide can cause unexpected polymerization. These are the advantages and disadvantages of this polymerization process and must be removed from the product. The presence of residual monomer (MMA) in PMMA is not allowed in products for biomedical applications, because MMA is allergies and have serious health implications. Therefore, it is necessary to do purification or washing. The purification process can be carried out by hydrolysis (adding acid-base) and washing with solvents. Nogueira et al. reported polymerization of PMMA using materials including MMA, PVA, and 2,2-azobisisobutyronitrile (AIBN) and water. After polymerization, PMMA purification was carried out using binary solvents (ionized water and methanol), then centrifuged several times to remove unreacted material and dried in a vacuum oven at 60°C for two days [3]. In another study, Godiya et al., the purification of PMMA was carried out using n-hexane solvent on the results of PMMA synthesis accompanied by stirring. The product is filtered and dried overnight in an oven at 70 °C [5]. The use of methanol and n-hexane solvents will require further purification to remove the solvent so that when they are used, it does not cause damage to the implant area where the PMMA is used.

In this study, we focused on washing with a suitable benign solvent, and this time with water. The choice of solvent was made based on the solubility of PVA, BPO, MMA and PMMA in the solvent and its effect on the PMMA product itself. The material to be removed must be soluble and non-dissolving or slightly soluble for the PMMA product. Water is a good solvent for polar or ionic materials. Polyvinyl alcohol (PVA), which is a dispersant in the manufacture of PMMA products, has good water solubility. In addition, BPO, which is the initiator, can also be dissolved in water (1 mg/ml at 25°C). Likewise, MMA, which is a monomer, has a water solubility of 15.7 g/L at 20°C. This research was to study the washing of synthesized product of PMMA produced by suspension polymerization use water as a solvent. PMMA products were characterized by Scanning Electron Microscopy (SEM), Particle Size Analyzer (PSA) and Fourier-transform infrared spectroscopy (FTIR) to understand the success of forming micron-size PMMA granules and the effectiveness of their washing.

2. Experimental

2.1. Material
The monomer, Methyl methacrylate (MMA) of analytical grade was purchased from Aldrich (Merck), with 99%. Polyvinyl alcohol (PVA) as a suspending agent and Benzyol peroxide (BPO) as initiator was purchased from Merck. Distilled water as a washing medium. Purging UHP Nitrogen (N₂) is used to remove oxygen in the reactor, was supplied by Samator. All materials are used without further treatment.

2.2. Method
The mixture of polyvinyl alcohol and distilled water (1 g/L) was added to 1.0 L a closed glass reactor, which was equipped with a mechanical stirrer and had a nitrogen inlet and a condenser. The mixture was heated until 85°C and stirred at 800 rpm. When the temperature is reached, a polymerization process is carried out by adding 150 gr of methyl methacrylate (MMA) and 1.0 g of benzyol peroxide (BPO) in the reactor. The polymerization time is 1 hour, 30 minutes. After the process is achieved, formed a white powder (PMMA). The powder is filtered and purified. PMMA product purification is carried out by washing it using distilled water. Washing was carried out at room temperature with a stirring speed of 200 rpm for 30 minutes and was washed three times. Washed products are dried using vacuum drying. The dry product was analyzed using SEM, PSA and FTIR analysis. SEM was done by
Hitachi Flexsem1000 with an accelerating voltage of 10 kV. PSA was measured in water using CILAS 1190 Liquid. FTIR analysis was conducted using Thermo Scientific Nicolet IS10.

Figure 1. Scheme the equipment of polymerization (a) and washing (b) of PMMA products

3. Result and Discussion

The visual macroscopic of PMMA powder after purification treatment is shown in Fig. 2. The powder of PMMA colour is completely white for all sample (1 and 2). All products have almost the same appearance, which is a fine white powder.

Figure 2. Photographs of PMMA products: (a) Sample 1 and (b) Sample 2 after purification treatment

The PMMA products that have been dried are analyzed by Particle Size Analyzer (PSA), which is to determine the size of the PMMA particles. Previous to analysis, PMMA powder product was first dispersed in ethanol and ultrasonic for 3 minutes to ensure a good particle dispersion. From
the results of the PSA analysis, sample 1 has an average particle size of 71.4 µm, and sample 2 has an average particle size of 57.5 µm so that the average size of the two samples is 64.45 µm.

In this study, the morphology of the resulting PMMA was obtained from Scanning Electron Microscopy (SEM) analysis. The SEM analysis results can be seen in Figure 3.

Figure 3. Scanning electron micrographs of PMMA particles produced by suspension polymerization: (a) Sample 1 and (b) Sample 2 [Magnification: 100x]

Figure 3 shows the surface morphology of sample 1 (3a) and sample 2 (3b). It can be seen that PMMA products for both samples have spherical in morphology. This shows that the PMMA polymerization result by suspension technique has been successfully produced even though it still coagulates and hardens during the process, which results in agglomeration. This agglomeration causes the particle size of the sample to be non-uniform, as shown in Figure 3a and 3b, there are less perfect (irregular) grain shapes and stick to each other. To avoid agglomeration, it is necessary to improve the stirring position. The diameter size of the PMMA particles was determined using the ImageJ software. It was found that the average particle sizes were 69.5 µm (sample 1) and 54.6 µm (sample 2) so that the average particle size of the two samples SEM analysis results was 62.05µm, where the particle size obtained tends to be the same as the PSA results.
Figure 4 shows the Fourier Transform Infrared Spectroscopy (FTIR) spectra of PMMA product after the purification process. From the results of FTIR analysis, Figures 4(a) and (b) have peaks at 1718.96 and 1719.79 cm\(^{-1}\) which is the characteristic peak of the carbonyl group (C = O) that characterizes PMMA with its molecular structure (C\(_5\)H\(_8\)O\(_2\)). It can also be seen that the MMA content with its molecular structure C\(_5\)H\(_8\)O\(_2\), is indicated by the peak in the range 1637 - 1654 cm\(^{-1}\), which is the C = C group. In the final PMMA product, no peaks were seen around the 3400 cm\(^{-1}\) peak which is the hydroxyl group (–OH) from PVA with its molecular structure (C\(_2\)H\(_4\)O), and 2960 cm\(^{-1}\) which is the aromatic group of BPO with its molecular structure C\(_{14}\)H\(_{10}\)O\(_4\). This shows that PVA and BPO in the PMMA powder surface have dissolved into the water during washing treatment. But a small amount of unreacted MMA is still be found in PMMA powder products. This is because, in this condition, MMA has relatively low solubility in water.

4. Conclusion
PMMA production by suspension polymerization has been successfully carried out, and the resulting PMMA powder is white. The SEM result shows that the PMMA product has spherical in shape and the average size of 64.45 µm. The SEM result was in accordance with PSA result that presents the average size of 62.05 µm. Purification using the washing method with water has also succeeded in removing PVA and BPO in the product.

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