The synthesis of polymethylmethacrylate (PMMA) by miniemulsion polymerization for bone cement application: the role of anionic surfactant and co-stabilizer virgin coconut oil concentration

Adil Putra Natanael Simorangkir[1], *Fitri* Kurniawati[2], *Ekavianty* Prajatelistia[1] and *Oka* Pradipta Arjasa[2*]

[1]Materials Science and Engineering Study Program, Faculty of Mechanical and Aerospace Engineering, Institut Teknologi Bandung, Indonesia
[2]National Research and Innovation Agency (BRIN), Indonesia

Abstract. Polymethylmethacrylate (PMMA), a widely used polymer, finds applications in various fields, including bone cement for orthopedic surgeries. In this study, we investigate the synthesis of PMMA via miniemulsion polymerization to enhance its suitability for bone cement applications. The focus lies on understanding the impact of two critical components: anionic surfactant and co-stabilizer virgin coconut oil concentration. The miniemulsion technique offers several advantages, such as improved monomer dispersion, reduced particle size, and enhanced mechanical properties. We systematically explore the influence of different anionic surfactant concentration on the polymerization process and the resulting PMMA properties. Significantly, we evaluate the novel role of virgin coconut oil as a co-stabilizer, aiming to enhance the stability of the PMMA miniemulsion system. Our findings reveal that specific anionic surfactant concentration significantly affect the polymerization kinetics, particle size distribution, and overall PMMA properties. Furthermore, the incorporation of virgin coconut oil as a co-stabilizer demonstrates promising results in terms of miniemulsion stability and final PMMA characteristics. This research contributes valuable insights into tailoring PMMA for bone cement applications, emphasizing the importance of surfactant selection and the potential benefits of using natural co-stabilizers.

1 Introduction

In orthopedic surgery, bone cements play a pivotal role in stabilizing implants and promoting bone healing [1–3]. Polymethylmethacrylate (PMMA) is a widely used polymer in bone cement formulations due to its biocompatibility, mechanical strength, and ease of processing [4]. However, traditional methods of PMMA synthesis often encounter challenges such as

* Corresponding author: okap001@brin.go.id

particle aggregation and poor dispersibility, which can affect the cement's mechanical properties and clinical performance [4,5].

Miniemulsion polymerization has emerged as a promising technique to overcome these limitations by allowing for the synthesis of PMMA nanoparticles with controlled [6,7]. In this process, the polymerization occurs in droplets stabilized by surfactants, resulting in stable colloidal dispersions. The choice of surfactants and co-stabilizers is critical as they influence the stability and properties of the miniemulsion, thereby impacting the final characteristics of the polymer [8].

Anionic surfactants are known for their ability to stabilize miniemulsions by forming a protective layer around the droplets, preventing coalescence and promoting uniform particle size distribution [9,10]. Additionally, co-stabilizers such as natural oils can enhance the stability and functionality of miniemulsions by interacting synergistically with surfactants. Virgin coconut oil (VCO), rich in medium-chain triglycerides and bioactive compounds, has shown promise as a co-stabilizer in various polymerization processes due to its stabilizing properties [11].

This study focuses on investigating the synthesis of PMMA via miniemulsion polymerization, specifically exploring the role of Sodium Dodecyl Sulphate (SDS) as a surfactant and its synergetic interaction of VCO as a co-stabilizer. By controlling the size and surface properties of these nanoparticles, we aim to enhance their suitability for bone cement applications. Understanding the influence of these parameters on the miniemulsion polymerization process and the resulting PMMA nanoparticles is crucial for advancing the development of improved bone cement materials with enhanced clinical efficacy and patient outcomes.

In this paper, we present a comprehensive investigation into the synthesis of PMMA nanoparticles using miniemulsion polymerization, highlighting the synergistic effects of SDS as a surfactant and VCO as a co-stabilizer. The interplay between surfactant, co-stabilizer, and nanoparticle properties provides valuable insights for optimizing PMMA-based materials in medical applications [4]. The findings contribute to the knowledge base of polymer chemistry and biomaterials science, aiming to pave the way for the development of next-generation bone cement formulations tailored for orthopedic applications.

2 Materials and Methods

2.1 Materials

The materials used in miniemulsion polymerization were methylmethacrylate (MMA, 99% purity) from Sigma Aldrich, SDS surfactant with >99% purity from Vivantis, VCO costabilizer from Purecoco, Potassium Peroxodisulfate (KPS) initiator from Sigma Aldrich, and aqua DM. The bone cement was made using solid components consisting of PMMA powder from the synthesis and BPO initiator from Sigma Aldrich, as well as liquid components consisting of MMA monomer and DMPT accelerator from Sigma Aldrich.

2.2 Miniemulsion Polymerization

PMMA was synthesized by adjusting the quantities of surfactant and stabilizer. For surfactant variation, surfactants were added at 0%, 1%, 3%, and 5% of the weight of MMA monomer. The surfactant was dissolved in 150 grams of deionized water (aqua DM), then 30 grams of MMA monomer was added and stirred at 1000 rpm for 5 minutes. The mixture underwent sonication for 10 minutes. KPS initiator was introduced, and the mixture was heated and

stirred at 1000 rpm for 3 hours at a temperature ranging from 60 ℃ to 90 ℃. The resulting product was subsequently dried in an oven at 60 ℃ for 5 hours.

In the case of stabilizer variation, 5% surfactant was dissolved in 150 grams of aqua DM, and stabilizer was added at 5%, 10%, 25%, 50%, and 100% of the weight of MMA monomer. Each synthesis used 30 grams of MMA monomer, following the same steps as described for surfactant variation.

Table 1. Miniemulsion polymerization with various surfactant concentration.

Sample name	MMA (gram)	Aqua DM (gram)	SDS (gram)	VCO (gram)	KPS (gram)
PMMA_Sur0%	30	150	0		0,3
PMMA_Sur1%	30	150	0,3		0,3
PMMA_Sur3%	30	150	0,9		0,3
PMMA_Sur5%	30	150	1,5		0,3

Table 2. Miniemulsion polymerization with various co-stabilizer concentration.

Sample name	MMA (gram)	Aqua DM (gram)	SDS (gram)	VCO (gram)	KPS (gram)
PMMA_Sur5%	30	150	1,5	-	0,3
PMMA_Sur5%_Cos5%	30	150	1,5	1,5	0,3
PMMA_Sur5%_Cos10%	30	150	1,5	3	0,3
PMMA_Sur5%_Cos25%	30	150	1,5	7,5	0,3
PMMA_Sur5%_Cos50%	30	150	1,5	15	0,3
PMMA_Sur5%_Cos100%	30	150	1,5	30	0,3

2.3 PMMA powder

The PMMA solid content was determined using equation 1, which involved measuring the weights of both the liquid and solid components obtained during PMMA synthesis. Characterization of PMMA included using FTIR (Prestige 21 Shimadzu) to identify functional groups and PSA (Cilas 170 Nano Dual Scattering Particle Size Analyzer) to measure the particle size of the synthesized PMMA.

$$Solid\ Content\ (\%) = \frac{Solid\ (g)}{Solution\ (g)}\ 100\% \qquad (1)$$

2.4 PMMA Bone Cement

PMMA bone cement was prepared using PMMA and MMA in a ratio of 1:2, with 2% BPO initiator and 1% DPMT accelerator relative to the MMA weight. The solid components, PMMA and BPO, were mixed separately from the liquid components, MMA and DMPT. These components were then combined and manually mixed by hand. During preparation, the temperature of the bone cement was monitored using a thermocouple, with measurements recorded every 10 seconds until the cement set. This temperature data aimed to ascertain the maximum temperature reached by the PMMA bone cement.

3 Result and Discussion

3.1 Miniemulsion polymerization

Table 3 outlines the outcomes of PMMA synthesis using miniemulsion polymerization with various surfactant concentrations. The study measured solid content and particle size. The findings reveal that adding surfactant increases the solid content of PMMA by generating more, smaller particles, thereby boosting polymerization rates. However, at surfactant concentrations of 3 wt% and 5 wt%, the solid content slightly decreased compared to 1 wt% surfactant.

Table 3. The result of miniemulsion polymerization with various surfactant concentration.

Sample name	Solid Content (%)	Particle size (nm)	PDI	FWHM (nm)
PMMA_Sur0%	11.5 ± 1.1	246.4	0.03353	100.5
PMMA_Sur1%	17.6 ± 0.8	80.9	0.02239	27.7
PMMA_Sur3%	17.0 ± 0.7	54.4	0.00916	11.9
PMMA_Sur5%	17.0 ± 0.8	43.0	0.01434	15.2

Solid content and particle size are crucial in polymer synthesis as they affect the polymer's physical and chemical properties. Higher solid content indicates more monomer conversion to polymer and may result in high molecular weight polymer. The results confirm that surfactant use in PMMA synthesis increases solid content by producing more, smaller particles, enhancing polymerization rates. However, excessive surfactant can prevent the water-soluble initiator from entering the droplets, thus slightly reducing the polymerization rate.

Additionally, the particle size of PMMA is influenced by surfactants. Higher surfactant amounts lead to smaller PMMA particle sizes. The polydispersity index (PDI) of all samples with surfactant falls within monodisperse region, ranging from Full Width Half Maximum (FWHM) 15.2 – 27.7 nm. For example, the PMMA_Sur3% sample has a particle size of 54.4 nm and PDI of 0.00916, indicating a more uniform particle size distribution. The PMMA_Sur5% sample, despite having a smaller particle size (43.0 nm), has a higher PDI (0.01434) than PMMA_Sur3% but still remains below 50 nm of FWHM.

These results support previous explanations that surfactants in miniemulsion polymerization increase the number of smaller particles, thereby boosting polymerization rates [10,12]. Surfactant stabilize droplets by increasing electrostatic repulsion, thus preventing Ostwald ripening [13]. However, surfactant concentrations above 2 wt% slightly decrease the polymerization rate, likely due to excess surfactant preventing the initiator from entering the droplets.

The addition of a co-stabilizer during PMMA synthesis (see Table 4) can significantly boost the solid content of the polymer. Experimental results show that using 5 wt% and 50 wt% co-stabilizer resulted in a solid content of 20%, indicating complete conversion of MMA monomer to polymer. The increase of co-stabilizer concentration is parallel with the increase of MMA polymerization indicates by the increase of solid content up to a maximum of ~20% shown by the PMMA_Sur5%_Cos50% and PMMA_Sur5%_Cos100%. The hydrophobicity of the VCO at 50% - 100% concentration was likely able to completely encapsulate and immobilized the MMA droplets in the micelle protected by the SDS and thus ensure the polymerization only occurred in the micelle. At lower concentrations of VCO, some of the MMA, which is slightly soluble in water [14], potentially existed outside the micelle, causing incomplete polymerization of the droplets. Additionally, higher amounts of co-stabilizer led to larger PMMA particle sizes due to monomer droplet swelling from the extra co-stabilizer [13]. Therefore, selecting the appropriate amount and type of co-stabilizer is essential for achieving high solid content and controlling PMMA particle size distribution during miniemulsion polymerization.

All of the experiment conducted show PDI ranging from 0.00916 – 0.03704 and FWHM ranging from 11.9 – 44.8 nm suggesting that the emulsion was kinetically stable and that Ostwald ripening was unlikely to occur.

Table 4. The result of miniemulsion polymerization with various co-stabilizer concentration.

Sample name	Solid Content (%)	Particle size (nm)	PDI	FWHM (nm)
PMMA_Sur5%	17.0 ± 0.8	43.0	0.01434	15.2
PMMA_Sur5%_Cos5%	17.0 ± 0.9	57.0	0.02056	18.9
PMMA_Sur5%_Cos10%	17.6 ± 0.7	58.2	0.01995	18.8
PMMA_Sur5%_Cos25%	18.9 ± 0.6	68.5	0.03427	28.6
PMMA_Sur5%_Cos50%	20.0 ± 0.7	95.5	0.03704	41.3
PMMA_Sur5%_Cos100%	19.5 ± 0.8	107.1	0.03469	44.8

3.2 Bone cement polymerization temperature

Bone cement made with PMMA synthesized using surfactants exhibited lower maximum temperatures compared to commercial bone cement and those synthesized without surfactants (see Table 5). This reduction in temperature can be attributed to residual surfactants on the PMMA particle surfaces, which likely slow down the polymerization reaction. Removing surfactants from particles synthesized with them is challenging, often necessitating special treatments to eliminate residual surfactants completely [15]. The lowest maximum temperature recorded was for bone cement using PMMA synthesized with 5 wt% surfactant, reaching 65.53 °C which is 30% lower than the 80 °C maximum temperature of commercial bone cement.

Table 5. Maximum bone cement polymerization temperature using PMMA powder synthesize with various surfactant concentration.

Sample name	Maximum temperature (℃)
PMMA_Sur0%	78,07±3,91
PMMA_Sur1%	66,86±3,27
PMMA_Sur3%	71,50±1,15
PMMA_Sur5%	65,53±0,67
PMMA Komersial	80 [16]

Although the reduction in curing temperature was significant, the 65.53 °C achieved is still not safe and can potentially cause thermal burns to organic tissue. Further investigation is needed to reduce the curing temperature to a safer region. Meanwhile, PMMA powder produced from miniemulsion with various co-stabilizer concentrations did not show any significant temperature change.

4 Conclusion

The synthesis of PMMA using miniemulsion polymerization with varying surfactant concentrations has shown significant impacts on solid content and particle size. Adding surfactant increases the solid content of PMMA by generating more, smaller particles, thus enhancing polymerization rates. However, at concentrations of 3 wt% and 5 wt%, excessive surfactant hinders the initiator's entry into the droplets, slightly reducing the polymerization rate. Optimal surfactant concentration is 1 wt%, which yields the highest solid content and smallest particle size with a uniform distribution. Surfactants also provide droplet stabilization, preventing Ostwald ripening by increasing electrostatic repulsion.

The use of costabilizers during PMMA synthesis can significantly boost the solid content, with 50 wt% and 100 wt% costabilizer achieving a ~20% solid content, indicating complete MMA monomer conversion. However, higher costabilizer concentrations led to larger PMMA particle sizes, likely due to monomer droplet swelling.

Bone cement made with PMMA synthesized using surfactants exhibited lower maximum temperatures compared to commercial bone cement and those synthesized without surfactants. The bone cement using PMMA synthesized with 5 wt% surfactant recorded the lowest maximum temperature at 65.53°C, which is 30% lower than the 80°C maximum temperature of commercial bone cement. Although this reduction is significant, the 65.53°C achieved is still unsafe and can potentially cause thermal burns to organic tissue. Therefore, further investigation is necessary to reduce the curing temperature to within a safe range. Meanwhile, PMMA powder produced from miniemulsion with various co-stabilizer concentrations did not show any significant temperature change.

In summary, careful selection of surfactant and costabilizer concentrations is crucial in optimizing the solid content, particle size, and thermal properties of PMMA for various applications. Further research is needed to refine these parameters to achieve safer curing temperatures and more efficient outcomes in bone cement and other PMMA applications.

References

1. S. Ramanathan, Y. C. Lin, S. Thirumurugan, C. C. Hu, Y. F. Duann, R. J. Chung. Poly(methyl methacrylate) in Orthopedics: Strategies, Challenges, and Prospects in Bone Tissue Engineering. Polymers (Basel). **16**, 367 (2024). https://doi.org/10.3390/polym16030367.
2. S. Deb. Orthopaedic bone cements. Woodhead Publishing Limited; (2008). https://doi.org/10.1533/9781845695170.
3. H. Orban, C. Cirstoiu, C. Zaharia, C. Cincu. Acrylic Cement Advantages or Disadvantages in Orthopaedic Surgery. Revista de Chimie. **59** (2008) https://doi.org/10.37358/RC.08.6.1856.
4. U. Ali, KJBtA Karim, N. A. Buang. A Review of the Properties and Applications of Poly (Methyl Methacrylate) (PMMA). Polymer Reviews. **55**, 678–705 (2015). https://doi.org/10.1080/15583724.2015.1031377.

5. Y. Sa, F. Yang, Y. Wang, J. G. C. Wolke, J. A. Jansen. Modifications of Poly(Methyl Methacrylate) Cement for Application in Orthopedic Surgery, p. 119–34. (2018). https://doi.org/10.1007/978-981-13-0950-2_7.
6. J. L. Mendoza-Castellanos, J. C. Pantoja-Espinoza, L. C. Rodríguez-Pacheco, F. Paraguay-Delgado. Synthesis of PMMA Microspheres with Tunable Diameters: Evaluation as a Template in the Synthesis of Tin Oxide Coatings. Polymers (Basel), **15**, 2419 (2023) https://doi.org/10.3390/polym15112419.
7. M. A. E. Hafizah, A. F. Riyadi, A. Manaf, Andreas. Particle Size Reduction of Polyaniline Assisted by Anionic Emulsifier of Sodium Dodecyl Sulphate (SDS) Through Emulsion Polymerization. IOP Conf Ser Mater Sci Eng. 515, 012080 (2019). https://doi.org/10.1088/1757-899X/515/1/012080.
8. ANMB El-hoshoudy. Emulsion polymerization mechanism. InTech; (2018). https://doi.org/10.5772/intechopen.68265.
9. Y. Zhang, H. Chen, Q. Zou. Anionic surfactant for silica-coated polystyrene composite microspheres prepared with miniemulsion polymerization. Colloid Polym Sci. **287**, 1221–7 (2009). https://doi.org/10.1007/s00396-009-2089-x.
10. G. A. Khoman, M. H. A. Kalijaga, N. Aisah, R. Fidyaningsih, J. Raharjo, O. P. Arjasa, et al. PMMA bone cement with L-arginine/nano fish bone nanocomplex for apatite formation. R Soc Open Sci. **11** (2024). https://doi.org/10.1098/rsos.231694.
11. S. S. Silva, L. C. Rodrigues, E. M. Fernandes, J. M. Gomes, A. Vilas-Boas, R. P. Pirraco et al. Approach on chitosan/virgin coconut oil-based emulsion matrices as a platform to design superabsorbent materials. Carbohydr Polym. **249**, 116839 (2020). https://doi.org/10.1016/j.carbpol.2020.116839.
12. E. M. Dogan-Guner, F.J. Schork, S. Brownell, G. T. Schueneman, M. L. Shofner, J. C. Meredith. Encapsulation of cellulose nanocrystals into acrylic latex particles via miniemulsion polymerization. Polymer (Guildf). **240,** 124488 (2022). https://doi.org/10.1016/j.polymer.2021.124488.
13. M. Antonietti. Polyreactions in miniemulsions. Prog Polym Sci. **27**, 689–757 (2002). https://doi.org/10.1016/S0079-6700(01)00051-X.
14. PubChem. PubChem Compound Summary for CID 6658, Methyl methacrylate. National Center for Biotechnology Information 2024.
15. D. Li, C. Wang, D. Tripkovic, S. Sun, N. M. Markovic, V. R. Stamenkovic. Surfactant Removal for Colloidal Nanoparticles from Solution Synthesis: The Effect on Catalytic Performance. ACS Catal. **2**, 1358–62 (2012). https://doi.org/10.1021/cs300219j.
16. E. Paz, Y. Ballesteros, J. Abenojar, J. C. del Real, N. J. Dunne. Graphene Oxide and Graphene Reinforced PMMA Bone Cements: Evaluation of Thermal Properties and Biocompatibility. Materials. **12**, 3146 (2019). https://doi.org/10.3390/ma12193146.