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Poly(methyl methacrylate)-microencapsulated clove oil slow release formulation

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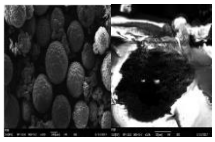
GRAPHICAL ABSTRACT



(b) SEM 100x for PMMA microencapsulated with clove oil
(c) SEM 3000x for PMMA microencapsulated with clove oil

ABSTRACT

Essential oils are known to have many uses such as for medicinal and pesticidal components but their high volatility limits their applications. Encapsulation or controlled release device is desirable for effective applications of essential oils. This study investigates the encapsulation of clove essential oil in porous polymeric particles to affect its slow release. Poly (methyl methacrylate) (PMMA) was prepared using free radical polymerization of methyl methacrylate. The material was characterized by NMR spectroscopy. The results have shown that the polymerization process was complete as evidenced by the absence of peaks for double bond at 6.0 and 5.5 ppm compared to those of the monomer. It was also confirmed by attenuated total reflection (ATR) infrared spectroscopy that indicated the presence of functional groups of the polymer. Meanwhile, clove oil was extracted from clove buds by hydrodistillation. Encapsulation was carried out by solvent evaporation method using oil in water (O/W) emulsion system. PMMA with encapsulated clove oil were formed using different PMMA: clove oil ratios. It was found that ratio of 1:1 resulted in the formation of beads but ratios of 2:1 and 3:1 did not form beads but clots instead. The presence of eugenol, an active component in clove oil, in the PMMA encapsulation was confirmed by gas chromatography with flame ionization detection based on comparison with the standard. Experiments on the slow release of PMMA-encapsulated clove oil were carried out and the weight loss was monitored at 10, 20, 30, 40, 50, 60, 120, 180 and 240 min. Similar experiments were performed using silica-clove, montmorillonite-clove and clove alone for comparison. It was found that PMMA-clove encapsulation showed the best performance followed by silica-clove, montmorillonite-clove and clove alone. Thus, PMMA encapsulation is highly potential as an effective formulation in controlled release of volatile compounds.

Keywords: microencapsulation, clove oil, poly(methyl methacrylate), emulsion, slow release control, extraction

1. INTRODUCTION

Currently, the use of synthetic chemicals to control insects and arthropods raises several concerns related to environment and human health. An alternative is to use natural products that possess good efficacy and are environmentally friendly. Among those chemicals, Essential oils, have long been reputed as antimicrobial and insects repellent [1].

The direct utilization of essential oils is limited because of their high volatile rate [2]. To overcome this drawback, the encapsulation of them with polymer is studies. By the encapsulation, the volatile rate of oils is reduced and controlled by applied it for external used [3]. Moreover, the essential oils are protected from light, air and heat. The selection of polymer shell depends on the application of the polymer capsule [4].

Encapsulated active substances can be effectively formulated into a protective coating [5]. The main advantage using microcapsules is that the release of active ingredients can be better controlled and that the mechanical properties of the coating can stay intact even at high concentrations of the active [6].

Microencapsulation is a process in which tiny particles or droplets are surrounded by a coating to give small capsules, of many useful properties. In general, it is used to incorporate food ingredients, enzymes, cells or other materials on a micro metric scale. Many methods have been used for the preparation of polymer capsule such as interfacial polymerization, phase inversion precipitation in-situ polymerization and solvent evaporation [7]. Among of them, solvent evaporation is one of the most famous methods due to its simplicity. Therefore, in this research, the preparation of PMMA microencapsulated clove oil was carried out by simple solvent evaporation method in oil in water (O/W) emulsion [8]. The influence of PMMA: clove oil weight ratio was studied [9]. This research will emphasize on synthesizing and characterizing the encapsulation with different ratio method at 1:1, 2:1 and 3:1 weight ratios of PMMA: clove oil [10]. Resulting show only 1:1 can proceed to characterization since 2:1 and 3:1 form clot products.

2. EXPERIMENTAL

The experiment was focusing on PMMA encapsulated with clove oil. So, two main ingredient which are PMMA and clove oil was prepared first. Clove oil was prepared through hydrodistillation and extract with diethyl ether $(C_2H_5)_2O$ through separating funnel. For PMMA it was prepared by bulk free radical polymerization using MMA as monomer and benzoyl peroxide as initiator. Ratio MMA: BPO is 1:1 and THF as solvent, and purging the reaction medium with an inert gas which is nitrogen for 30 min and the reaction will let for 24hour for reaction of polymerization occur as scheme 1. Water and methanol used to precipitate the polymer. PMMA presence of functional group and was analyse by using ^{1}H NMR and ATR. The encapsulation was done by dissolved PMMA in THF. PMMA with encapsulated clove oil were formed using different PMMA: clove oil ratios which are 1:1, 2:1 and 3:1. PMMA and clove oil will form homogenous solution and the solution was added dropwise to 1% aqueous polyvinyl alcohol which act as surfactant and stabilizer. The PMMA encapsulated by cove oil was characterized by analyse morphology by using SEM. GC-FID was used to determine present of essential oil in encapsulated, and lastly Experiments on the slow release of PMMA-encapsulated clove oil were carried out and the weight loss was monitored at 10, 20, 30, 40, 50, 60, 120, 180 and 240 min. Similar experiments were carried using silica-clove, montmorillonite-clove and clove alone for comparison.

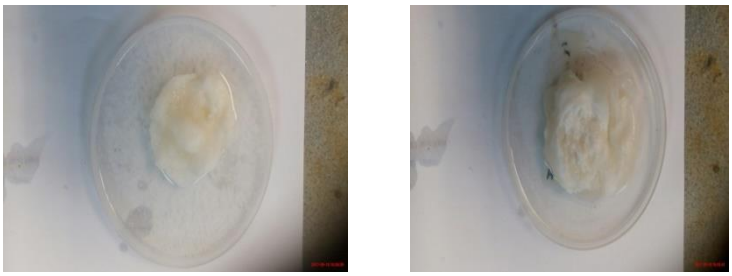
3. RESULTS AND DISCUSSION

3.1: Result Formation Microencapsulated with Different Ratio

Emulsions with high colloidal stability were obtained in all cases as shown in Figure 1 (a-c). It was found that only 1:1 weight ratio is suitable for formation PMMA microencapsulated clove oil Figure 1 (a). Clotted obtain because formation agglomeration before adding to emulsifier which is PVA. The clotted happen because agglomeration, the agglomeration was form during mixing PMMA and oil with Ratio 2:1 and 3:1 of PMMA: clove in the solution means increases of PMMA as double and triple respectively. Presence of PMMA as bulky will form interaction among them and form big molecule. This make the molecule has high interfacial tension. Then, when the solution added to emulsifier it will disperse in clotted form Figure 2 (a) and (b) showed clotted after filter the solvent for ratio 2:1 and 3:1. The increases of PMMA as double and triple respectively cause's increases of hydrophobic substance in the system and it rapidly crush out or precipitate as clotted.

(a) (b) (c)

Figure 1: (a) 1:1 ratio of PMMA: clove oil, (b) 3:1 ratio of PMMA: clove oil,(c) 3:1 ratio of PMMA: clove oil



(a) (b)

Figure 2: (a) 2:1 ratio of PMMA: clove oil after filter, (b) 3:1 ratio of PMMA: clove oil after filter

3.2. Characterization of PMMA

3.2.1 FT-IR of MMA and ATR of PMMA

From Figure 3(a) and (b) we can see both MMA and PMMA has absorption for C=O ester at 1724 cm^{-1}. Therefore, it can be seen that there is a distinct absorption band at 1145 cm^{-1} for both, which can be attributed to the C–O–C stretching vibration. The band at 2949 cm^{-1} can be attributed to the bending vibration of the C–H bonds of the –CH sp3 group hich also present for both monomer and polymer.

From the spectrum we can see that from MMA there are two main peak is missing, C = C and C-H sp^2 which has a value of 1620 cm^{-1} and 3050 cm^{-1} respectively are not appear on PMMA. On the basis of the above discussions, it can be concluded that the prepared polymer was indeed PMMA from MMA. We also can observed the absorption band C-H sp^3 for MMA weaker compare to PMMA at 2949 cm^{-1} because there only one C-H sp^3 bonding MMA before polymerization

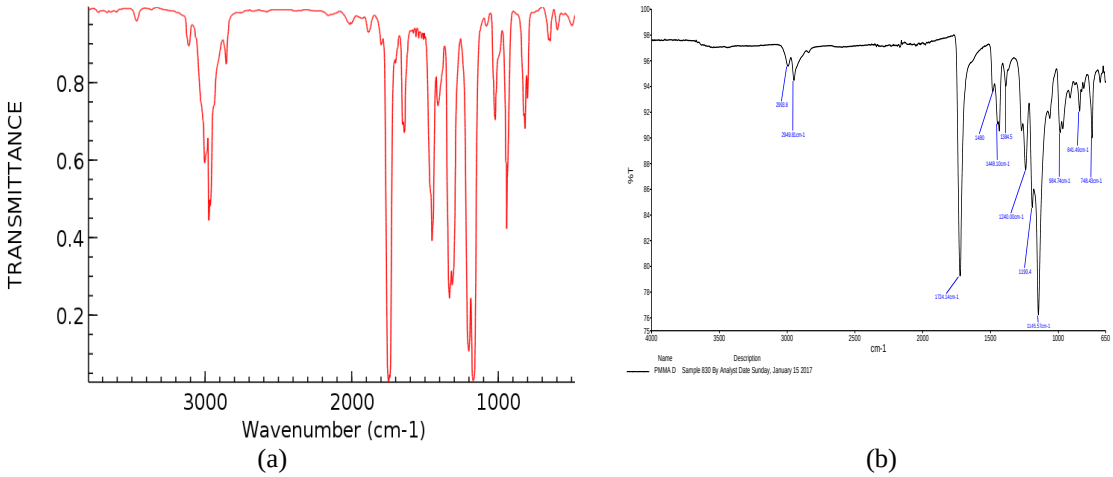


Figure 3: (a) FT-IR spectrum of PMMA (b)ATR spectrum of PMMA

3.2.2 ^{1}H NMR of methyl methacrylate (MMA), crude polymethyl methacrylate (PMMA), and solid (PMMA)

We can see all three spectrums showed peak at 7.27 ppm, its due to the solvent $CDCl_3$. Figure 4(a) for MMA ^{1}H spectrum show two main peak peak values at 6.0 and 4.98 ppm belong to the vinyl group as mention on the table. Presence peak at 3.65 ppm is for methoxy CH_3-O functional group.

After 24 h of polymerization, ^{1}H NMR for crude gave spectrums in Figure 4(b), we can see that the sample has same peak values at 6.0 and 4.98 ppm lie spectrum of MMA. The values belong to the vinyl group as mention on the table. This proved that presence of peak vinyl which means on the solution there were some MMA left unreacted during polymerization

After wash the crude sample with a solvent and it will form precipitated. The purpose of the wash using a solvent is to make it precipitate, it also remove unreacted monomer. That is why on the result of Figure 4(c) for sample solid , peak at 6.0 and 4.98 have disappeared completely and this indicates that vinyl group had gone or disappeared, and has formed polymer. Having ensured that our sample was pure PMMA then we can proceed with further reaction. Peak of 3.65 ppm is for absorption of methoxy CH_3-O, peak arises at 1.05 ppm and 1.65 ppm for CH_3-C and CH_2-C respectively has confirm there no unsaturated bond anymore so we can proceed to further reaction.

3.3 Characteristic PMMA encapsulation clove oil

3.3.1 SEM analysis for PMMA and PMMA microencapsulated clove oil

For Figure 5 (a) SEM of PMMA it showed it has been observed that the particles had regular shapes. Then it's also have smooth surface and order of shape of particle in PMMA seem not orderly it random arrangement..

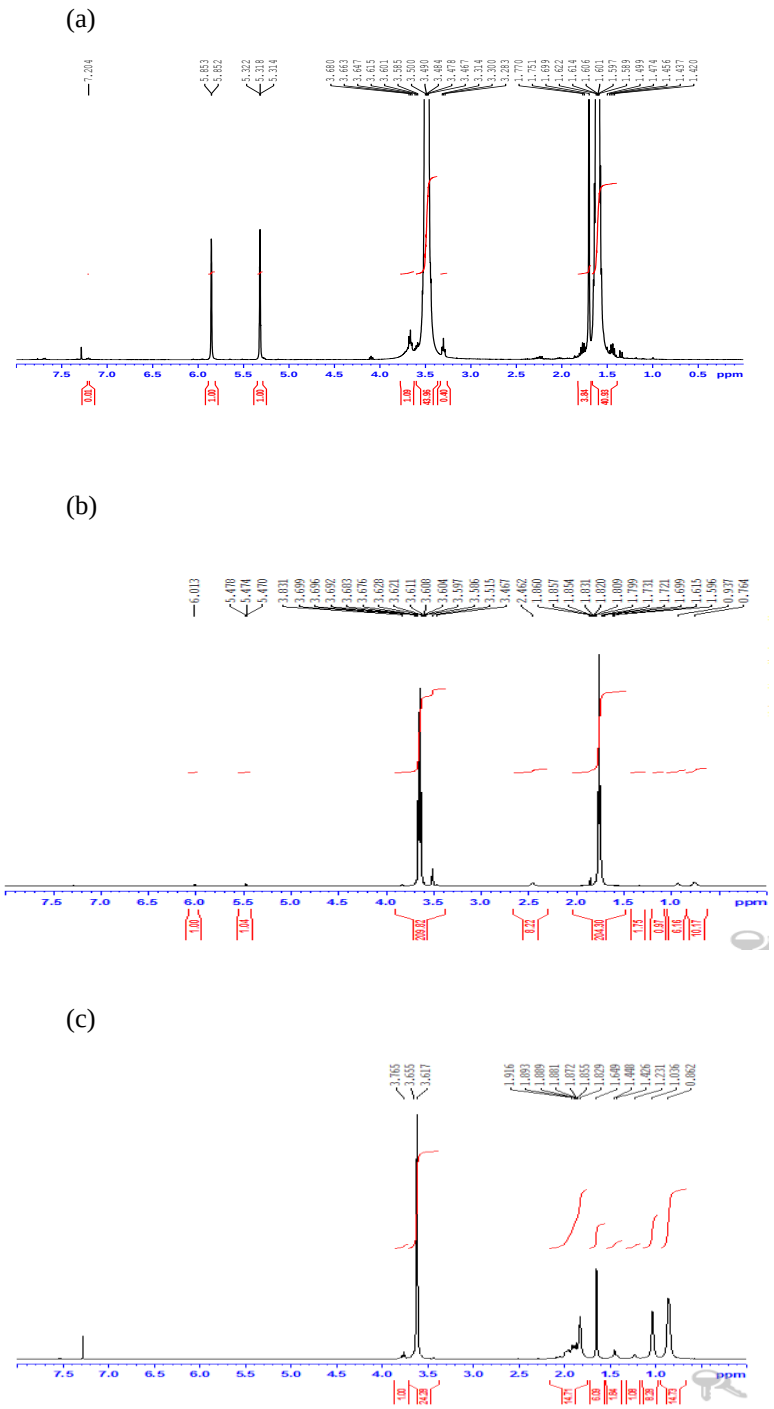
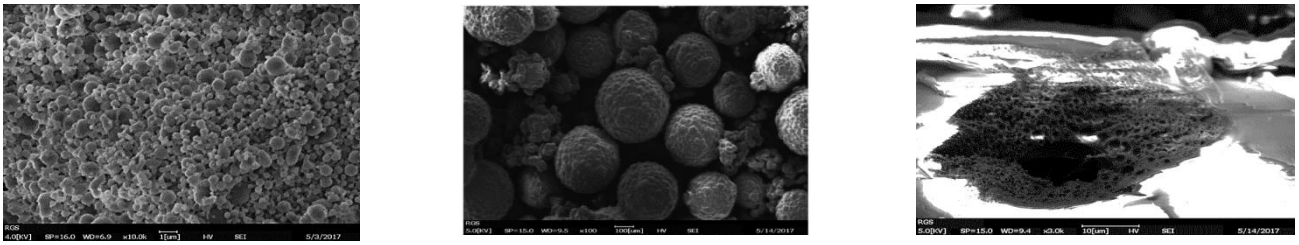


Figure 4(a): ^{1}H NMR spectrum of methyl methacrylate (MMA) solution; (b): ^{1}H NMR spectrum of polymethyl methacrylate (PMMA) crude and (c): ^{1}H NMR spectrum of polymethyl methacrylate (PMMA) solid using $CDCl_3$ as solvent

The images obtained by SEM from Figure 5 (b) and (c) used to observe the external morphology and the average size of the microcapsules after deposition of the microcapsules in the PMMA. For Figure 5 (b) which 100x the morphology microcapsule is composed of a core material (closed) and closing material, having the ability to develop an insulating wall which protects the core material. For the mean size of the microcapsules based on volume distribution is 10 µm. Microcapsules showed a rough surface and loss of the spherical shape. It also shows pore formation in Figure 5 (c) in the PMMA walls, allowing the controlled release of the encapsulated clove oil. The microcapsules are distributed individually without excessive agglomeration, and no visible oil residues on the surface of the microcapsules can be seen.



(a) (b) (c)

Figure 5: (a) SEM for PMMA (b) SEM 100× for PMMA microencapsulated with clove oil (c) SEM 3000× for PMMA microencapsulated with clove oil

3.3.2: GC-FID analysis for clove oil containing in PMMA microencapsulate

In order determine the encapsulated clove oil contain in PMMA encapsulated, the polymer particles was extracted with methanol and the solution was analysed by GC. This approach takes advantage on the porosity of the obtained polymer microcapsules. The principal compound detected qualitatively by GC-FID analysis in the clove essential oil which dominated by eugenol. The eugenol showed a retention time of 4.8 min while methanol (solvent) was eluted at 1.9 min in the chromatogram as shown in Figure 6.

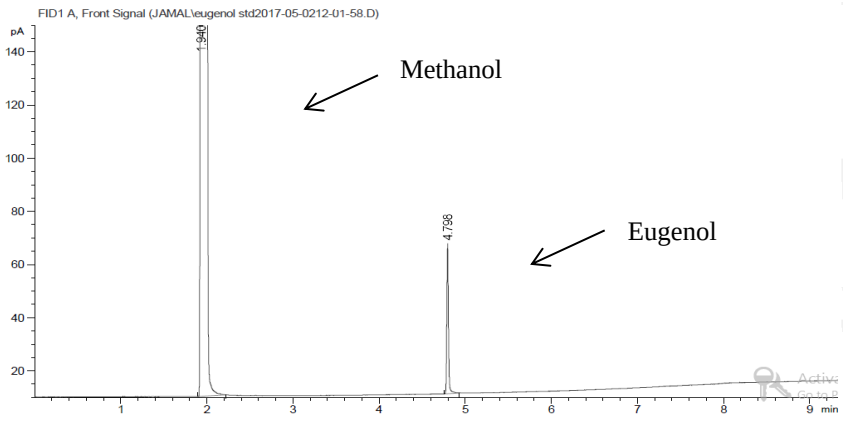


Figure 6 : GC-FID chromatogram of standard eugenol solution. GC conditions:HP-5 capillary column (30 m × 320 µm ID, 0.25 µm film thickness); temperature program initial temperature 110°C, increased at 15°C/min to 210°C held for 2 min; detector temperature 310°C

The PMMA microencapsulated essential oil was extracted with methanol with sonication at room temperature (30˚C) for 5-10 min and the extract was analysed by GC. A GC chromatogram of the extract of PMMA microencapsulates is shown in Figure 7. The chromatogram showed identical peak at retention time of 4.8. This indicated that the sample contained eugenol, which is a major component of clove essential oil.

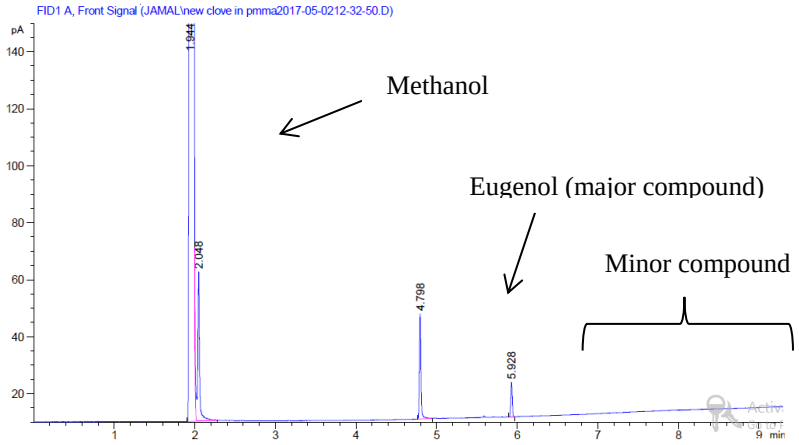


Figure 7: GC-FID chromatogram of clove oil contained in PMMA encapsulate dissolved in methanol

3.4 Weight loss of volatile compound.

From Table 1, results show that PMMA encapsulated clove oil is the best for the control release of clove oil compared to other absorbents because weight loss of volatile compound only 0.0023g/240 min, which is the lowest compared to the other three. Silica-clove oil is the second best follow up by montmorillonite-clove oil and lastly clove oil itself. As expected, without any medium that can bind or hold it, the clove oil was vaporized quickly since it contains volatile compounds. Silica is better than montmorillonite as absorbent to hold clove oil is because pore size and particle size. Mesoporous silica nanoparticle adsorbent (200 nm particle size, pore size 4 nm) is better than montmorillonite which is microsporous. For PMMA the encapsulation makes it better than silica even it only micropore. Since the active agent or clove oil inside the capsule so it make the essential oil more difficult to vaporize.

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Table 1: Weight loss of volatile compounds at different times

Time (min)	Mass sample (g)			
	PMMA encapsulate clove oil	Silica- clove oil	Montmorillonite-clove	Clove oil
0	1.0015	1.0046	1.0034	1.0001
10	1.0015	1.0045	1.0027	0.9990
20	1.0015	1.0037	1.0017	0.9980
30	1.0014	1.0031	1.0014	0.9970
40	1.0013	1.0027	1.0007	0.9957
60	1.0011	1.0019	0.9987	0.9800
120	1.0004	1.0009	0.9953	0.9764
180	0.9999	0.9993	0.9931	0.9701
240	0.9992	0.9986	0.9904	0.9684
Weight loss*	0.0023	0.0062	0.0130	0.0317

* Weight loss = final weight (g) – initial weight (g)

4. CONCLUSION

Polymethyl methacrylate (PMMA) encapsulated with clove oil was successfully synthesize by using solvent evaporation of oil water emulsion system. Polymer and essential oil was prepared by bulk free radical polymerization and hydrodistillation respectively. For PMMA it was characterized by using ATR and 1H NMR, it necessary to make sure polymerization is occurring and then can proceed for encapsulation. For PMMA encapsulate clove oil was characterized by SEM to identify its morphology and GC-FID used to determined present clove oil as qualitative analysis.

It can be concluded that 1:1 ratio of PMMA: clove oil is better compare 2:1 and 3:1 ratio for preparing microencapsulation since only 1:1 ratio form beads while other two ratio did not form beads instead clots. Besides that, PMMA encapsulate clove oil was successfully be slow release control agent since it performed better compared to silica-clove, montmorilinite-clove and clove oil itself in term of weight loss of vaporized compound.

CONFLICTS OF INTEREST

All authors have declared that there is no conflict of interest.

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