GINGER ESSENTIAL OIL ENCAPSULATION IN PMMA MICROCAPSULES – PART II

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The aim of this study was the encapsulation of ginger essential oil in polymer crosslinked particles. The encapsulation of the ginger essential oil was made in poly(methyl methacrylate) (PMMA) through suspension polymerization. A tetra functional monomer triethylene glycol dimethacrylate (TEGDMA) was used along with MMA for polymer particle crosslinking and for increasing the polymerization rate. The parameters that were varied in the process of encapsulation were the concentration of AIBN initiator and the concentration of the essential oil. The obtained materials were characterized by SEM which revealed an increase of the particles size with the initiator concentration. GC and TGA analysis showed the amount of encapsulated oil and the oil composition. It was noticed that a higher oil concentration introduced in the reaction leads to a lower encapsulation efficiency due to the reactive double bonds present in the oil components which react with the free radicals formed by the initiator.

Keywords: ginger essential oil, poly(methyl methacrylate), encapsulation, SEM, GC/MS

1. Introduction

Essential oils are volatile, natural, complex compounds with specific pleasant odours and are formed by aromatic plants as secondary metabolites. The

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extraction of these oils from the plant material is usually made by distillation, but more modern methods use carbon dioxide or microwaves [1-3].

Ginger essential oil is a product valuable not only for its specific fragrance, but also for the biological properties it possesses: antimicrobial, antifungal, antibiotic etc [4-8]. As this oil has highly volatile components (α-pinene, β-pinene) that are lost during storage and use, it is very important to increase its stability. By increasing the stability of the ginger essential oil, it is possible to widen the range of applications for this valuable product.

A very good way to increase the stability of essential oils is by encapsulation in polymer matrixes that protect the oil from the various factors that cause its degradation. By microencapsulation, the valuable substances (liquids, solids or gases) are turned into micrometric products with spherical form, protected by a membrane from the environment. This technique is useful for the protection of sensible substances, as in the case off essential oils, from the surrounding conditions, and also the development of controlled release of active substances [9]. The stabilized essential oil can then be used in applications (cosmetic products, application on textiles), the structure of the polymers ensuring a controlled release of the oil over time.

The novelty of this study consists in the encapsulation of the ginger essential oil in polymethyl methacrylate (PMMA) crosslinked with TEGDMA through suspension polymerization and the characterization of the obtained product in order to notice possible applications for it in the cosmetic or textile industry.

2. Experimental

2.1. Materials

Methyl methacrylate (MMA) (Merck) was purified by vacuum distillation (presure = 100 mmHg, temperature = 47°C). Azoisobutyronitrile (AIBN) (Fluka) was recrystallized from methanol. Triethyleneglycoldimethacrylate (TEGDMA) (Sigma Aldrich), the suspension agent, poly(vinyl alcohol) (PVA) (Mw = 85,000-124,000 Da, 88% hydrolyzed), were used as received. The ginger essential oil was obtained through a microwave assisted hydro-distillation process, using an optimized procedure similar to the literature [10].

2.2. Methods

2.2.1 MMA suspension polymerization

0.2 g of PVA were added to 10 mL of distilled water in a round bottom flask and heated to 75°C under continuous stirring for the complete dissolution of the stabilizing agent. Separately, the specific amount of initiator was dissolved in the monomer solution (2 mL of MMA and 2 ml TEGDMA). This solution is

dropwisely added to the first aqueous solution, and the mixture was stirred for 4 h. After this interval, the particles were centrifuged, washed several times with distilled water and dried until a constant mass was attained.

2.2.2 Suspension polymerization of MMA in the presence of ginger essential oil extract

This synthesis was realized as in the case 2.2.1 with an organic phase containing various amount of essential oil (5% - 0.25 mL, 10 % - 0.5 mL, 20% - 1 mL). The rest of the following steps were similar.

2.3. Characterization

The morphology of polymer particles has been investigated through XL-30-ESEM TMP scanning electron microscope (SEM). The samples were sputtered with a thin layer of gold prior to imaging.

The TGA analysis has been performed on Pyris 1 TGA Instruments equipment, under nitrogen atmosphere, with a heating rate of 5°C/min from the room temperature to 500°C.

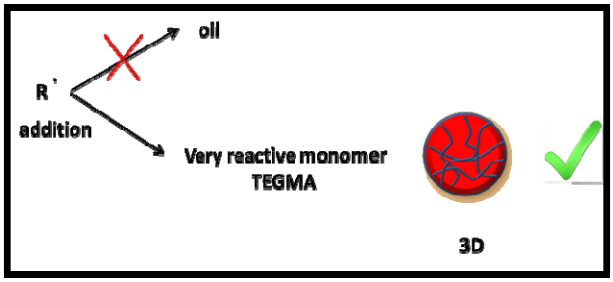
The essential oil content in the PMMA microcapsules was determined using a HP6890 gas chromatograph equipped with: capillary column (DB-1, GW Scientific, 30 m x 0.025 mm, 0.5 microns) and FID detector. The identification of the samples analyzed by gas chromatography was carried out by comparing the sampled spectral peaks with the spectra from a Wiley database.

The GC-MS equipment used for the qualitative analysis of the essential oil was Agilent 5975, composed of a gas chromatographer and a mass spectrometer with a quadruple filter. A DB-EUPAH column was used, with a length of 60 m, an internal diameter of 0.25 mm and a film thickness of 0.25 microns. The carrier gas was helium, with a 1.8 mL/min flow. The temperature program used was as follows: the start temperature was 30°C (3 min) followed by an increase of 4°C/min until reaching the final temperature of 280C (10 min). The temperature of the injector was 250°C, that of the transfer line 280°C, and that of the quadrupole was 150°C. The detection of the components was performed in the range of 10 – 500 m/z. Each chromatographic signal was analysed using MSD Chem Station software and Nist databases for the compound identification. For each analysis, 30 µL of sample were injected.

3. Results and discussions

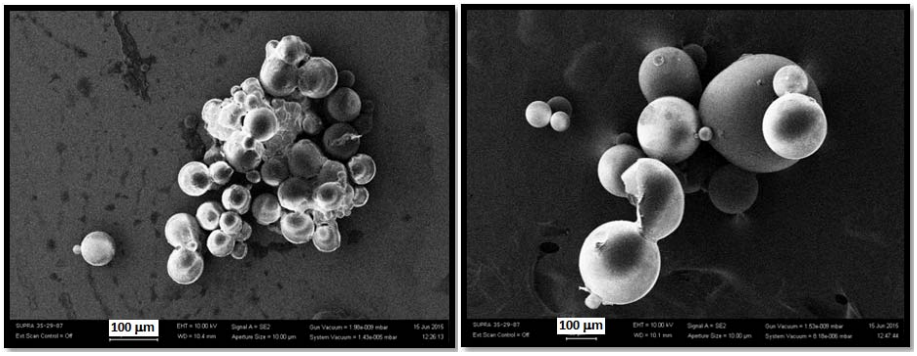
This study presents an optimization of the ginger oil encapsulation in PMMA microcapsules through in situ polymerization. Our previous study [11] revealed a moderate conversion for suspension polymerization, respectively the encapsulation of a small percentage of oil in the polymer particles which do not

retain their spherical shape for high concentrations of initiator. These limitations were due to the reactivity of the double bonds, contained by the components of the ginger essential oil, which consumed a part of the free radicals thus, decreasing both the polymerization rate as well as the conversion value. Therefore, a competition between the addition reaction of the free radicals to the monomer units and their interaction with the reactive components of the oil takes place. In order to limit the drawbacks of this competitive process, it is necessary to use a co-monomer with an increased reactivity for radical polymerization. Thus, acting also as crosslinking agent, TEGDMA was chosen as co-monomer for MMA. As expected, the reactivity of TEGDMA is higher than MMA and through the realization of a 3D network structure, a higher retention of the essential oil inside the polymer particles can be achieved (**Scheme 1**).

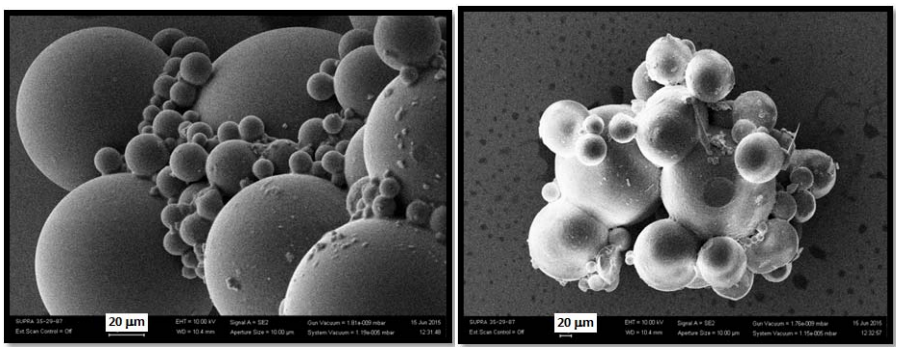


Scheme 1: The optimization of the polymerization in the presence of ginger oil

The first stage of this study consisted in the morphology analysis of the synthesized particles obtained using 5%wt. ratio of ginger oil and different initiator concentrations.



a) **b)**



c) **d)**

Fig. 1: SEM analysis of the particles obtained using 5% wt. ginger oil and different initiator concentrations: a) 0.015 mol/l; b) 0.03 mol/l; c) 0.06 mol/l; d) 0.09 mol/l

In Fig. 1 a-d, a high dimensional polydispersity can be observed in all cases, however with the increase of the initiator concentration the percentage of larger particles also increases. Considering that the stirring and suspension agent concentration were kept constant, this modification can be attributed to the modification of the initiator concentration. A higher initiator concentration leads to a faster polymerization rate. At high polymerization rates, the particles do not undergo self-stabilization resulting in their coalescence [12] and thus particles with larger dimensions result from increased initiator concentration.

Nevertheless, the aim of this study was to encapsulate an increased amount of essential oil in the polymer particles. Thus, the next step consisted in the realization of the suspension polymerization process in the presence of 20% wt. ginger oil. As mentioned in the above paragraph, the most suitable initiator concentration was the lowest (0.015 mol/L). The morphology of the obtained particles was investigated by SEM analysis.

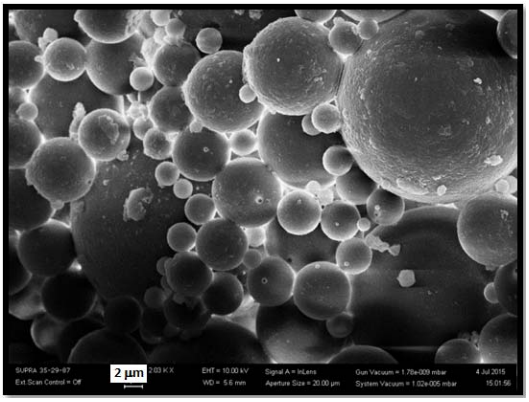


Fig. 2: SEM analysis of the polymer particles obtained using 0.015 mol/l initiator and 20% wt. ginger oil

The analysis of Fig. 2 reveals that the particles dimensions are smaller than the experiments made in the presence of a lower concentration of ginger oil (Fig. 1a). This aspect can be explained by the decrease of the polymerization rate, due to the consumption of the free radicals by the components of the essential oil. This assumption was confirmed in our previous study [11]. An important aspect is that spherical particles were obtained in the presence of a high quantity of ginger oil by in situ polymerization, which represents a novelty in this research field.

In order to highlight the encapsulation of the ginger oil in the polymer particles, thermogravimetric analyses were performed (Fig. 3).

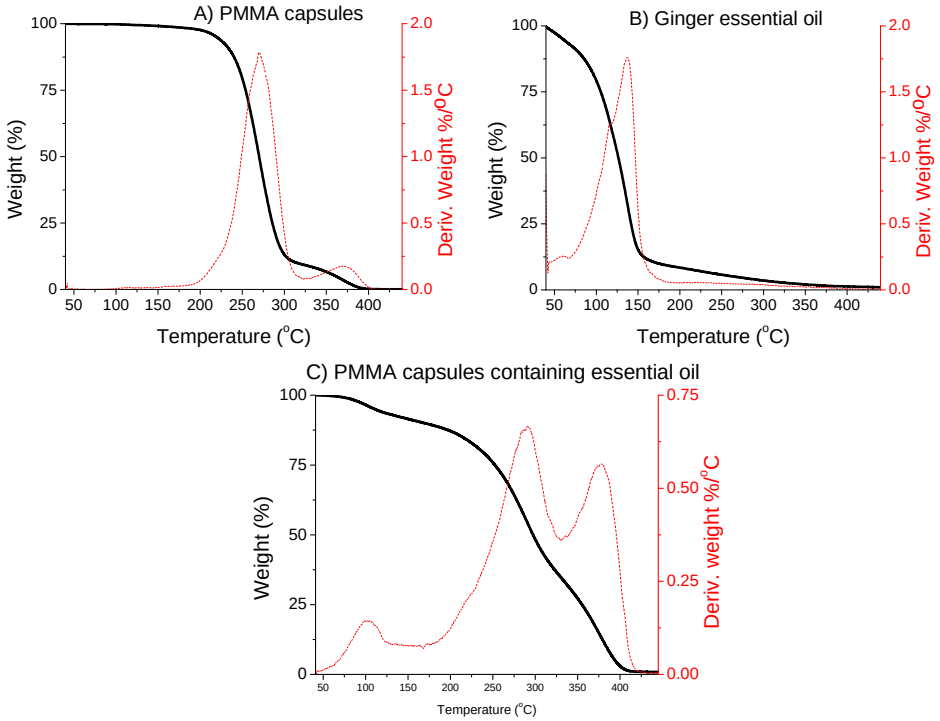


Fig. 3: TGA analysis for A) PMMA microcapsules; B) ginger essential oil; C) microcapsules containing 20% wt. ginger essential oil.

The analysis of the TGA curves in Fig. 3 reveals a 90% weight loss for PMMA around 300°C and for the essential oil around 150°C. The polymer microcapsules containing ginger oil present a weight loss in 3 steps: 10 % weight loss around 150°C, 70% weight loss around 300°C and around 380°C complete decomposition of the material. The weight loss up to 150°C is attributed to the encapsulated essential oil. The second weight loss step at 300°C is correlated with the PMMA matrix which starts its decomposition sooner due to the structural

defects resulted from the release of the volatile oil. The last step registered in the TGA analysis at 380°C corresponds to the rest of the residual compounds obtained through analogous reactions. This method has put into evidence the encapsulation of the ginger oil in the polymer particles.

In order to properly asses the total concentration of encapsulated oil, the polymer particles were suspended in solvent and the extract was characterized by GC analysis. The results of the analyses are presented in **Table 1**.

Table 1

GC analyses results for variation in AIBN concentration

Retention time	Compound	Conc. in oil %	Capsules with 5% ginger oil				Capsules with 20% ginger oil and 0.015 mol/L AIBN
			AIBN amount, mol/L				
			0.015	0.03	0.06	0.09	
9.49	a-Pinene	1.33	2.43	1.26	1.01	0.81	2.31
10.07	Camphene	0.39	9.38	26.23	33.3	40.79	-
10.81	Limonene	3.45	2.06	1.6	1.61	4.91	2.35
12.94	Eucalyptol	1.27	2.25	0.76	0.72	0.63	1.35
13.82	cis-Carveol	3.28	-	3.6	3.48	2.83	3.57
14.21	b-Citral	7.01	-	8.76	8.19	5.44	8.08
17.27	a-Curcumene	9.29	19.84	11.36	11.49	11.63	12.34
17.48	Zingiberene	32.07	30.55	25.99	17.63	10.98	32.92
17.65	a-Selinene	8.59	16.08	11.05	9.65	9.11	12.11
17.72	b-Bisabolene	1.74	6.94	1.45	1.01	1.22	2.57
17.84	b-Sesquiphellandrene	14.94	1.64	1.66	1.67	1.59	2.03
19.71	g-Eudesmol	1.01	1.45	0.6	1.18	0.75	1.07
The total concentration of the essential oil in the polymer microcapsules (% wt.)			**0.22**	**1.74**	**2.59**	**2.19**	**13.67**
Ginger oil encapsulation efficiency (% wt.)			**4.40**	**34.80**	**51.80**	**43.80**	**68.35**

The data presented in Table 1 reveals that the percentage of encapsulated oil increases with the initiator concentration up to a certain value followed by a decrease. Probably a polymerization rate too high limits the time for the encapsulation process to take place. Thus, considering that the initial monomer-oil solution contained 5% wt. oil an encapsulation yield of approximately 52% was achieved. In order to confirm these results, an encapsulation polymerization using an initial oil concentration of 20% wt. was performed (using 0.015 mol/L AIBN concentration). The GC analysis revealed 13.67% wt. oil concentration to the polymer particles which corresponds to an oil encapsulation yield of 68%.

Taking into account the reactivity of the double bonds of essential oil, the next step consisted in the suspension polymerization of MMA particles in the presence of different concentrations of ginger oil. The GC/MS analysis results for the obtained PMMA microcapsules are presented in the Fig. 4.

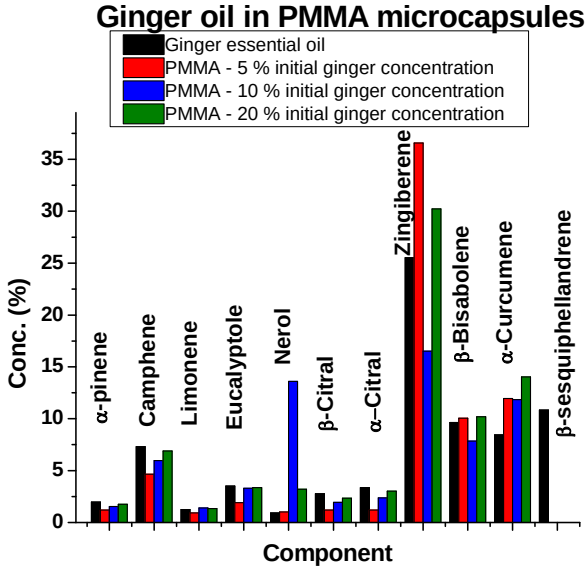


Fig. 4: The GC/MS results for PMMA microcapsules obtained using different initial essential oil quantities (5% - 0.25 mL, 10% - 0.5 mL and 20% - 1 mL)

For the PMMA capsules obtained using different initial essential oil concentration, the main components detected by GC/MS as components that are released from the capsules by extraction in methanol are: Zingiberene (17-37%), α-Curcumene (12-14%), β-Bisabolene (8-10%). There are also some higher volatile components detected, such as α-Pinene (1-2%), Camphene (5-7%), Eucalyptol (2-3%), α- and β-Citral (each 1-3%). β-Sesquiphellandrene is reported to be one of the major constituents of ginger essential oil [12] and the GC/MS analysis confirmed the presence of this compound in the essential oil (11%) and the absence of it in the polymer particles. Literature data [13] on ginger essential oil showed that Zingiberene and β-Sesquiphellandrene can be converted into Curcumene during storage of the essential oil. It is very possible, considering the close structures of these compounds, that Zingiberene, β-Sesquiphellandrene, Curcumene and also Nerol change one into another during the encapsulation process, as their sum in each of the cases is constant (46% for ginger oil, 50% for 0.25 ml oil, 42% for 0.50 ml oil and 48% for 1.00 ml oil) (Fig. 5).

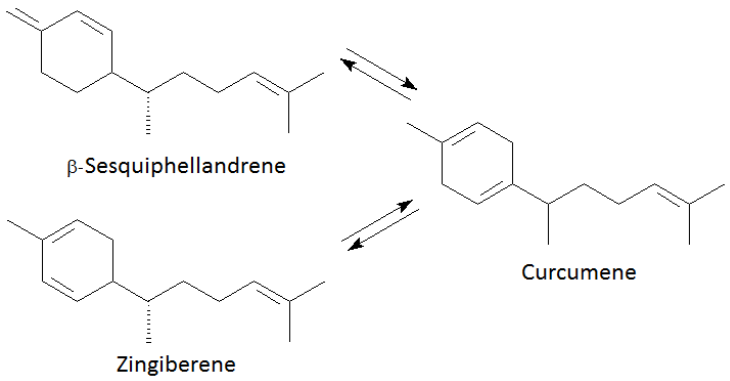


Fig. 5. Posibility of conversion of Zingiberene and β-Sesquiphellandrene into Curcumene during storage of the essential oil [12]

From **Fig. 4**, it can be noted that an increase of the initial essential oil concentration leads to a decrease of the encapsulation efficiency (11.92% for 0.25 ml oil, 5.55% for 0.50 ml oil and 1.94% for 1.00 ml oil). This is due to the higher number of reactive double bonds present in the oil composition which react with the free radicals formed by the initiator, creating a poor encapsulation environment.

4. Conclusions

This study presents an improved encapsulation process of ginger essential oil through the use of a tetra functional monomer and MMA. The purpose of using this other monomer is the crosslinking of the polymer particles and the increase of the polymerization rate, thus avoiding any possible side reactions. As the initiator concentration increases, the size of the particles formed increases, this being explained by the polymerization rate. The encapsulation of the essential oil was underlined by TGA and GC/MS, obtaining 13.67% in the case of 20% initial essential oil.

The encapsulation efficiency decreases (11.92% for 0.25 ml oil, 5.55% for 0.50 ml oil and 1.94% for 1.00 ml oil) through the introduction of a larger amount of essential oil in the polymerization process. This trend can be explained by the increased number of reactive double bonds present in the oil composition, which react with the free radicals formed by the initiator, thus creating a poor encapsulation environment.

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