Ginger Essential Oil Encapsulation in PMMA Microcapsules. I

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The aim of this study was the encapsulation of ginger essential oil in polymer particles. The chosen method was suspension polymerization of methyl methacrylate. In all cases, the polymerization process in the presence of ginger essential oil leads to decrease of the conversion at similar reaction intervals. The different reactivity of the essential oil components towards the free radicals generated by the thermal decomposition of AIBN was determined using GC/MS headspace analysis. The amount of encapsulated oil was determined by thermogravimetrical and GC analyses. TGA provided less reliable data about the total encapsulated essential oil. However, the extraction and GC analysis of the samples confirmed a higher content of essential oil in sample 2 (0.03 mol/L AIBN), and the lowest in sample 4 (0.09 mol/L AIBN).

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

Essential oils, also known as essences or volatile oils, are substances biosynthesized by living organisms. They can be liberated from the material which contains them by distillation, pressing or extraction with a suitable solvent. They have found uses in fragrance, food, cosmetic and pharmaceutical industry [1, 2].

Essential oils can be obtained through different conventional methods such steam distillation, hydro-diffusion, hydro-distillation, destructive distillation, cold expression as well as novel innovative techniques such as supercritical fluid extraction [3], turbo distillation, ultrasound-assisted extraction, microwave-assisted extraction, instantaneous controlled pressure drop technology [2, 4].

The microencapsulation consists in the isolation of the active substances (liquid, solid or gaseous), for the obtaining in general of spherical products with micrometric dimensions, in which the active material, or core, is protected from the environment by a membrane, a protecting shell [5]. This technique can be applied for different purposes such as: protecting sensitive compounds from environmental degradation, development of controlled release properties, masking of unpleasant taste or smell of active components, avoiding dilution of the core when small quantities are required or transformation of liquid compounds into mobile solids.

Microencapsulation allows the formation of a physical barrier between the core and the shell material for the protection of sensitive ingredients (flavors, antioxidants, oils, vitamins, medicine etc.) from the environment, in particular moisture, pH and oxidation. The controlled release of the microparticles can be triggered through breaking, solubilization, heating, *p*H or enzymatic action [6, 7].

One of the most important targets for encapsulation process is fragrance compounds. In the last decade, the demand for perfumed products is constantly increasing and it is considered that in the future it will intensify and diversify. The following are typical examples of perfumed consumer goods: odorants, bath additives, candles, decorative cosmetics, deodorants, antiperspirants, soaps, perfumes, hair care products, household products, oral hygiene, personal care, shaving, skin care and laundry products (detergents, balsams) [1].

This study presents a novelty in this research direction dealing with the encapsulation of ginger essential oil in poly(methyl methacrylate) through suspension polymerization, as well as the characterization of the obtained materials for multiple possible applications.

Experimental part

Materials and methods

Methyl methacrylate (MMA) (Merck) was purified by vacuum distillation (p=100 mmHg, T=47°C). Azoisobutyronitrile (AIBN) (Fluka) was recrystallized from methanol. The suspension agent, poly(vinyl alcohol) (PVA) (Mw=85 000-124 000 Da, 88% hydrolyzed), was utilized as received. The ginger essential oil was obtained through a microwave assisted hydro distillation process, using an optimized procedure similar to the literature [8].

MMA suspension polymerization

In a round bottom flask 0.2 g of PVA were added to 10 mL of distilled water and heated to 75°C under continuous stirring for the complete dissolution of the stabilizing agent. Separately, in 2 mL of MMA was dissolved the specific amount of initiator. This solution is added dropwise to the first aqueous solution and the mixture was stirred for 2 h. After this interval, the particles were centrifuged, washed several times with distilled water and dried until a constant mass was attained.

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

This synthesis was realized as in the previous case with the modification that the organic phase contains 0.5 mL essential oil, also. The following steps were identical.

Characterizations

The morphologies of polymer particles have been investigated through XL-30-ESEM TMP scanning electron

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microscope (SEM). The samples were sputtered with a thin layer of gold prior to imaging.

The TGA analysis has been performed on Q500 TA Instruments equipment, under oxygen atmosphere, using either an isothermal regime at 30°C or a heating rate of 20 °C/min from room temperature to 500 °C.

The GC/MS headspace analyses were performed using of a Thermo Electron Corporation Focus GC gas chromatograph with a Macrogol 20 000 R column (film thickness 0.25μm); l = 60 m; ∅= 0.25 mm. The mobile phase used was helium with a debit of 1.5 mL min^{-1}, while the sample injection volume was 0.2μL. A Thermo Electron Corporation DSQII mass spectrometer was used for detection. The identification of the samples analyzed by gas chromatographically was carried out by comparing the sampled spectral peaks with spectra from a Wiley database.

The essential oil content in the PMMA microcapsules was determined using a gas chromatograph apparatus HP6890 series equipped with: capillary column (DB-1, GW Scientific, 50 mX0.250 mm, 0.5 microns) and FID detector.

Results and discussions

The suspension polymerization reactions of MMA were realized using 4 different concentrations of AIBN initiator, in the presence or absence of essential oil. First, we will discuss the influence of the initiator concentration on the conversion (fig. 1), respectively on the morphology of the obtained particles in the absence of the essential oil (fig. 2).

The analysis of figure 1 reveals the conversion increase with the concentration of the initiator. This aspect can be easily explained by a higher polymerization rate, respectively higher monomer consumption. The final value is relatively low due to the short reaction time (2h) and the total consumption of the monomer is not being reached. For supplementary information on the morphology of the particles, SEM analysis was employed (fig. 2).

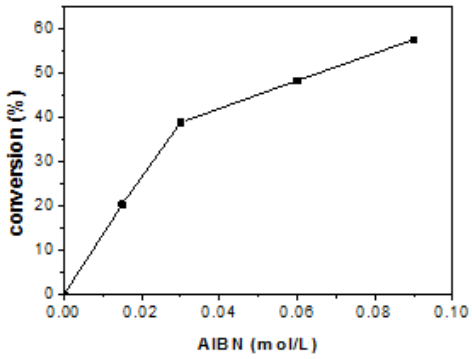
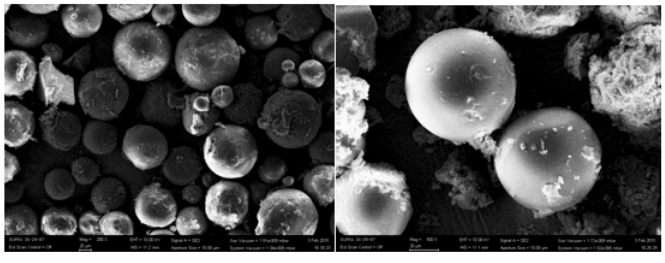


Fig. 1. AIBN concentration influence on the conversion in the absence of essential oil



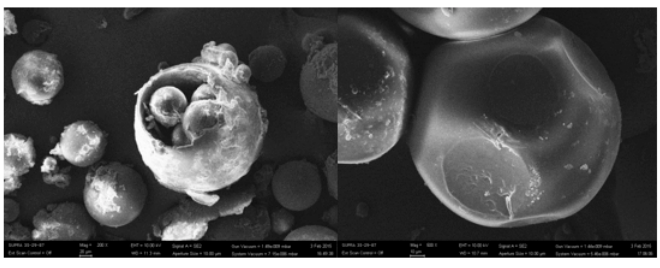


Fig. 2. SEM images of the PMMA particles for the 4 AIBN initial concentrations: a)0.015 mol/L; b) 0.03 mol/L; c) 0.06 mol/L; d) 0.09 mol/L

A small increase in the particles dimensions with the increase of the AIBN initial content can be observed from the analysis of figure 2 (a, b, c and d). This aspect can be explained by the increase of the final conversion reached [9].

The polymerization reactions in the absence/presence of the ginger oil were realized using poly(vinyl alcohol) as suspension agent. The parameters were kept constant in the presence of the essential oil and the conversion evolution as a function of AIBN concentration is presented in figure 3.

As for the previous cases, the conversion increases with the initiator concentration, but the values reached are significantly lower. This aspect suggests a degree of inhibition/delaying of the polymerization reaction, which can be explained by the chemical interaction of the essential oil components with the initiator. In order to better understand these interactions the chemical structure of the ginger essential oil components are presented in scheme 1.

Form the analysis of the chemical structures presented in scheme 1, we can conclude that the majority of the constituent's present reactive double bonds capable of interaction with the free radicals generated the AIBN thermal decomposition. In order to highlight this interaction, GC/MS/HS was performed on the ginger oil and on the PMMA microcapsules.

Using GC/MS/HS analysis, we have determined that the principle components of the extracted ginger essential oil are: camphene (36-38%), α-pinene (15-16%), limonene (14-16%), eucalyptol (1,8-cineole 11-12%). The initial ratio between the oil components (α-pinene/camfen/b-pinen/b-mircen/Limonene/Eucalyptol-Cis-carveol/b-citral/a-Curcumene/Zingiberene 16.73/35.45/1.54/3.81/17.92/7.54/

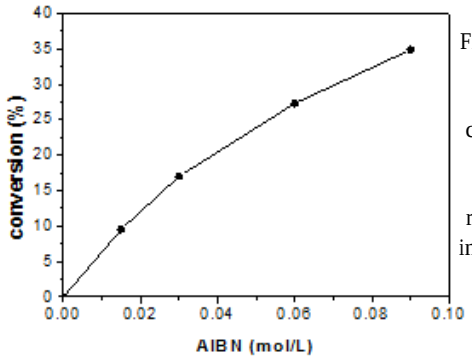
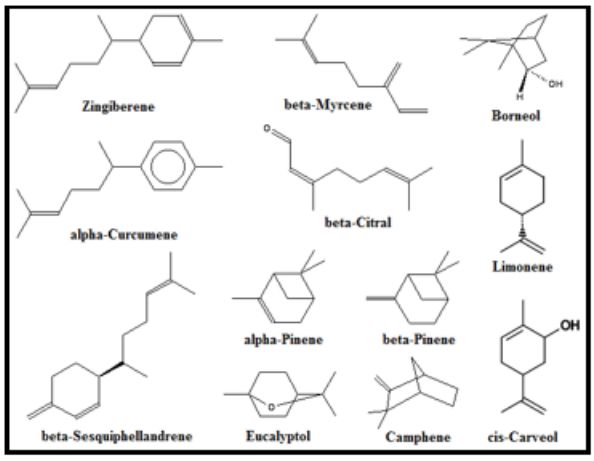


Fig. 3. Conversion evolution vs initiator concentration for the polymerization reaction realized in the presence of essential oil



Scheme 1 Chemical structures of ginger oil main components

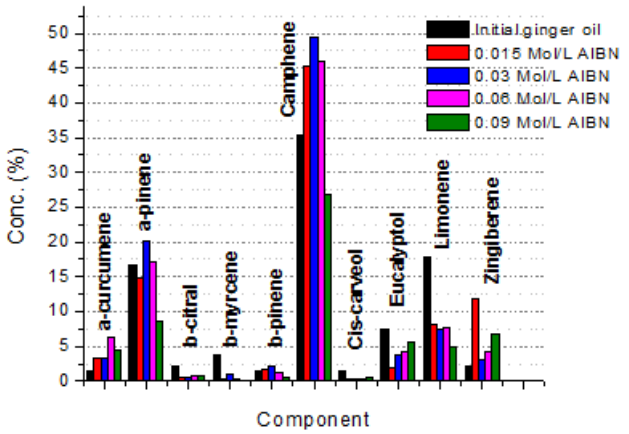


Fig. 4.The GC/MS/HS analysis of the ginger extract and PMMA microcapsules containing essential oil

1.52/2.27/1.51/2.09) should remain constant if there are undesirable reactions taking place.

Analyzing the ratio between the ginger oil components, in the case of PMMA microcapsules, we observe that â-citral, β-myrcene, cis-carveol and limonene are consumed with preponderance from the oil composition, which confirms the reactivity of the components with the free radicals from AIBN thermal decomposition and explains the decrease of the conversion value (scheme 2).

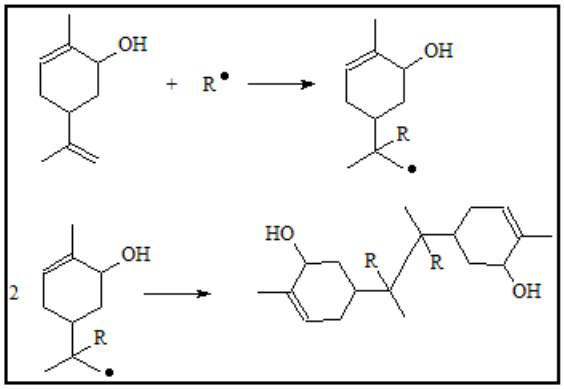
An important aspect to note is that the major components of the ginger essential oil appear to be affected to a lesser extent (fig. 4). Nevertheless, the polymerization inhibition/delaying caused by the oil components is the explanation for the utilization of an AIBN concentration in order of 10^{-2} mol/L compared to a classical radical initiator content of 10^{-3} mol/L. For supplementary information on the morphology of the particles, SEM analysis was employed (fig. 5).

In the case of figure 5a the porosity of the particles caused by the initiator decomposition and N_2 release can be easily observed. Increasing the AIBN concentration, in figure 5b we observe the formation of a number of smaller particles which adhere to large ones. The significant particle sized difference in this case can be correlated with the polymerization inhibition. The adhesion of the particles is due to the *free* oil which serves as adhesive between the different polymer particles formed. For the next samples figure 5c and 5d, we observe a relative low number of particles embedded in a continuous polymer mass. In these cases, the suspension is unstable due to some thermodynamic issues (APV quantity, suspension stirring speed).

In order to determine the essential oil content in the polymer particles, TGA analysis in isothermal regime (30°C) for 100 min has been performed.

In figure 6, it can be observed that at a constant temperature of 30°C, the most significant loss (0.94% wt. loss) is registered for the microcapsules obtained using the lowest initiator concentration. The next samples offer differentiated results, thus the second highest weight loss (0.65 % wt. loss) is recorder for the samples prepared using the highest AIBN concentration (0.09 mol/L). However, these values do not allow the determination of a correlation between the efficiency of the encapsulation and initiator concentration. Thus, the TGA analysis was performed on larger temperature interval (fig. 7).

The highest weight loss is registered for the sample containing the highest initial initiator concentration, whereas the smallest weight loss is recorded for the sample containing the lowest initiator concentration. The important



Scheme 2. Possible reactions of the free radicals formed with cis-carveol

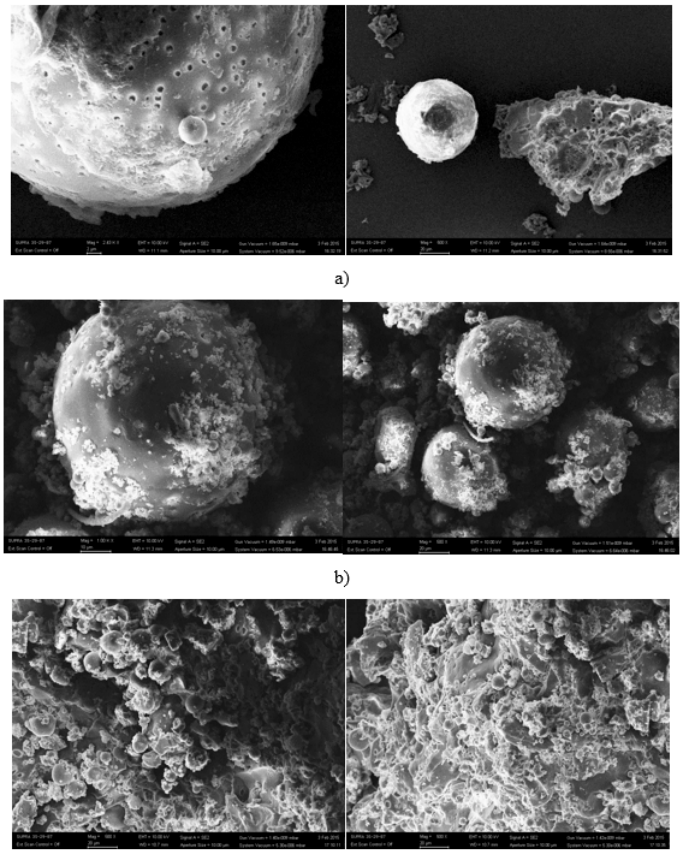


Fig. 5. SEM analysis of PMMA microcapsules containing essential oil for the four concentrations of ginger essential oil:a) sample 1 (0.015 mol/L); b)sample 2 (0.03 mol/L); c)sample 3 (0.06 mol/L); d)sample 4 (0.09 mol/L)

weight loss takes place after 200°C, when the PMMA thermal degradation begins following a two steps process [10].

Thus, both TGA analysis offer uncertain information on the quantity of encapsulated ginger essential oil inside the polymer microcapsules. In order to solve this problem and to better determine the quantity of encapsulated oil, we have extracted the polymer particles with methanol and analyzed the solutions by GC. This approach takes advantage on the porosity of the obtained polymer microcapsules.

The principal compounds detected by GC analysis in the ginger essential oil are zingiberene, α-curcumene, β-sesquiphellandrene, β-citral, limonene, α-selinene, camphene and cis-carveol, results which are in accordance with literature data [11, 12]. In the case of limonene, eucalyptol, borneol, cis-carveol and β-citral, the highest concentrations are registered for microcapsules prepared using 0.03 mol/L AIBN, whereas for α-Selinene

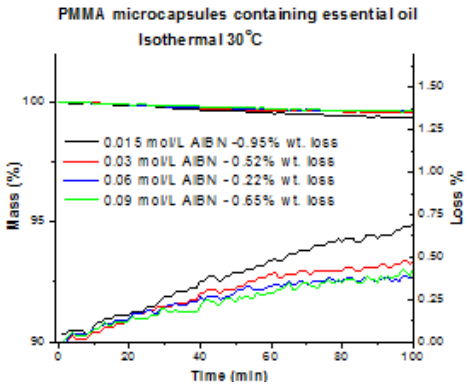


Fig. 6. TGA analysis isothermal regime (30°C)

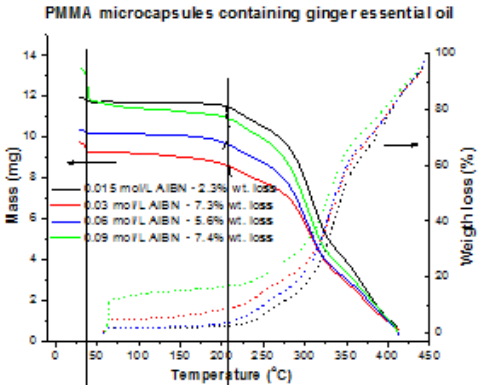


Fig. 7. TGA analysis of the PMMA microcapsules containing ginger essential oil up to 400°C

Retention time	Compound	Conc. in oil %	Capsules with ginger oil – initiator amount			
			0.015 mol/L AIBN	0.03 mol/L AIBN	0.06 mol/L AIBN	0.09 mol/L AIBN
10.26	α-Pinene	1.34	1.53	1.82	1.38	1.07
10.52	Camphene	5.69	6.13	7.75	5.65	4.55
11.84	Limonene	7.72	2.13	3.06	3.34	4.71
13.94	Eucalyptol	1.59	0.18	0.46	0.63	1.16
14.24	Borneol	1.01	0.11	0.21	0.30	0.51
14.82	cis-Carveol	4.16	0.87	1.63	2.23	3.68
15.20	β-Citral	8.49	2.00	3.86	5.24	6.06
16.73	Geraniol acetat	0.98	0.49	1.02	0.93	0.78
18.25	α-Curcumene	10.50	17.49	16.21	18.56	10.77
18.45	Zingiberene	19.87	33.55	21.09	22.66	27.76
18.63	α-Selinene	7.73	14.12	13.24	15.29	11.76
18.81	β-Sesquiphellandrene	12.51	2.77	2.81	3.99	3.04
19.13	γ-eudesmol	1.14	0.22	1.13	0.83	0.60
The total concentration of the essential oil in the polymer microcapsules (% wt.)						
			6.13	**9.13**	**7.49**	**4.84**

Table 1
GC ANALYSES RESULTS

and β-Sesquiphellandrene the proportion increases for the experiments realized using 0.06 mol/L AIBN. In the case of Zingiberene, which is the major constituent detected in the ginger essential oil, the highest concentration was obtained for the particles obtained with the smallest initiator concentration. These results justify the difference in reactivity of the essential oil components with the free radicals generated by the AIBN thermal decomposition.

The GC analysis revealed that the highest essential oil concentration (9.13% wt.) in the case of the polymer microcapsules obtained using 0.03 mol/L AIBN (sample 2), whereas the lowest (4.84% wt.) encapsulated oil concentration was in the case sample 4 (0.09 mol/L AIBN initial concentration).

Conclusions

In all the suspension polymerizations experiments realized in the presence of ginger essential oil a decrease of the conversion for the same reaction time was observed. This observation can be explained by the decrease of free radicals concentration and hence the polymerization rate. The existence of reactive double bonds in the constituents of the ginger essential oil leads to the decrease of the free radical concentration, thus reducing the polymerization rate and therefore the conversion.

Through GC/MS/HS analysis, the different reactivity of the essential oil components towards the free radicals generated by AIBN thermal decomposition was established. The thermogravimetrical analyses did not afford reliable data about the total encapsulated essential oil. However, by extraction and GC analysis of the samples, the highest essential oil content was determined in the sample 2 (0.03 mol/L AIBN), while the lowest was in the case of sample 4 (0.09 mol/L AIBN).

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