EFFECT OF STIRRING SPEED ON THE PREPARATION OF UREA-FORMALDEHYDE MICROCAPSULES FILLED WITH ROSE OIL BY INTERFACIAL *IN SITU* POLYMERIZATION METHOD

Stanislav G. Bayryamov[1], Maria P. Nikolova[2]

[1]*Department of Repair, Reliability, Mechanisms, Machines, Logistic and Chemical Technologies, Agrarian and Industrial Faculty University of Ruse "Angel Kanchev", 8 Studentska St., Ruse 7017, Bulgaria, sbayryamov@uni-ruse.bg (S.B.)*
[2]*Department of Material Science and Technology Faculty of Mechanical and Manufacturing Engineering University of Ruse "Angel Kanchev", 8 Studentska St., Ruse 7017, Bulgaria, mpnikolova@uni-ruse.bg (M.N.)*

Received 23 July 2024
Accepted 13 November 2024
DOI: 10.59957/jctm.v60.i4.2025.2

ABSTRACT

In this paper, rose oil was microencapsulated by the chemical process of in situ interfacial polymerization using urea and formaldehyde as monomers serving as the capsule wall building material. As is found, in the process of microencapsulation by in situ polymerization, the emulsification step is one of the most important, which is why the authors pay special attention to it. Based on their preliminary studies, they divided this step into two sub - steps, considering the influence of reaction conditions separately in each one of them. The presented work examines the influence of stirring speed in the emulsification step (sub - step A and sub - step B), on the process efficiency, yield and quality of the obtained microcapsules, thus the authors hope to contribute to the optimization of the conditions for obtaining better quality microcapsules and with a higher yield.

Keywords: microencapsulation, in-situ polymerization, rose oil, urea, formaldehyde, mono methylol urea, pre - polymer, emulsification step.

INTRODUCTION

It is well known that rose oil is the face of Bulgaria, which means that our country is famous with the production of the best quality rose oil. Due to the current topic related to the microencapsulation of essential oils and their diverse application in various fields, our efforts were focused on the microencapsulation of this product. Thus, rose oil was microencapsulated by the chemical method of *in situ* polymerization using urea and formaldehyde to build the capsule shell. Unfortunately, there is not much data on the study of the different reaction conditions with the aim of optimizing them, specifically regarding the encapsulation of rose oil. This has led us to study these conditions during the emulsification step, which is one of the most important in this microencapsulation method. The condition studied was the different stirring speed of the reaction medium. This aimed to optimize the conditions for obtaining microcapsules with desired properties. Thus, varying the conditions of the process, depending on the application of the microcapsules, their design and synthesis could be realized.

The inability of an active substance to maintain both its stability and its action over an extended period is one of many significant problems in modern industry. This instability is due to the constant exposure of the substance to adverse environmental conditions, such as temperature fluctuations, direct sunlight, temperature, various oxidizers, as well as

other chemical agents. One of the ways to increase the stability, and to preserve the action and long - lasting effect of the substance through its controlled release, is the application of the microencapsulation process [1 - 4]. The microencapsulation technique depends on the physical and chemical properties of the material to be encapsulated [1 - 4]. Many review works describe the different methods for obtaining microcapsules, their analysis, as well as application in different fields, depending on their properties. For instance, in the review of Zhao and Zhang, the microencapsulation of phase change materials (MEPCMs) was considered, together with capsules fabrication, their characterization and applications in various areas of the economy and industry [5]. In another literature review, different microencapsulation methods based on emulsification were concerned - for producing pharmaceutical products [6]. A variety of microencapsulation techniques as well as the factors influencing the encapsulation efficiency was summarized by Jyothi et al. [7]. Another work discussed different microencapsulation methods for delivery of protein drugs and their application in medicine and pharmacy [8]. On the other hand, the microcapsules with thermal energy storage compounds can be suitable for smart textile, thus the microencapsulation technology finds a wide application in textile industry [9]. Moreover, Poncelet summarized microencapsulation as fundamental achievement in the contemporary industry, discussing different methods for microcapsule synthesis and their applications in various areas [10]. Also, Venkatesan et al. reviewed the different approaches for microencapsulation and differentiated them as a vital technique in novel drug delivery system [11]. A review of microencapsulation methods for microencapsulation of phase change materials as a thermal energy storage medium was discussed by Jamekhorshid et al. [12], whereas V.V. Tyagi et al. reviewed the development of phase change materials based microencapsulated technology for buildings [13]. In their literature review, Platte et al. studied the microencapsulation of alkaline salt hydrate melts for phase change applications by surface thiol-michael addition polymerization [14]. The development of cosmetic textiles using microencapsulation technology was reviewed by Cheng et al. [15]. Also, the fact that bioactive compounds can be preserved by microencapsulation is one of the important achievements in modern industry [16]. In their review, Aloys et al. [17] as well as Timilsena et al. [18] paid a huge attention on the preparation of microcapsules by one of the most important methods namely complex coacervation. In their work they considered at the different principles, mechanisms, methods, techniques, benefits and various applications of obtained microcapsules by complex coacervation. A variety of microencapsulation methods and the industrial applications of the obtained microcapsules as drugs in medicine and pharmaceutical industry were concerned by Benita [19]. Another review, written by Kaushik et al., examined the various methods of microencapsulation and characterization of omega-3 fatty acids due to the presence of some specificities in these compounds [20].

The choice of material making up the capsule wall is made according to the final characteristics of the capsule shell, the function it is to perform and the conditions under which the capsule is required to be resistant. In addition, depending on the type and properties of the encapsulated substance, the method and conditions related to this should also be selected. For example, in some cases substances need to be encapsulated to enclose the main material by means of the stable shell of the capsule and preserve it for a certain period [15]. In other cases, due to the properties of the core material, it has been necessary to encapsulate it in such a way that the active substance was released either gradually through the walls of the capsule, known as controlled release or diffusion, or by changing the external conditions (pH, ionic strength, heat, mechanical impact, light, ultrasound or other radiation) to cause the capsule shell to break, melt or dissolve [6, 8, 11, 16 - 19]. Such active substances are different dyes, drugs, fragrances, detergents, cosmetics, foods and nutritional supplements, etc.

Different microencapsulation methods are characterized by some specifics that make each method unique. In this case, during the *in-situ* polymerization between urea and formaldehyde, a preliminary synthesis of a pre - polymer (mono methylol urea) takes place in the first step, its subsequent adsorption on the surface of the microdroplets formed in the second step and its further polycondensation throughout the microencapsulation step in the final urea-formaldehyde co - polymer, simultaneously with the self - wrapping

of the previously obtained microdroplets of the core substance [21 - 25]. The pre - polymer (mono methylol urea) was obtained by addition of one molecule of urea to one molecule of formaldehyde, after which the newly formed pre - polymer molecules were adsorbed on the surface of the microdroplets obtained during the emulsification step [21]. When the reaction of the media changes because of lowering the pH, polycondensation takes place between the molecules of mono methylol urea to urea - formaldehyde polymer. [21 - 25]. The microcapsules formed by this way, built from a urea - formaldehyde polymer wall, were characterized by good qualities, allowing on the one hand to keep the substance stable for a long period of time and on the other hand, through its controlled release to have a long - lasting effect according to its purpose. Depending on the stirring speed in the emulsification step, the yield of microcapsules and the quality of the capsule shell were different, which was the subject of consideration in the present scientific work.

Finally, the nature of the encapsulated substance is also important, the main role of which is evident in the initial selection of conditions and materials. In the case of the microencapsulation of essential oils, their sensitivity to sudden changes in conditions must be considered, as well as their specific behaviour, depending on the material used for its microencapsulation, i.e. the material making up the capsule shell. This should be considered when selecting the material making up the capsule wall, as well as when choosing the conditions for carrying out the process itself.

Like any method for the preparation of microcapsules, the *in-situ* polymerization method is characterized by several disadvantages. One such drawback is the formation of a by - product, leading to a decrease in yields. During the encapsulation of substances by in situ polymerization, along with the formation of microcapsules, a side process of microparticle formation of the corresponding polymer takes place [21]. These two types of particles form two masses, and the resulting microcapsules are located on the surface of the reaction medium, while the microparticles of the polymer forming the shell of the capsule fall to the bottom. Increasing the amount of microparticles leads to a decreasing in the efficiency of the encapsulation process, and the goal of modern research is to minimize the amount of microparticles as much as possible. This could be achieved through optimizing the conditions of the *in-situ* polymerization by changing individual process parameters [26 - 28]. This optimization of the conditions could only be achieved after the process was run and studied under a different change in these conditions. Here we propose a dependence of the encapsulation efficiency on the stirring speed in the emulsification step, which could contribute to the optimization of these conditions to reduce the amount of microparticles. This, in turn, would lead to the redirection of the material making up these microparticles into its use for a thicker and better-quality capsule wall, leading to an improvement in resin efficiency.

Pre - polymer synthesis

The first step of the microencapsulation procedure was the synthesis of pre - polymer (mono methylol urea), obtained by reacting urea with formaldehyde through an addition reaction. The preparation of the pre - polymer solution was carried out according to the method of Rochmadi et. al. [21], Xiong et al. [29], Yang and Pan [30], Matson [31], as well as with our modifications [32, 33]. The stability of the formed mono methylol urea was influenced by the conditions of its preparation. When synthesized at a higher pH (11 - 13), regardless of the other conditions (temperature, molar ratio), as well as regardless of whether it was stored in solution or in the solid state, the resulting pre - polymer was very stable and could be used repeatedly [34]. Presumably, substances are more stable in solid state than in liquid state or in solution. However, when it was synthesized at a lower pH, in the range between pH 7 - 9, it was unstable for a long period of time and was desirable to use it immediately.

The synthesis was carried out in a three - necked round - bottom flask equipped with a thermometer, a reflux condenser and a mechanical or electromagnetic stirrer. A precisely determined amount of urea was placed in it, to which, with vigorous stirring, a pre - neutralized 37 % formalin solution was added, and the pH of the solution was adjusted to pH 8 - 8.3 by slowly adding drops of a 10 % sodium hydroxide solution. The preliminary neutralization of the formalin solution was required due to the presence of impurities of formic acid obtained because of oxidation of formaldehyde. The reaction mixture was heated in a water bath and

the temperature should not exceed 70°C. Heating at this temperature was continued for about 1 h, and after cooling, the reaction mixture was diluted with distilled water to 250 mL of pre - polymer solution. It was important to know that the pH of the reaction mixture decreased during the reaction, which is an indication of the formation of a product of the addition reaction (pre - polymer). This lowering of the pH of the reaction mixture was not desirable because it created conditions for the formation of insoluble undesired by - products [34 - 38]. Therefore, it was necessary to maintain it in the range between 8 - 8.3 by adding dropwise of dilute sodium hydroxide solution.

Emulsification step

The preparation of the microcapsules was according to the method of Rochmadi et. al. [21], Xiong et al. [29], Yang and Pan [30], Matson [31], Vassiliades [39], as well as with some of our modifications [32, 33] changing the stirring speed (500 rpm, 750 rpm, 1000 rpm, 1250 rpm, 1500 rpm and 2000 rpm) during the emulsification step. In addition, the process was carried out using an emulsifier (3 % of sodium dodecyl sulfate, SDS). The microencapsulation step was the same as in the procedure of Bayryamov and Nikolova [32, 33]. The essential oil was encapsulated after dilution with a given solvent (concretely medical paraffin), aiming on the one hand to reduce the cost of the encapsulated substance, on the second - to stabilize the core material and on the third - to increase the efficiency of the process, which could lead to higher yield and better quality of the obtained microcapsules. The effect of solvent on microencapsulation efficiency will be discussed elsewhere.

According to the procedure of Bayryamov and Nikolova, the emulsification step can be divided into two sub - steps: A. Micro droplet formation; B. Adsorption of pre - polymer molecules on the droplet surface [32]. The stirring speed (500, 750, 1000, 1250, 1500 and 2000 rpm) was changed both during the first sub - step and the second sub - step of the emulsification step. When stirring speed was varied (at the emulsification step), the temperature, the time and the emulsifier concentration (3 %) were constant. In the first sub - step, when the stirring speed was varied, the temperature was 70°C and the time was 3.5 h. In the second sub - step, after receiving the milk - like emulsion, when the stirring speed was varied, the temperature was lowered to 45°C and the time was 2.5 h.

The stirring speed during the emulsification step plays a key role, especially on the size of the microdroplets, determining the size of the microcapsules obtained afterwards. In physico - chemical and chemical methods, regardless of the microencapsulation method, data show that with increasing stirring speed, especially during the emulsification step, the size of the capsules decreases, and their yield, quality and stability increase [7, 22, 26, 28, 40 - 42].

However, there were studies that shown that the very high stirring speed i.e. over 500 rpm led to a decrease in the yield of microcapsules, which was due to frequent collisions believed to occur between the particles causing the deposition of poly(urea - formaldehyde) and the alkyd resin derived from palm oil on the stirrer and the reactor wall [25]. Of course, these known exceptions were due to the specific properties derived from the alkyd resin (from palm oil) as the core substance, from the method and its accompanying protocol, from the type of surfactant, as well as from the material used to build the microcapsule shell.

In this regard, efforts were aimed at carrying out research related to the influence of different stirring speeds during the two sub - steps (stages A and B) of the emulsification step, on the efficiency of the microencapsulation process and the quality of the obtained microcapsules.

Initial studies show that the higher speed has a positive effect on the process and quality of the capsules [32]. In turn, the capsule yield increased while the encapsulation efficiency (EE, %) also increased and the encapsulated substance content (core content %, E% core), decreased. Since decreasing values of this quantity indicated that the mass of the encapsulating substance of the insoluble shell was rising, it follows that the density of the material making up the shell (shell quality) was increasing. These results indicated the increase in the amount of adsorbed pre - polymer particles on the surface of the forming microdroplets.

Microencapsulation (polymerization) step

During this step, the synthesis of the microcapsules is realized, which takes place because of the polycondensation (pH < 7) of the mono methylol urea molecules, adsorbed on the surface of the microdroplets

formed in the second step. While the addition reaction between one molecule of urea and one molecule of formaldehyde leading to the formation of mono methylol urea (pre - polymer) proceeds at a higher rate in an alkaline media at pH 7 - 8, the polycondensation reaction (in the microencapsulation step) between the pre - polymer molecules is favoured in acidic conditions at pH = 3.

This step is affected by the same factors, namely temperature, stirring speed and time. The temperature and the time have a huge effect on the microencapsulation process as well as on the yield and quality of the obtained microcapsules. Since the polycondensation reaction leading to the formation of the polymer capsule wall is an exothermic reaction, increasing the temperature slows down this reaction. Furthermore, the high temperature causes desorption of the mono methylol urea pre - polymer molecules, resulting in a lower yield of the microcapsules and a thinner, low - quality shell.

As for the influence of the time in this step, the third step, i.e. the microencapsulation step may take 5, 6, or 3 h [21]. At pH 3, along with the formation of microcapsules, polymer microparticles were formed during the polymerization step. According to Rochmadi et. al. at lower pH, the rate of microparticle formation is higher than the rate of microcapsules obtaining together with the high speed of the polymerization reaction in general [21]. Thus, the main goal of the authors worldwide is to reduce the amount of non - adsorbed pre - polymer particles, which could be done by controlling the molar ratios of substances as well as the other parameters (stirring speed, temperature, time, type and concentration of surfactant, type of solvent, type of linker etc.) during the second step of the process (emulsification step) and also by controlling the pH during the polymerization step. For this reason, it is also necessary to study the influence of pH during all steps of microencapsulation, especially during the polymerization step, based on which to select the optimal pH - value to minimize the process of formation of microparticles at the bottom of the reaction mixture of the sample. This is best seen by the encapsulation factor (EF) characteristic, giving the ratio of the total weight of microcapsules on the surface of the sample reaction mixture to the total weight of microparticles at the bottom of the sample reaction mixture (m_{mcs}/ $m_{mps,}$ see below). Also, Rochmadi et. al. described that the microencapsulation time influences on the resin efficiency [21]. However, this was observed until the third h, after which resin efficiency was increased very little from 47.6 % at the 3rd h to 53.8 % at the 6th. According to us, these data indicated that the density of the shell slightly increased after the 3rd h. Studies on the effect of microencapsulation time on this parameter are to be done and will be described elsewhere.

EXPERIMENTAL

Methods and materials

The following materials and reagents were used in the current work: Technical urea, recrystallized from ethyl alcohol; formalin as a 37 % formaldehyde solution; rose oil purchased from licensed Bulgarian producers; the pre - polymer resin was obtained in an alkaline media as a solution of mono methylol urea at a specified concentration; 10 % NaOH solution, 1N NaOH solution, and 10 % citric acid solution were used to adjust the pH throughout the process. The solutions were prepared just before the microencapsulation procedure using the commercial reagents.

The reaction of the mixture with respect to pH was monitored and controlled using a professional benchtop pH - meter: BANTE Instruments, Model 920 - UK with a combinative pH electrode with BNC coupling. The pH - meter includes temperature compensation in the temperature range of 0°C to 100°C. Operating conditions: from 0°C to 50°C with relative humidity up to 95 %. Division of pH = 0.001 pH units, range: from pH = - 2.000 to pH = 20.000, accuracy (at 20°C) pH ± 0.002.

For agitation of the reaction mixture and for control of the stirring speed, an electromagnetic stirrer with heating was used with an included temperature probe to control the actual temperature, brand DIAB, Model MS7 - H550 - S with a temperature range of + 30 - 550°C, stirring speed 0 - 1500 rpm, power 1030 W; as well as homogenizer for solid and liquid media Velp Scientifica, model OV5 with a stirring speed of 1000 - 22000 rpm.

Weight analyses including microcapsule yield (%), encapsulation efficiency (EE, %), % sample (% encapsulated compound, core content, E% core), resin efficiency (RE, %) and encapsulation factor (EF) were

performed by weighting various components on an analytical and precise balance with internal calibration - "KERN" model ABJ 120 - 4NM, range 120 g, accuracy 0.0001 g, plate diameter: d = 91 mm; as well as using an analytical and precise balance with internal calibration - "KERN" model ABJ 220 - 4NM, range 220 g, accuracy 0.0001 g, plate diameter: d = 91 mm.

In terms of their shape, morphology and approximate size, the microcapsules were analysed with a light microscope CARL ZEISS JENA, model 30 - G0020a, with magnifications of 12.5 x, 25 x, 40 x and 100 x, as well as a reflective optical metallographic microscope Nikon, included in the equipment of CSEM Scratch tester (Switzerland) and digitized with a 14 - megapixel camera. The size of the microcapsules as well as their size distribution were determined using a laser diffraction apparatus brand MICROTRACK MRB model SYNC, with a working range of 0.01μm - 4mm.

FT-IR analyses of rose oil microcapsules were carried out on PerkinElmer Spectrum™ 3 FT-IR apparatus (21 CFR Part 11 Compatible) operating at the wavelength range between 7800 cm^{-1} - 225 cm^{-1}. Before the analysis, the microcapsules were broken by grinding in a porcelain mortar or with ultrasound. The spectra of the prepared microcapsules were obtained after freeze drying of the broken microcapsules' mixture using KBr pellets or NaCl crystals.

Preparation of microcapsules

Pre-polymer synthesis step. General procedure

60 g of urea (Mm = 60.06 g mol^{-1}; 1 mol) were placed in a 500 mL three - necked round bottom flask fitted with a thermometer, reflux condenser and mechanical or electromagnetic stirrer. To these, with vigorous stirring, 120 mL of 37 % formalin solution (44.4 g formaldehyde, Mm = 30.03 g mol^{-1}; 1.48 mol) were added, as the pH of the solution was adjusted to pH 8 - 8.3 by slowly adding drop wise 10 % sodium hydroxide solution. The reaction mixture was heated in a water bath as the temperature must not exceed 70°C. Heating at this temperature was continued for about 1 h, after which the water bath was removed, and the flask was left under reflux at room temperature. After cooling, the reaction mixture was diluted with distilled water to 250 mL of pre - polymer solution. It is important to know that the pH of the reaction mixture decreases over the course of the reaction, and therefore it is necessary to maintain it in the range of 8 - 8.3 by drop wise addition of dilute sodium hydroxide solution. This decrease in the pH of the reaction mixture is not desirable due to the creation of conditions for the formation of insoluble undesirable side by - products. To this end, various alkali reaction salts, such as: ammonium carbonate, sodium acetate and its mixture with citric acid and others, may be used instead of sodium hydroxide solution. Ammonium chloride may also be used as well as urotropine, melamine, TRIS. HCl or TRIS - base, triethanolamine, urotropine and similar.

Emulsification step, general procedure

In an Erlenmeyer flask, 3 % SDS was added to 100 mL of pre - polymer solution at different stirring speeds: (500, 750, 1000, 1250, 1500 and 2000 rpm). The resulting pre - polymer and surfactant solution was transferred to a 500 mL round - bottom flask equipped with a thermometer, a reflux condenser, and a mechanical or electromagnetic stirrer. Then, 5 mL of essential rose oil, preliminary diluted with a medical paraffin (rose oil : medical paraffin - 1 : 49, 0.1mL : 4.9mL) were added to the pre - polymer and surfactant (SDS) solution, varying in the same range of the stirring speed (500, 750, 1000, 1250, 1500, and 2000 rpm) at a temperature of 70°C. The duration of the emulsification step from its beginning to obtaining a milky white emulsion (stage A) was 3.5 h and then to the end of the emulsification step (stage B) was 2.5 h.

Microencapsulation (polymerization) step

The stirring speed of the reaction mixture was reduced to 750 rpm for about 20 min., after which a solution of citric acid was added to the emulsion (to achieve pH 3), at a temperature of 45°C. The reaction mixture was stirred for 3 h under the same conditions, after which the resulting microcapsules were filtered, washed with distilled water and dried at room temperature or in a dryer at a temperature of 55 - 60°C for 6 h. To harden the microcapsules, after the expiration of the time, the solution was cooled to room temperature (or previously obtained capsules were placed in water), with constant stirring, 2 mL of a 37 % alcoholic solution of formalin was added, and the stirring was continued for another 15 min until their solidification. Then, the obtained microcapsules were filtered, washed with distilled water and dried under the conditions mentioned above.

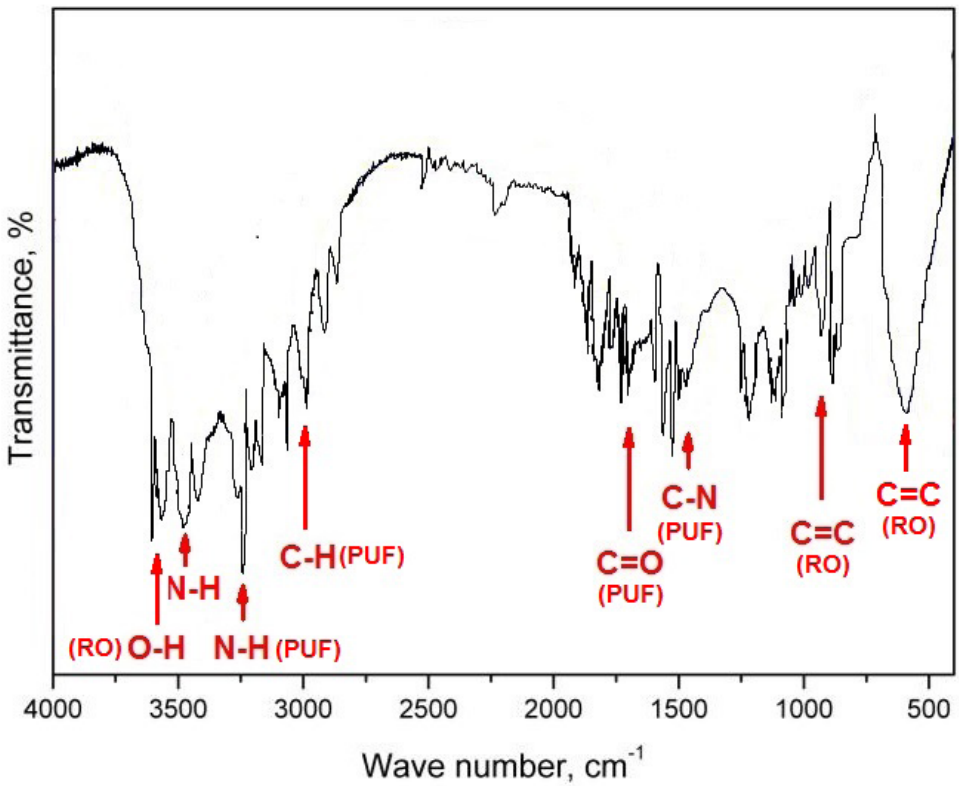

Fig.1. FT - IR spectrum of urea - formaldehyde microcapsules filled with rose oil. PUF: poly(urea-formaldehyde), RO: rose oil.

Product analysis

FT-IR spectroscopic analysis

The infrared spectra of the microcapsules, with the characteristic absorption bands of the urea - formaldehyde polymer forming the wall of the microcapsules, are at 3500 cm^{-1}, 3400 cm^{-1}, 2870 cm^{-1} and 2800 cm^{-1}, 1620 cm^{-1} and 1530 cm^{-1}, corresponding to C-H, N-H and C-N vibrations, respectively as well as the N-H of the amine are at 3250 cm^{-1} and 3300 cm^{-1} respectively [25, 29, 42 - 44]. The O-H vibrations of the hydroxyl groups of the rose oil essential alcohols are at 1050 cm^{-1}, 1340 cm^{-1}, 1375 cm^{-1}, 1430 cm^{-1}, 3375 cm^{-1}, 3580 cm^{-1}, 3610 cm^{-1} and 3650 cm^{-1}. The vibrations for the C=O groups of the essential oil aldehydes of the rose oil are at 1375 cm^{-1}, 1710 cm^{-1}, 1725 cm^{-1}, 1735 cm^{-1}, 2745 cm^{-1} and 2785 cm^{-1}; and from the ethereal ketones: 1610 cm^{-1}, 1710 cm^{-1} and 1720 cm^{-1}. The characteristic bands for C=C bonds are at 580 cm^{-1}, 970 cm^{-1} and 1640 cm^{-1}; and for C=C-H: 3075 cm^{-1} and 3085 cm^{-1} [45].

Weight analysis

In turn, the yield of the microcapsules (%) was calculated based on the ratio of the total weight of the dried product over the total weight of the raw materials required to form the microcapsules Eq. (1).

$$Yield\% = \frac{m1}{m2 + m3}.100 \quad (1)$$

where: m_1 is the total weight of the microcapsules, m_2 is the starting weight of the encapsulated substance, m_3 is the weight of the starting material used to encapsulate the substance

There are several methods for determining the yield of components of the reaction mixture in the preparation of microcapsules. According to literature data, the yield of the encapsulated substance in the microcapsules was determined by solvent extraction [14]. The microcapsules were torn by grinding in a porcelain mortar, using a mixture of acetone and ethanol

(or hexane instead of the extraction mixture) to extract the encapsulated substance. The resulting dry residue, which was the wall of the microcapsule, insoluble in the extraction solvents, was filtered, washed several times with a mixture of acetone and ethanol (or hexane instead of the extraction mixture) and dried at 70°C for 24 h in a vacuum oven. The percentage of the microencapsulated substance (the core content of the microcapsule) was calculated using the following Eq. (2):

$$E\%core = \frac{m_{sp} - m_{sh}}{m_{sp}}.100 \quad (2)$$

where: m_{sp} is the total weight of the sample and msh is the weight of the insoluble shell

Here we introduce a new, fast and simple method to analyse the encapsulation efficiency by the yield measurement of the encapsulated substance. It is based on a weight analysis by measuring the mass of the starting material to be encapsulated and the mass of the non - encapsulated substance after the encapsulation process. The difference between the masses of the starting material and the non - encapsulated substance gives the mass of the encapsulated compound. The ratio between the weight of the encapsulated substance and the weight of the starting material intended for encapsulation, multiplied by 100, gives a percentage yield of the encapsulated substance, named encapsulation efficiency (EE%, Eq. (3)):

$$EE\% = \frac{m_a - m_b}{m_a}.100 \quad (3)$$

where: m_a is the total weight of the substance to be encapsulated, m_b is the weight of the non-encapsulated substance.

The resin efficiency (%) obtained from the ratio between the weight of the polymer resin in the product (forming the capsule shell) and the initial total weight of the pre-polymer material (resin) in the solution multiplied by 100 was calculated using the following Eq. (4):

$$RE\% = \frac{m_{Rprod}}{m_{Rsol}}.100 \quad (4)$$

where: RE is the resin efficiency; m_{Rprod} is the weight of resin in product (microcapsule wall); $m_{Rsol.}$ - the initial weight of resin in solution (mono methylol urea).

The encapsulation factor obtained based on the ratio between the total weight of microcapsules on the surface of the sample reaction mixture and the total weight of microparticles at the bottom of the sample reaction mixture was introduced by Bayryamov and was calculated using Eq. (5):

$$EF = \frac{m_{mcs}}{m_{mps}} \quad (5)$$

where: EF is the encapsulation factor; m_{mcs} e is the total weight of microcapsules on the surface of the sample reaction mixture; m_{mps} is the total weight of microparticles at the bottom of the sample reaction mixture.

Particle size analysis

The average diameter, size distribution and standard deviation were determined from at least 150 measurements. The average diameter was calculated as arithmetic mean value of the particle size range automatically measured by the laser diffraction apparatus.

Standard deviation was calculated using the following Eq. (6):

$$s = \sqrt{\frac{\sum_{i-1}^{n}(x_i - \bar{x})^2}{(n-1)}} \quad (6)$$

where x_i is the i measurement of the determining element; x - mean value from n measurements; n - number of measurements

RESULTS AND DISCUSSION

Effect of stirring speed in the first sub-step (stage A) of the emulsification step on the characteristics of the obtained rose oil microcapsules

The process of microencapsulation of the rose oil was carried out at different stirring speeds of the reaction mixture (500, 750, 1000, 1250, 1500 and 2000 rpm). As can be seen from the data given below (Tables 1 and 2, Figs. 2, 3, 5 and 6), the stirring speed during the first and second sub-steps (stages A and B) of the emulsification step has a similar effect on the characteristics of the obtained microcapsules. Increasing this speed leads to an improvement in these

Table 1. Effect of stirring speed during the first sub - step (stage A) of the emulsification step on the characteristics of the obtained rose oil microcapsules.

№	Stirring speed, rpm	Yield, %	EE, %	$E\%_{core}$	RE, %	EF	Size, μm
1	500	37.9	58.3	64.8	32.8	0.68	120 - 80
2	750	40.6	63.3	65.2	36.9	0.75	80 - 60
3	1000	47.5	70.5	44.6	43.3	0.96	45 - 35
4	1250	54.2	78.2	40.7	50.4	1.25	30 - 20
5	1500	63.5	82.1	38.4	59.2	1.84	25 - 15
6	2000	63.4	81.5	38.2	59.7	1.88	20 - 15

Other conditions: 3.5 h at temperature: 70°C; surfactant concentration (SDS): 3 % (w/w).

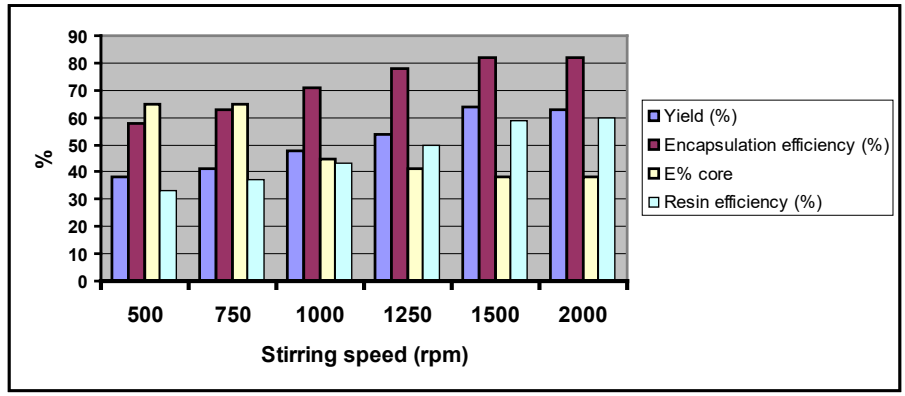

Fig. 2. Effect of stirring speed during the first sub - step (stage A) of the emulsification step on the characteristics of the obtained rose oil microcapsules.

characteristics, especially in terms of capsule size. The higher this speed, the smaller the average value of the diameter of the capsules. The smallest sizes are the capsules obtained at a stirring speed of 1500 and 2000 rpm, and between these two values of the stirring speeds, the differences between the sizes of the capsules are insignificant, and in many cases, they are absent (Tables 1 and 2, Figs. 3, 4 and 6.) This suggests the existence of a limit in the dependence of the size of the capsules on the stirring speed during the first and second sub-steps (stages A and B) of the emulsification step. Speed of 2000 rpm appears as a restriction in relation to the diameter of the microcapsules (20 - 15 μm), and finally, the other properties should be highlighted: yield (%), encapsulation efficiency (%) and content of the encapsulated substance (E% core). As mentioned, since no significant differences are observed in the parameters of the obtained microcapsules between the stirring speeds of 1500 and 2000 rpm, the authors prefer the speed of 1500 rpm, because of the futility of applying the higher speed.

As can be seen from the data in Table 1 and Fig. 2, an inverse relationship between the yield (%) and the encapsulation efficiency (%) is observed in relation to the content of the encapsulated substance (E% core). With the increase in the stirring speed of the reaction mixture, there is an increase in the values of the first two characteristics and a decrease in the value of E% core. This indirectly indicates that the quality of the microcapsule wall as well as its thickness increases, which is directly exposed by the results given in Table 1 and Fig. 2. It can be seen from them that as the stirring speed increases, the resin efficiency (RE, %) of the obtained microcapsules also increases.

According to the encapsulation factor giving the ratio of $m_{mcs}/m_{mps.}$ i.e. between the total weight

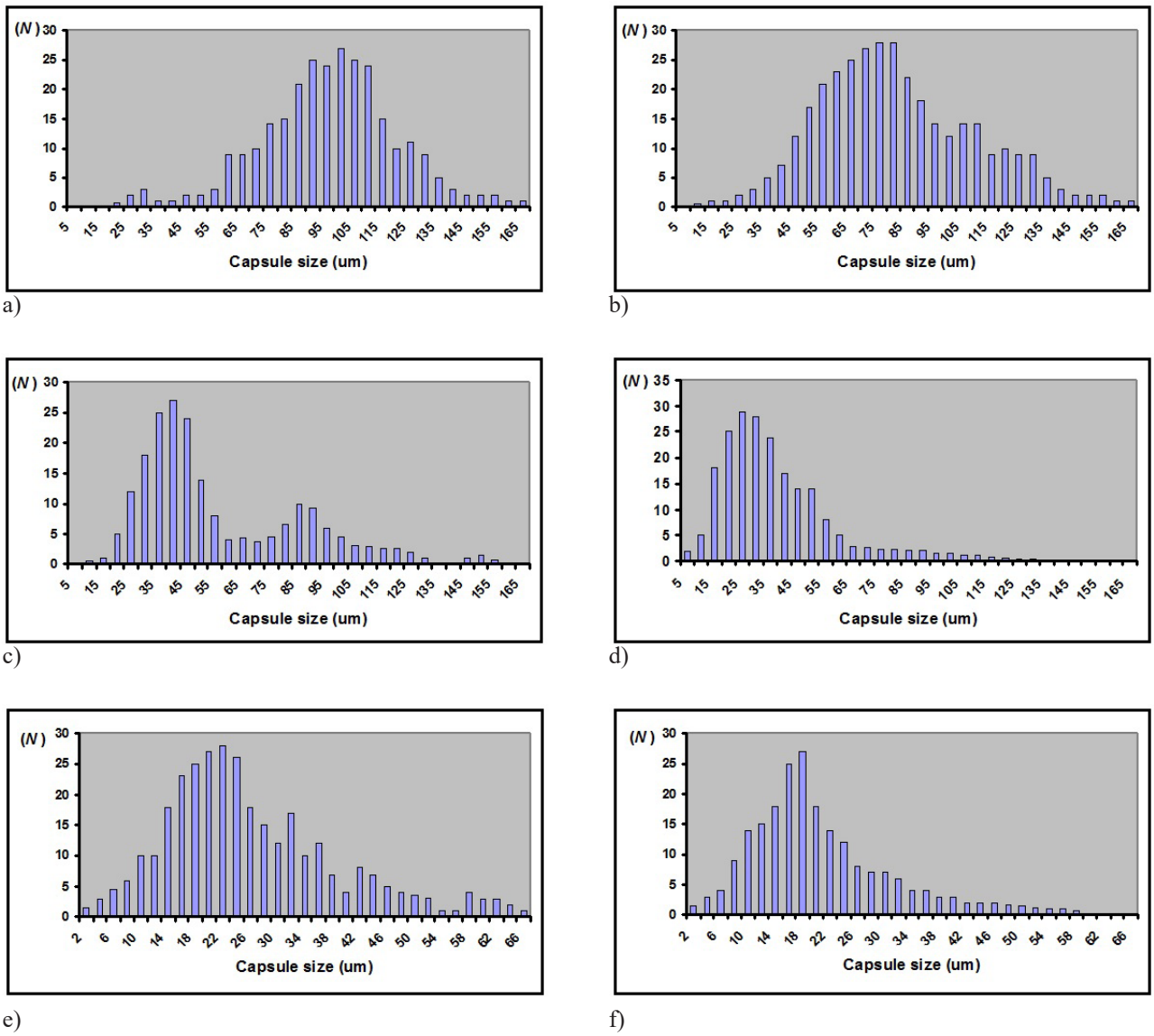

Fig. 3. Influence of the stirring speed during the first sub - step (stage A) of the emulsification step on the size of the obtained microcapsules of rose oil, represented by the average value of the diameter, in μm, (a) 500 rpm; (b) 750 rpm; (c) 1000 rpm; (d) 1250 rpm; (e) 1500 rpm; (f) 2000 rpm.

of microcapsules on the surface of the sample reaction mixture and the total weight of the polymer microparticles at the bottom of the sample reaction mixture, it is also directly related to the yield (%) of the microcapsules. At this characteristic, as shown by the data in Table 1, an increase in values was also observed as the stirring speed of the reaction mixture increased, indicating that most of the polymer particles served to microencapsulate the target substance. As mentioned above, due to the lower density of rose oil compared to water, giving a correspondingly lower density to the microcapsules, they float to the surface of the sample, unlike the polymer microparticles, which due to their higher density compared to the water, remain at the bottom of the reaction mixture.

Effect of stirring speed in the second sub - step (stage B) of the emulsification step on the characteristics of the obtained rose oil microcapsules

The high stirring speed of the reaction mixture during the first sub - step (stage A) of the emulsification step has a positive effect on the microencapsulation

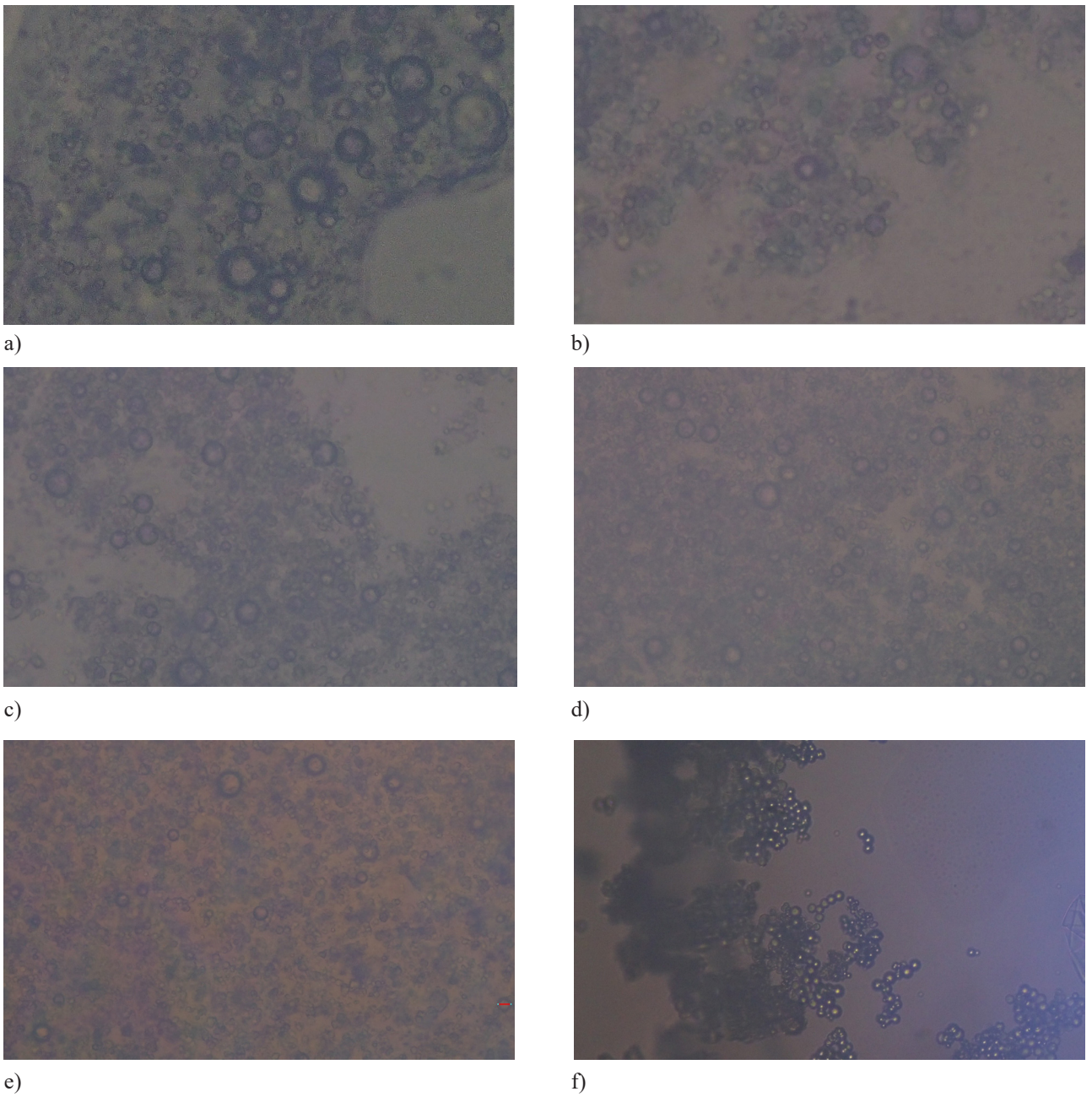

Fig. 4. Photographs of the rose oil microcapsules taken at different stirring speeds during the first sub - step (stage A) of the emulsification step: (a) 500 rpm, (b) 750 rpm, (c) 1000 rpm, (d) 1250 rpm, (e) 1500 rpm and (f) 2000 rpm.

process, expressed by relevant characteristics such as yield (%), encapsulation efficiency (EE, %), content of the encapsulated substance (E% core), size of the capsules obtained, resin efficiency (RE, %) and encapsulation factor (EF). Likewise, following the microencapsulation process of rose oil through the second sub - step (stage B) of the emulsification step in order to establish the dependence of the process characteristics and the product obtained on the stirring speed, the process was carried out using the same stirring speeds of the reaction mixture (500, 750, 1000, 1250, 1500 and 2000 rpm). As the data shown (Table 2, Fig. 5 and Fig. 6), similar dependencies were also observed during the second sub - step (stage B) of the emulsification step, i.e. at lower speeds, the microencapsulation process was not the most efficient,

which also affected the relevant characteristics. As the stirring speed increased during this sub - step of the emulsification step, the size of the capsules decreased, i.e. the speed was reflected on this feature (the size of the capsules is directly related to their quality). Furthermore, higher stirring speeds of the reaction mixture prevented agglomeration (clumping) of the microdroplets initially obtained in the stage A of the

Table 2. Effect of stirring speed during the second sub - step (stage B) of the emulsification step on the characteristics of the obtained rose oil microcapsules.

№	Stirring speed, rpm	Yield, %	EE, %	$E\%_{core}$	RE, %	EF	Size, μm
1	500	41.4	61.8	68.3	36.7	0.77	100 - 90
2	750	44.5	64.4	68.7	40.2	0.83	80 - 65
3	1000	51.1	74.1	48.2	48.0	1.15	40 - 30
4	1250	57.7	81.7	44.1	53.4	1.76	30 - 20
5	1500	63.5	82.1	38.4	59.6	1.87	25 - 15
6	2000	63.9	84.9	38.2	58.0	1.95	20 - 15

Other conditions: 2.5 h at a temperature of 45°C; surfactant concentration (SDS): 3 % (w/w).

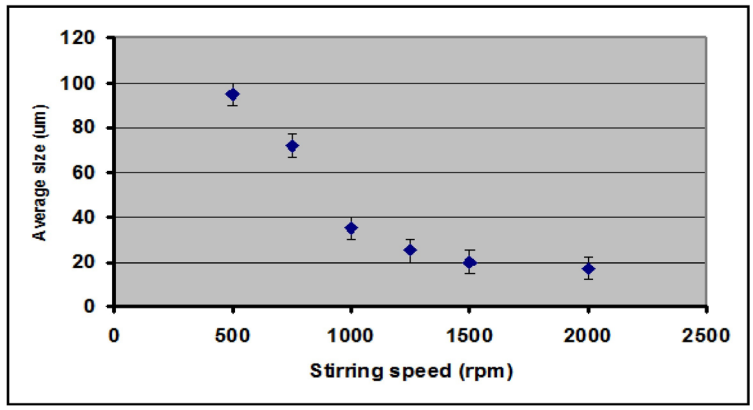

Fig. 5. Effect of stirring speed during the second sub - step (stage B) of the emulsification step on the characteristics of the obtained rose oil microcapsules.

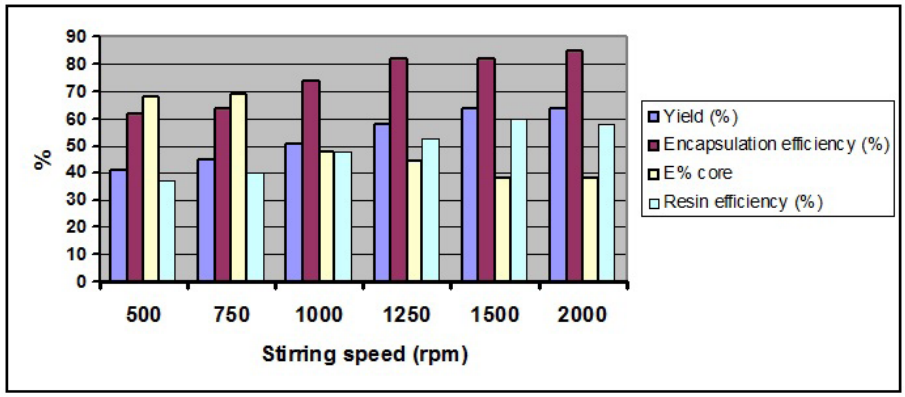

Fig. 6. Effect of stirring speed during the second sub - step (stage B) of the emulsification step on the size of the obtained microcapsules of rose oil, represented by the average value of the diameter, in μm.

emulsification step.

For example, at a speed of 500 rpm the size of the capsules was 100 - 90 μm (Table 2, Fig. 6). As the stirring speed increased, the size of the capsules decreased and at a speed of 1500 rpm, the size of the capsules reached 25 - 15 μm (Table 2, Fig. 6). Applying a stirring speed of 2000 rpm, the size of the capsules decreased slightly, for example to 20 - 15 μm (Table 2, Fig. 6). It is important to note that the increasing in stirring speed from 1250 rpm up also had no significant effect, as at 1250 rpm, the size of the capsules varied from 30 - 20 μm (Table 2, Fig. 6). For this reason, a speed of 1250 rpm can also be used in microencapsulation.

The other characteristics also improved with increasing stirring speed during the second sub - step of the emulsification step, with the yield (%) and encapsulation efficiency (EE, %) increasing, while the content of the encapsulated substance (E% core), which moved inversely compared to the first two characteristics, decreased. As for the resin efficiency (RE, %) and the encapsulation factor (EF), they also rose with increasing stirring speed (Table 2, Fig. 5).

Due to what has been said so far, it is concluded that it is necessary in the stage B of the emulsification step to maintain a high stirring speed during the adsorption process of the pre - polymer on the surface of the initially obtained microdroplets to avoid agglomeration and sticking of the microdroplets and increasing their size. We know that the size of the micro-droplets obtained during the emulsification step determines the size of the obtained microcapsules. In addition, other parameters such as yield (%), encapsulation efficiency (EE, %), encapsulated substance content (E% core), resin efficiency (RE, %) and the encapsulation factor (EF) are also affected from the stirring speed in the second sub - step.

CONCLUSIONS

This article represents the preparation of rose oil microcapsules by *in situ* polymerization of urea - formaldehyde pre - polymer to urea - formaldehyde polymer forming the wall of the microcapsules.

The authors pay attention to the influence of the main factors on the encapsulation process and prove their importance, thus it can be controlled with the aim of creating capsules with desired yields and qualities. Thus, a successful design of the capsules could be realized, both in terms of their size and in terms of the type, thickness and quality of the shell that builds them.

Specifically, in this paper, the influence of the stirring speed in the emulsification step, on the efficiency of the microencapsulation process and the quality of the obtained microcapsules was investigated. The effect of stirring speed was studied by examining the various characteristics such as yield (%), encapsulation efficiency (EE, %), E% core, resin efficiency (RE, %), encapsulation factor (EF) and microcapsules size, presented by the average diameter value of the microcapsules. From the data presented, during both sub - steps (stages A and B) of the emulsification step, the increase in stirring speed up to 1500 rpm leads to an increase in the yield, and a further increase in the stirring speed has no significant effect on the yield of the obtained microcapsules. The dependence of encapsulation efficiency (EE, %) and resin efficiency (RE, %) on stirring speed is also analogous.

As can be seen mainly from the content of the encapsulated substance (E% core), the stirring speed at the emulsification step has the significant influence on its content. As stirring speed increases (from 500 to 1500 rpm), E% core decreases, indicating a denser and better-quality capsule wall. Since E% core represents the percentage ratio of the mass of the encapsulated substance to the mass of the capsule, this means that reducing the value of this ratio gives information about the quality of the shell obtained, i.e. by changing these parameters to obtain the value of this ratio in descending order, it becomes denser. When the stirring speed increases above 1500 rpm the E% core does not change visibly, and the decrease in the value of the content of the encapsulated substance is insignificant.

An increase in the stirring speed also positively affects the size of the microcapsules, and the dependence of the average diameter of the microcapsules on the stirring speed, like E% core, also has an inversely proportional characteristic. As the stirring speed increases, the size of the capsules decreases. The size of the substance microdroplets obtained in the emulsification step determines the size of the microcapsules. Since the authors point to the second step as the most important, since then microdroplets are formed on the surface of which the pre-polymer

is adsorbed, therefore research is focused on this step of the process. Due to their specificity, it is necessary to carefully refine the conditions in the emulsification step, which is why the authors divide it into two sub - steps: Stage A. Microdroplet formation; Stage B. Pre - polymeric molecular adsorption on the surface of the resulting microdroplets. The authors believe that the first sub - step (stage A) of the emulsification step is one of the most important, because then the microdroplets are formed. At the second sub - step of the emulsification step the pre - polymer molecules are adsorbed on the surface of the obtained microdroplets, which is also one of the most important.

The efficiency of the microencapsulation process is also determined by the undesired lateral process of formation of polymeric microparticles (without packaged substance), due to that the pre - polymer and polymer particles are desorbed from the surface of the microdroplets during the emulsification (II) step and the polymerization (III) step of shell formation of the microcapsule. As can be seen from the data, during both sub - steps (stages A and B) of the emulsification step, increasing the speed has a positive effect on the encapsulation factor (EF). As this speed increases and through both stages of the emulsification step, due to the reduction in the size of the microdroplets, their total surface area increases, resulting in a greater amount of adsorbed pre - polymer particles on the surface of these microdroplets. The formation of polymeric microparticles without packaged product (microencapsulated substance) is probably because during the emulsification step and microencapsulation step, at a higher temperature, a large part of the pre - polymeric particles are desorbed from the surface of the microdroplets. Therefore, this step is of particular importance that also depends on time and temperature. A study of the effect of the temperature and time on the emulsification step (stage A and stage B) is forthcoming, which will be discussed in another article.

Acknowledgements

This research was funded by Research Science Fund of University of Ruse (Project 2024-AIF-02)

***Authors' contributions**: All experimental results, including pre-polymer synthesis, microcapsule preparation, weight analysis, particle size analysis, and IR analysis, were performed by the first author: S.G.B. The microscopic analysis performed by a reflective optical metallographic microscope Nikon, was fulfilled by the second author: M.P.N..*

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