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PRODUCTION OF ESSENTIAL ORANGE OIL MICROCAPSULES: COMPARISON OF THE USE OF SURFACTANTS CETILTRIMETILAMONOUS BROMIDE AND POLYSORBATE 20 BY ELECTRONIC SCAN MICROSCOPY

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Abstract: *Commercial applications of microcapsules began to appear in the textile industry in the late 1990s increasing investments in research to develop functional tissues, with a special focus on value aggregation, coating them with various active substances for the development of innovative products and according to fashion. Microcapsules have been presented as an alternative with regard to the encapsulation of essential oils since it is one of the most effective methods to achieve the goal of controlled release. The orange essential oil has biocidal properties and has been used microencapsulated as an ecological botanical insecticide. The characteristics of microcapsules containing aromatic oils, such as morphology and particle size distribution, depend on the preparation conditions such as the type of emulsifier used and the viscosity of the core material. Thus, for the microcapsules to be effectively used for the development of innovative products in the textile industry, studies on their formulation and characterization are necessary. This article proposes to compare the use of cetyltrimethylammonium bromide and polysorbate surfactants by means of their morphology, by scanning electron microscopy analysis on the formulation of microcapsules whit melamine formaldehyde shell with core of orange essential oil (citrus sinensis) combined with a non-volatile oil Medium Chain Triglycerides produced by interfacial polymerization method. At the end, the microcapsules were analyzed by microcoscopies and the differences in microcapsule morphologies were observed according to the kind of surfactant used.*

Key words: *Microcapsules. Essential Orange Oil. Electronic Scan Microscopy. Textile.*

1. INTRODUCTION

In the textile industry, commercial applications of microcapsules began to appear in the 1990s, more specifically in 1999, with the launch of the first fabric with microcapsules applied onto textile fibers [1]. This has contributed to a significant increase in investment in research to develop functional fabrics, developing textile materials with specific properties, adding value to the products by coating them with active substances, resulting in innovative and fashionable products [1] [2] [3] [4]. Also, worth mentioning are studies on the controlled release of fragrances for the development of textile products with long lasting fragrances, which is seen as a challenge for industries that use perfumes in their products, due to the great attraction of consumers [4] 5] [6] [7] [8]. Through microencapsulation it is possible to encapsulate a wide range of substances that impart different properties related to the nature of the product [4] [7], thus being able to combine core and shell materials, also giving visual, tactile and olfactory characteristics, but specifically in the sector Of textile finishes with fragrances has been an important commercial target and a challenge [3]. Therefore, the use of microcapsules has been presented as an alternative to achieve satisfactory results with regard to encapsulation of fragrances and active substances such as biocidal agents [2] [3] [9] [10] [11] [11] 12].

Orange essential oils have been used for medicinal purposes since the fourth century [13] [14]. The biocidal properties of citrus essential oils are well known and historically [11] [13] [14], as for example, antifungal [15] [16] and insecticides [16]. The orange essential oil (citrus sinensis) is a citric oil, and like all others of this nature, contains an extremely wide variety of compounds, being able to vary between 20 and 60, composed mainly of monoterpenes (limonene: 32-98%), , Sesquiterpene hydrocarbons, oxygen derivatives thereof, as well as aliphatic aldehydes, alcohols and esters [14] [18]. The antifungal capacity has been attributed mainly to the presence of limonene, linalool or citral [18]. As for insecticide properties, studies have shown that orange essential oil has its proven and proven insecticidal activities and is recognized as safe by the United States Food and Drug Administration (FDA) [17]. The orange essential oil also has strong activity against some insects and its components may be potential candidates for new botanic insecticides [17], because the oil, when microencapsulated can aid in the application, being an economically feasible, fast and effective method, besides leaving minimal residues [19]. Another advantage of the use of orange oil is that the crop of the genus Citrus, of which orange is a part, is the largest in the world (100 million cubic tons per year), oranges account for 60% of the total product volume [15]. After processing the oranges, approximately 45% are available as a sub-product and can create environmental problems, especially water pollution due to the presence of biomaterials such as essential oil, pectin and sugars [15]. In this case the use of the essential oil represents a decrease in the disposal of this material.

The use of microcapsules has been presented as an alternative with respect to the encapsulation of essential oils and other active substances. Using this microencapsulation technology, it is one of the most effective methods to achieve the goal of controlled release [5] [20]. To solve restrictions on the material to be encapsulated, the microencapsulation of aromatic oils plays important roles, for example: it captures the fragrance in its original form with minimal alteration and maximum retention; protects the fragrance from interaction with an uncontrolled environment and from premature release during storage; and completely releases the fragrance, when desired [1].

Therefore, special attention should be paid to the shell that envolve the core material, as this is the material that is susceptible to the outside and may increase the stability of the microcapsule. Preparing microcapsules of melamine formaldehyde (MF) resin for the aromatic oil shell material increases the durability of the perfume [8], in addition, the cured MF resin is non-toxic and can be used in both wet and dry environments [6]. Thus, MF resin has been extensively studied and applied in the elaboration of functional products, such as microcapsules containing essential oils, and due to its excellent performance, its fields of application are being expanded [6].

For the microemcapsulation of aromatic oils are used the chemical methods, among them, the interfacial polymerization [1] [6] [8] [21]. In interfacial polymerization many types of polymerization reactions can be induced to occur in interfaces resulting in microcapsules [8]. It is a widely used method that allows the manufacture of microcapsules from two immiscible liquids (oil / water emulsion) by forming thick polymer walls around liquid droplets [21].

The preparation conditions such as the type of emulsifier used and the viscosity of the core material directly influence the characteristics of the microcapsules containing aromatic oils such as morphology and particle size distribution [22], therefore, it is important to analyze the morphologies of the microcapsules. In this case, we can use the Scanning Electron Microscope (SEM), one of the most versatile instruments available for the observation and analysis of the microstructural characteristics of solid materials [23]. Among the main advantages of the SEM are to allow increases of 300.000 times or more, keeping the depth of field compatible with the observation of rough surface and provide information quickly on morphology [23]. Another advantage is the ease with which a particular region of interest in the sample can be chosen and located at low magnification [24]. Therefore, SEM is one of the most versatile instruments available for the observation and analysis of micro-structural characteristics of solid objects, this is mainly due to the high resolution that can be obtained when the samples are observed [23]. One of the most important characteristics of the SEM is the three-dimensional appearance given to the images of the samples, only possible because of their large depth of field, and the possibility of doing the small exam with a great depth of focus [23]. This ability to confer a three-dimensional appearance and the possibility of obtaining small increases with great depth of focus, which facilitates the morphological analysis of the microcapsules.

Thus, for the microcapsules to be effectively used for the development of innovative, functional and sensorial products in the textile industry, studies on its formulation and characterization are necessary, so this article proposes to compare the use of cetyltrimethylammonium bromide surfactants (CTAB) and polysorbate 20 (Tween 20) by means of its morphology, performed by scanning electron microscopy (SEM) analysis in the formulation of melamine formaldehyde (MF) shell microcapsules with orange essential oil nucleus (citrus sinensis) combined with a fixed oil medium-chain triglycerides (MCT) produced by interfacial polymerization method.

2. MATERIALS AND METHODS

Materials: Essential orange oil (*citrus sinensis*), surfactants CTAB and Tween 20, all was purchased from Sigma-Aldrich®.; MF; MCT was purchased from Delaware®. Preparation of microcapsules: Microcapsules containing essential orange oil combined with a MCT (1:1) and surfactants Tween 20 and CTAB with MF resin as shell material were synthesized by interfacial polymerization technology. To characterization of microcapsules: SEM FEI model Phenom (Fei, Oregon, USA).

The microcapsules were obtained by the interfacial polymerization method. To prepare the emulsion was placed in a beaker, deionized water with surfactant. The mixture was stirred on a mechanical stirrer (Fisatron 713D), after stirring the essential oil was added and brought to the ultrasound (Cole Parmer model CV33). The pH was adjusted to 4.5 using a solution of acetic acid. The emulsion was reserved. The prepolymer was prepared in another beaker containing deionized water and formaldehyde, after using a magnetic stirrer (TE-085) at a temperature of 70 ° C, while maintaining gentle agitation was added the melamine. The pH was adjusted to 8.5. The prepolymer was reserved.

For the preparation of the microcapsules the jacketed beaker containing the emulsion was connected to the thermostatic bath with a temperature of 70 ° C. This emulsion was subjected to a mechanical stirrer. During this stirring the prepolymer was slowly added to the emulsion. After addition of the prepolymer the mechanical stirrer timer was adjusted, also adjusting the pH to 9.0. After of shaking, the solution was placed in a centrifuge (Quimis, Tubes Centrifuge) at its maximum speed for phase separation. The microcapsules were filtered and washed with deionized water. After the microcapsules were taken to the desiccator (ARSEC). The obtained method was tested with different surfactants, CTAB and Tween 20 in proportion (1:1) with essential oil. At the end of the production, the microcapsules were analyzed by micrococopies and the differences in microcapsule morphologies were observed according to the kind of surfactant used.

3. RESULTS AND DISCUSSION

The conditions of preparation of the microcapsules, more specifically, the use of the two surfactants (CTAB and Tween 20) directly influenced the characteristics, according to the images obtained by SEM. In Figure 1, SEM images of the orange essential oil microcapsules with CTAB surfactant are ob- served. It is observed that the CTAB surfactant interacted well with the core material (orange essential oil), forming microcapsules of regular morphology, according to Figure A(C), that is, the formation of regular capsules, in addition, are evenly distributed in the sample, according to Figures 1(A) and 1 (B), indicating a satisfactory formation. In Figure 2, in SEM images of the orange essential oil microcapsules with the change of surfactant to Tween 20 and the same formulation of the previous production, it is observed that the surfactant Tween 20, unlike CTAB, did not interact well with the orange essential oil, forming irregular microcapsules, according to Figure 2(B), in addition, the microcapsules formed, according to Figure 2(C), present some pores, according to Figure 2(C), that can come from formation of foam in the emulsion. Unlike the previous sample, Figure 1, the microcapsules produced with Tween 20 surfactant, as in Figure 2(A), are not uniformly distributed in the sample, in addition to the formation of agglomerates of microcapsules, indicating an unsatisfactory formation.

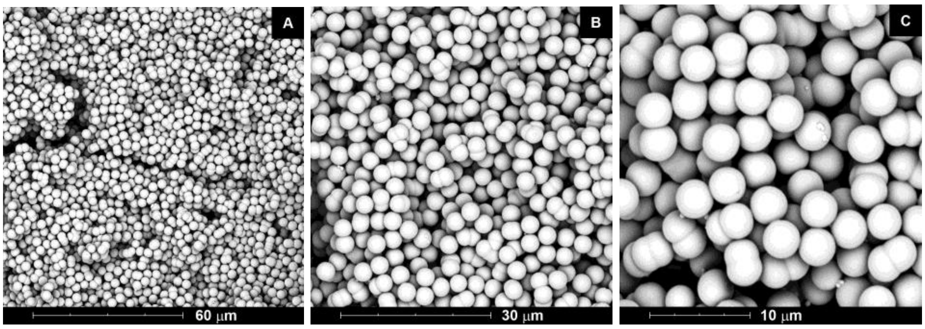

Fig. 1*: SEM of microcapsules with* surfactant CTAB, *(A) images with magnification 2000x, (B) images with magnification 4000x and (C) images with magnification 8000x.*

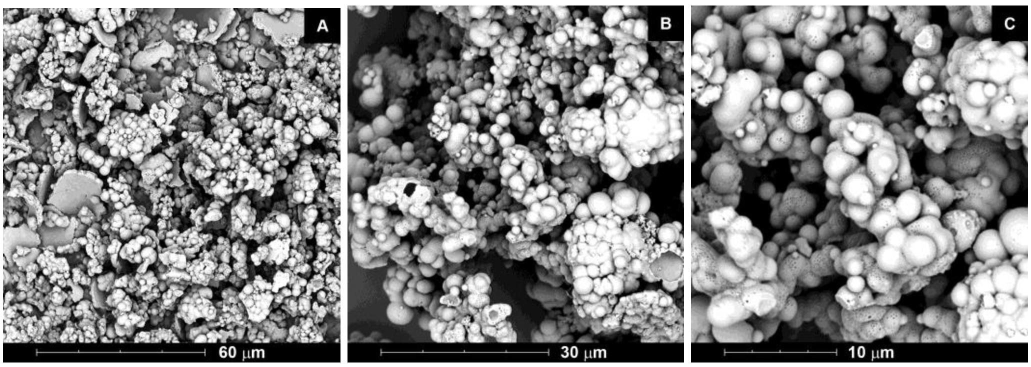

Fig. 2*: SEM of microcapsules with* surfactant Tween 20, *(A) images with magnification 2000x, (B) images with magnification 4000x and (C) images with magnification 8000x.*

3. CONCLUSIONS

At the end of the work by comparing the images obtained by SEM with different magnifications, it was possible to observe the differences in the morphologies of the microcapsules according to the type of surfactant used.

The use of SEM allowed us to understand the influence that the use of different surfactants produced on the morphological characteristics of the analyzed microcapsules, emphasizing the importance of the analysis of microcapsule morphologies.

By means of SEM, it is possible to obtain magnifications of 2000 times, 4000 times and 8000 times, conserving the depth of field of the samples and providing information on their morphology in different regions of interest, both in larger planes (2000 times) and In more detail (8000 times), with three-dimensional appearance and great depth of focus, which facilitated the morphological analysis of the microcapsules.

Through the analyzes the morphological differences of the microcapsules related to the surfactant were realized. The CTAB, according to the images obtained by the SEM, interacted well with the core material (orange essential oil), forming microcapsules of regular morphology and evenly distributed in the sample, indicating a satisfactory formation. After modification of the surfactant type for Tween 20, it was observed that the surfactant Tween 20, unlike CTAB, did not interact well with the orange essential oil, irregularly forming microcapsules, in addition to the formation of pores, were not uniformly distributed in the sample, forming agglomerates of microcapsules, indicating an unsatisfactory formation.

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