SAT-CR-P-2-CT(R)-15

CHARACTERIZATION TECHNIQUES FOR MICROCAPSULES IMMOBILIZED ON TEXTILES

Assoc. Prof. Maria Nikolova, PhD
Department of Material Science and Technology,
University of Ruse "Angel Kanchev", Bulgaria
E-mail: mpnikolova@uni-ruse.bg

Assist. Prof. Stanislav Bayryamov, PhD
Department of Repairing, Reliability, Mechanisms,
Machines, Logistic and Chemical Technologies,
University of Ruse "Angel Kanchev", Bulgaria
E-mail: sbayryamov@uni-ruse.bg

Abstract: *Microencapsulation of fragrances or other active substances for industrial application in textiles is vastly used for development of innovative textile products. The elaboration of such new products with addied-value properties can increase their competitiveness, durability, stability, permeability, fire-resistance, chemical protection, bactericidy, etc. To achieve the desired mechanical and physicochemical properties the textiles containing immobilized microcapsules should be properly characterized at laboratory and industrial scale. For that reason, the paper covers the basis and theory of immobilized microcapsule characterization methods and it could be used as refrence recource for material scientists, chemists and engineers to chose which techniques could be appropriate for particle characterization needs.*

Keywords: *Microcapsules, Morphology, Characterization methods, Release, Aroma*

INTRODUCTION

Microcapsules (MCs) are available with a wide range of industrial products. Microcapsules can be applied to textiles by spraying, coating, padding or immersing. By incorporation suitable binders, the microcapsules can be chemically applied to textiles which make them durable to washing or handling. The properties imparted to the fabric by encapsulation are lasting antimicrobial, antifungal, insect-repellent, cosmetic, medical (cell encapsulation, drug delivery, etc.), fire-retardants, photochromic, thermochromic or aroma textiles. In selecting active substances for encapsulation, it must be ensured that these substances are effective, well encapsulated, stored and immobilized, and follow a sustain release under controlled conditions. The objective of this work is to study the characterization techniques after production of microcapsules (MCs) at laboratory and/or industrial scale and final product characterization in terms of resistance to cleaning cycles, abrasion, combustion or antimicrobial activity.

EXPOSITION

Encapsulation and release of moieties

It is important to know the encapsulation efficiency in order to determine the amount of free substance and where the encapsulation yield improvement is necessary. The encapsulation yield of microcapsules could be determined from the mass of capsules (dried product) as a percentage of the total mass of the ingredients (raw materials) used. Similar calculation could be done after washing of immobilized MCs (Man, Y.C., Irwandi, J. & Abdullah, W.J.W., 1999). Alvim and Grosso (Alvim, I.D., & Grosso, C.R.F., 2010) proposed calculation the encapsulation efficiency (EE, %) by the ratio of encapsulated core weight and total core weight according to equation 1:

$$EE, \% = \frac{\text{encapsulated core weight}}{\text{total core weight}} . 100 \quad (1)$$

The encapsulated core weight was determined by the difference between the total core, as weighed initially, and the core weight that was lost throughout processing. The non-encapsulated core residues should be carefully removed with anhydrous ethanol from the homogenizer rod and baker.

Extraction through less polar organic solvents is commonly employed technique to measure free hydrophobic substances. For example, simple extraction by cyclohexane of the encapsulated oil by the polymer (of hydroxypropylmethylcellulose/sodium carboxymethylcellulose with various consentrations of sodium dodecylsulfate) is proposed by Sovili et al. When 1 g of microcapsules are dispersed in 100 ml of cyclohexane (left for 40 min on a magnetic stirrer) after filtering the samples, the amount of the released oil could be determined spectrophotometrically (Sovilj, V.J., et al., 2010). In another study, known amount of microcapsules of urea-formaldehyde were taken in 20 ml vial, crushed with glass rod and immersed with 15 ml solvent (toluene). After filtering and washing several times with solvent, the mixture with solid residue put on filter paper was dried at 70°C for 24 hours. The weight of the filter paper before and after extraction was used to calculate the core content by equation 2 (Ullah, H., Azizlia, K., Man, Z.B. & Ismail, M.B.C., 2016):

$$core\ content = \frac{W_{iC} - W_{fc}}{W_{fc}} . 100 \quad (2)$$

Where W_{ic} is the initial weight and W_{fc} is the weight of microcapsules after washing with toluene.

Similarly, ruptured with a pestle in a mortar microcapsules (of poly(urea-formaldehyde)) containing alkyd resin were mixed with acetone and ethanol - solvents used to extract and dissolve the core. The insoluble shell was filtered and thoroughly washed and dried at 70 °C for 24 h in a vacuum oven. The core content (E_{core}) was calculated by using equation 3 (Shahabudin, N., Yahya, R. & Neon Gan, S., 2016):

$$E_{corr} = \frac{W_S - W_m}{W_S} . 100 \quad (3)$$

Where W_S refers to the weight of the sample, and W_m is the weight of the insoluble shell.

By using similar methodology, the release profile of MCs could also be determined. For example, samples containing one and the same quantity of dried gelatin/gum Arabic/chitosan microcapsules (5 mg) were suspended in 95 ml of buffer (pH 6.4) and kept at 10 °C. At various time intervals (1, 5, 10 and 15 days) the oil was extracted (in ether) with a separating funnel. The total amount of encapsulated coriander oil is similarly extracted with petroleum ether. The cumulative amount of oil released can be determined by the equation 4 (Dima, C., Creţu, R., Alexe, P. & Dima, Ş., 2013):

$$Q\% = \left(1 - \frac{m_i}{m_o}\right) . 100 \quad (4)$$

Where m_i is the mass of oil released and m_o is the total mass of encapsulated coriander oil.

However, depending on the cross-linking chemistry, density, and shell thickness, certain microcapsules are too fragile to be analyzed by solvent extraction methods. Gas chromatography (GC) can be used to separate the components in MCs and to determine their relative amounts with high precision if these components could be vaporized without decomposition. The separation and analysis of volatile components is done by using NIST library search method. The method could compare the percentage of each component in the liquid phase and the percentage of each component in the gas phase of the fragrance released from the microcapsules. When

using headspace-GC, analysis of the internal phase of microcapsules could be done without direct sampling of the matrix. The original component concentration can be determined by calibration. The purpose of the analysis is to evaluate individual components and to relate the chromatographic profiles to odor or aroma characteristics. The mass of the encapsulated perfume is calculated using mass balance. For example, the yield of encapsulation could be calculated based on the equation 5 (Rodrigues, S.N., et al., 2009):

$$Encapsulation\ efficiency\ (\%) = \frac{m_{total} - m_{out}}{m_{total}} .100 \quad (5)$$

Where m_{total} is the amount of loaded perfume (g) and m_{out} is the amount of non-encapsulated perfume (g). The analysis could be combined with different number of dry washing or abrasion cycles. By coupling the gas chromatograph with mass spectrometer (GC-MS) complex mixtures of organic compounds can be separated, identified and quantified (Fig. 1). The method is capable of determining trace levels of organic moieties. For example, to analyze immobilized MCs, the textile could be cut into small pieces and enclosed into vials that are closed and placed into water bath at certain temperature and time (simulating washing). When the fibers were withdrawn and introduced into the heated chromatograph injector of GC-MS, the initial result (peak area) of the textile without washing (M_1) could be compared with that after washing or displacing several days (M_2). The loss ratio of fragrant component could be calculated using equation 6 (Hu, J., Xiao, Z., Zhou, R., MA, S., Wang, M. & Li, Z., 2011):

$$L = \frac{M_1 - M_2}{M_1} .100 \quad (6)$$

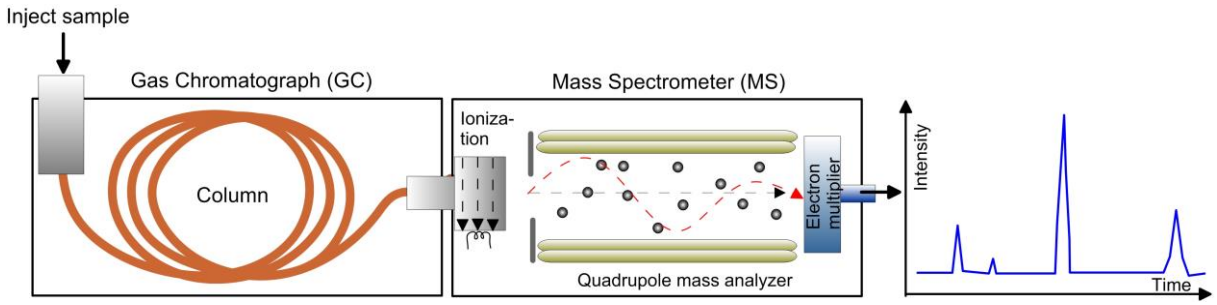

Fig. 1. Diagram of gas chromatograph with attached mass spectrometer

Except for gas chromatography, odor assessment can be performed by electronic nose analysis. It constitutes electronic sensing system capable to detect odors or flavours. The detection system consists of 18 non-specific semiconductor gas sensors that could be used for analysis of aromas released in the air from fabrics impregnated with MCs. Each sensor is sensitive to all volatile molecules but in a specific way. The sensors commonly used in electronic noses include metal oxide semiconductors, conducting polymers, polymer composites, etc. Electronic nose analysis could be used to evaluate the effect of washing cycles (in standard detergent (3% owf) at 40°C in automatic washing machine (according to ISO 6330-1984) on the aroma release of MC impregnated textiles (Hu, J., Xiao, Z., Zhou, R., MA, S., Wang, M. & Li, Z., 2011). Another way of fragrance evaluation of MC impregnated textiles is Lewis procedure. Before and after 10 washing cycles followed by air drying for 24 hours (according to ISO 105-C01:1989), textile specimens could be tested for the presence of fragrance using five judges. The fabric was placed on a flat hard board and scratched with fingernail on an area of 3 × 3 cm in size to break some of the capsules and immediately smelled. The results were recorded with "yes" (subdivided into strong, medium or weak fragrance) or "No" (Van Soest, J.G.J., 2007; Lewis, J., 2003).

Thermal, thermodynamic properties and air permeability

Thermodynamic analysis provides appropriate criteria for predicting the physical stability of MCs and intrinsic properties of encapsulated moieties and shell. Differential scanning calorimetry (DSC) is a thermoanalytic technique based on analysis of the difference in heat flow of a sample and reference when the former undergoes physical transformation such as phase transition. By scanning at different heating rates, the obtained curves indicate the crystallization points and their peak temperatures of degradation could be determined. The method analyzes the microcapsules' thermo-oxidative stability in nitrogen flow usually in the rage -60 up to +300 °C and could also be used to determine the encapsulation efficiency (Mayya, K.S., Bhattacharyya A., & Argillier, J.-F., 2003). Thermogravimetric analysis (TGA) is another thermal analysis which measures the change in the mass of the samples over time as the temperature increases. Thus, it can investigate the weight fraction of constituents in different composites. This thermal analysis in nitrogen atmosphere is held in non-isothermic or isothermic conditions while drying the microcapsules. Then the mass loss is calculated. In the obtained curve (temperature (°C) - mass loss (%)) of non-isothermal analysis, the mass loss is associated with decomposition of the shell, followed by evaporation of the organic solvent and decomposition of the liquid. Different microparticles with various encapsulated volumes or different polymer stability in solutions can be compared (Bolimowski, P.A., Kozera, R. & Boczkowska, A., 2018). Usually, TGA could not be used to determine the amount of shell and core accurately because of their overlapping temperature rages of thermal degradation.

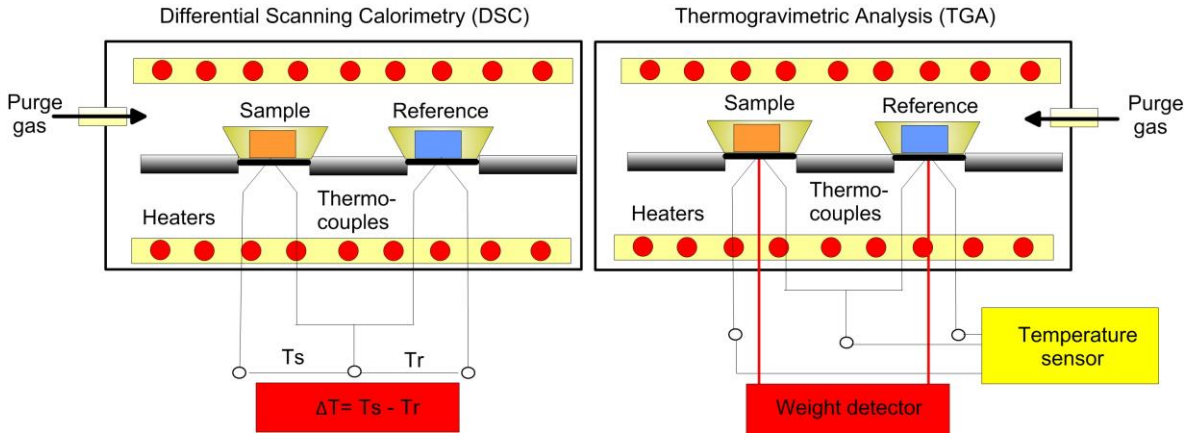

Fig. 2. Scematic drawing of main components of typical DSC (left) and TGA (right) furnace

Various fibers react differently to fire exposure. For impregnated textiles with flame retardant microcapsules, to ensure efficient and safe burner operation, combustion test could be held. A technique that studies the combustion performance of textiles is vertical burning test in a burning chamber according to the DIN 53906 standard. The glow time and burning time though the whole length of the samples are determined. The samples are classified as non-flame resistant, fire-retardant and flame-resistant. The combustion performance could be also studied by calculating limited oxygen index (LOI) in a limited oxygen index camber according to standard ASTM D 2863 (Golja, B., et al., 2014). The percentage of LOI should be at least 26 to consider the samples to be flame retardant.

The air permeability determines the rate of air flow passing perpendicularly through a known area under a prescribe air pressure. This is an important factor for the performance of different textile materials used as filters, air bags, clothing, parachutes, sails, tentage, etc. The air permeability could change with the amount of impregnated MCs compared to pristine textiles. The test gives the rate of air flow through a material under a differential pressure between both faces of the fabric. It expresses the quality of air in cm^3 passing per second through one cm^2 (ASTM - D737. Standard Test Methods for Air Permeability of Textile Fabrics, 2012; Jeyaraj, J.M., Arumgam, M. & Kulandaiappan, V., 2016).

Antimicrobial properties

Common problems in health care institutions are related to transmission and spreading of microbial contamination of textiles causing a potential risk for serious infections, cross-infections, and, subsequently, extra costs to healthcare services. Therefore, it is of prime importance to protect medical textiles such as gowns, masks, caps, hospital linen, etc., by meeting the demand for antimicrobial protection. Moreover, antimicrobial functionalization could add therapeutic value to textiles making them suitable for would healing application. To impart antimicrobial properties and develop biomedical products, MC functionalized textile materials with different capabilities of action are developed. The way of action could be by contact (for permanently attached substances or so called "bound antimicrobials") and by diffusion (for slowly released agents with controlled-release mechanism or so-called "leaching antimicrobials"). The antimicrobial agents can be biocidal (causing death of microoorganisms) and biostatic (inhibiting microorganism growth) and the mode of action strongly depends upon the concentration of the immobilized bioactive moieties such as triclosan, polyhexamethylen biguanide, N-halamine compounds, silver and silver conpounds, natural compounds, chitosan, etc. The commonly applied standard test methods for evaluation of impregnated antimicrobial fibrous surfaces include:

-Qualitative tests - ISO 20645-2004, and parallel streak method AATCC TM147 - both are based on the agar diffusion method where the agar surface is covered by a strip of the tested textile that is previously inoculated with the test culture. After incubation for 24 or 48 hours, the bacterial growth is examined underneath and around the edges (zone of inhibition) of the sample. For covalently bonded agents that do not diffuse into the agar, a zone of inhibition is not observed. The zone of inhibition becomes apparent when the agent diffuses into the agar indicating certain release rate (Ristić, T., et al., 2011). The methods are quick, inexpensive and well-defined but the different diffusion rates through agar depending on antimicrobial agent, weight and texture of the fabric hinder the efficient comparison of different agents. Colorimetric MTT assays can also be used for measuring bactericidal activity of functionalized textiles (Grethe, T., et al., 2015). AATCC TM30, 2017, qualitative test is usually applied against filamentous fungi where textile samples are placed on potato dextrose agar and inoculated with *A. niger*. The fungal growth and zone of inhibition are measured after 7 days of incubation (part III). Different procedure using humidity jar and treated, untreated and dry strip of nutrient-immersed textile sprayed with spore suspension calculates the percentage of coverage by fungal growth after incubation (part IV).

-Quantitative tests - ASTM E 2149 Shake flask method determines the antimicrobial activity of immobilezed agents under dynamic contact conditions. The sample is immersed in an inoculum (bacterial concentration around 10^5 mL^{-1}) in an agitated flask for one hour. After that, the aliquot of the buffer is plated on the agar, incubated overnight and counted for the number of colonies versus untreated control. It is appropriate for non-leaching antimicrobials and ensures contact of the inoculum with the treated surface, sensitive and realistic results. However, there is no correlation between this method and other quantitative tests and the tests conditions do not replicate real-life use. Other quantitative tests on similar principle are ISO 20743, JIS 1902 (both use low in nutrients broth to reduce neutralization of antimicrobials with proteins), AATCC TM100 (that uses rich nutrient broth) (Ristić, T., et al., 2011). They are applicable to all textile products and allow comparision among various antimicrobial agents and different treatments.

The accuracy and reproducibility of all methods depends on the standardized conditions (that are frequently modified and inconsistent amongst laboratories) and efficiencies of the microbial extractions from the textile samples.

-Real-time count methods such as polymerase chain reaction (PCR) and/or immunoassays. By using PCR, DNA sequences are exponentially amplified and, therefore, both PCR and bacterial growth are very similar (Fig. 3a). When the number of DNA copies obtained when bacteria were grown with the presence of antimicrobial agents is compared with the copies without inhibition, the inhibition over the growth kinetic can be measured. Immunoassays are

antibody-based reactions with high sensitivity that can be used for detection of bacterial markers and bacterial growth. The reaction produces detectable signal such as color change that could be analyzed optically (Fig. 3 b). Both methods are considered fast and highly accurate although expensive.

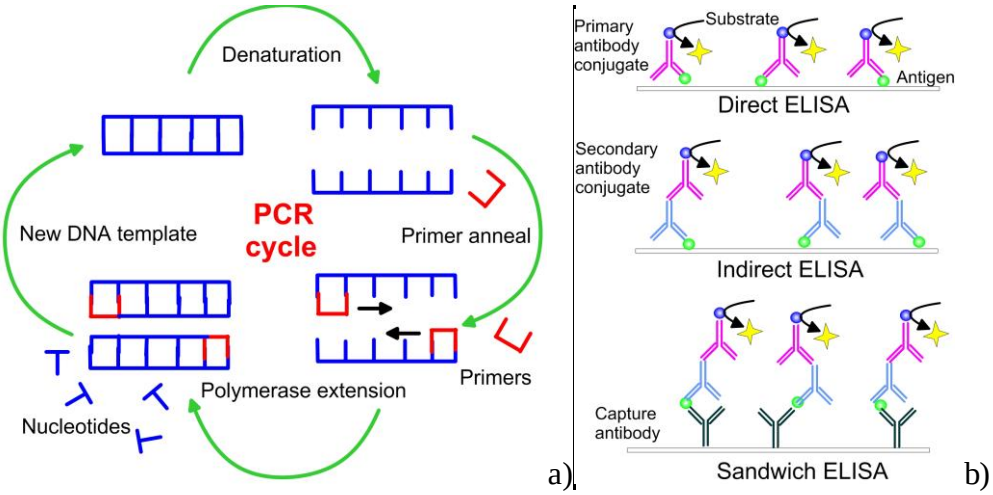

Fig. 3. Scematic diagrams showing: a) principle of polymerase chain reaction (PCR); b) concepts in Enzyme-Linked Immunosorbent Assay (ELISA)

CONCLUSION

Various characterization techniques have been used for examination of the encapsulation efficiency, effectiveness of immobilization, and properties of MC impregnated textiles depending on the intended application. In order to ensure the efficiency of functionalization of textiles, appropriate method with successful criteria for characterization should be chosen. Knowledge of the components is important for chosing methods for testing the thermal stability of wall material/core composites and their controlled-release behavior. Antimicrobial efficiency of medical textiles offers new opportunities for developing products with large future applications. However, the toxicity, allergenicity, and degradability of the included chemicals into MCs within the environment should also be taken into account.

Acknowledgments: This research was funded by Research Science Fund of University of Ruse (Project 2018-RU-08, 4048)

REFERENCES

AATCC 147, Assessment of Textile Materials: Parallel Streak Method, https://members.aatcc.org/store/tm147/554/

AATCC TM30-2017, Antifungal Activity, Assessment on Textile Materials: Mildew and Rot Resistance of Textile Materials, https://members.aatcc.org/store/tm30/491/

Alvim, I.D., & Grosso, C.R.F., (2010). Microparticles obtained by complex coacervation: influence of the type of reticulation and the drying process on the release of the core material, *Ciênc. Tecnol. Aliment. Campinas*, 30(4), 1069-1076. http://dx.doi.org/10.1590/S0101-20612010000400036

ASTM E 2149 Standard Test Method for Determining the Antimicrobial Activity of Antimicrobial Agents Under Dynamic Contact Conditions, https://www.astm.org/Standards/E2149.htm, DOI: 10.1520/E2149-13A

Bolimowski, P.A., Kozera, R., Boczkowska, A., (2018). Poly(urea-formaldehyde) microcapsules - synthesis and influence of stirring speed on capsules size, *Polimery*, 63(5) 339-346. DOI: dx.doi.org/10.14314/polimery.2018.5.2

DIN 53906: 1974-02, Testing of textiles - Determination of the burning behaviour. Vertically method; Ignition by application of + ame to base of specimen. St. Gallen: SNV (1971) https://www.beuth.de/de/norm/din-53906/11617607

Dima, C., Creţu, R., Alexe, P., Dima, Ş., (2013). Microencapsulation of coriander oil using complex coacervation method, *St. Cerc. St. CICBIA*, 14(3), 155 - 162, ISSN 1582-540X

Golja, B., Sumiga, B., Boh, B., Medved, J., Pusik, T., Tavcer, P.F., (2014). Application of flame retardant microcapsules to polyester and cotton fabrics, *Materials and technology* 48 105-111. ISSN 1580-2949

Grethe, T., Haase, H., Natarajan, H., Limandoko, N., Mahltig, B. (2015) Coating process for antimicrobial textile surfaces derived from a polyester dyeing process. *J Coatings Technol Res. Springer US*, 12, 1133-1141. https://doi.org/10.1007/s11998-015-9709-9

Hu, J., Xiao, Z., Zhou, R., MA, S., Wang, M., Li, Z., (2011). Properties of Aroma Sustained-release Cotton Fabric with Rose Fragrance Nanocapsule, *Product Engineering and chemical technology, Chinese Journal of Chemical Engineering*, 19(3) 523-528. https://doi.org/10.1016/S1004-9541(11)60016-5

Jeyaraj, J.M., Arumgam, M., Kulandaiappan, V. (2016). A Study on Silk and Its Mixed Fabric for Functional Properties, *Walailak J Sci & Tech*, 13(11), 913-922

ISO 6330-1984 T Textiles, Domestic washing and drying procedures for textile testing, https://www.iso.org/standard/12626.html

ISO 105-C01:1989 Textiles, Tests for colour fastness - Part C01, Colour fastness to washing: Test 1, https://www.iso.org/standard/3801.html

ISO 20645:2004 Textile fabrics, Determination of antibacterial activity - Agar diffusion Plate test, https://www.iso.org/standard/35499.html

Lewis, J. (2003) *Effect of curing method on the durability of microencapsulated fragrant finishes:* master's thesis. Institute of Textile Technology, Manchester, England

Man, Y.C., Irwandi, J., Abdullah, W.J.W., (1999). Effect of different types of maltodextrin and drying methods on physico-chemical and sensory properties of encapsulated durian flavour. *Journal of the Science of Food and Agriculture*, 79, 1075-1080. https://doi.org/10.1002/(SICI)1097-0010(199906)79:8<1075::AID-JSFA329>3.0.CO;2-Q

Mayya, K.S., Bhattacharyya A., & Argillier, J.-F. (2003). Micro-encapsulation by complex coacervation: influence of surfactant, *Polym Int*, 52, 644-647. DOI: 10.1002/pi.1125

Ristić, T., Zemljič, L.F., Novak, M., Kunčič, M.K., Sonjak, S., Cimerman, N.G., Strnad, S. (2011). Antimicrobial efficiency of functionalized cellulose fibres as potential medical textiles, Science against microbial pathogens: communicating current research and technological advances A. Méndez-Vilas (Ed.), Formatex

Rodrigues, S.N., Martins, I.M., Fernandes, I.P., Gomes, P.B., Mata, V.G., Barreiro, M.F., Rodrigues, A.E., (2009). Scentfashion®: Microencapsulated perfumes for textile application, *Chemical Engineering Journal* 149, 463-472. doi:10.1016/j.cej.2009.02.021

Sovilj, V.J., Milanović, J.L., Katona, J.M., Petrivić, L.B. (2010). Preparation of microcapsules containing different contents of different kinds of oils by a segregative coacervation method and their characterization, *J. Serb. Chem. Soc.* 75(5), 615-627. DOI: 10.2298/JSC091008042S

Shahabudin, N., Yahya, R., Neon Gan, S., (2016). Microcapsules of poly(urea-formaldehyde) (PUF) containing alkyd from palm oil, *Materials Today: Proceedings* 3, S88 - 95. DOI: 10.1016/j.proeng.2016.06.519

Ullah, H., Azizlia, K., Man, Z.B., Ismail, M.B.C., (2016). Synthesis and Characterization of Urea-formaldehyde, Microcapsules Containing Functionalized Polydimethylsiloxanes, *Procedia Engineering*, 148, 168 - 175. DOI: 10.1016/j.proeng.2016.06.519

Van Soest, J.G.J., (2007). *Flavours and fragrances - chemistry, bioprocessing and sustainability*. Berger, Berlin; Heidelberg New York: Springer, p. 439 DOI 10.1007/978-3-540-49339-6