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Preparation and Characterization of Tung Oil Loaded Melamine Formaldehyde Microcapsules

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ABSTRACT

In this study microcapsules were prepared by in-situ polymerization route with melamine formaldehyde as a shell material and tung oil as core material. Melamine formaldehyde (MF), a thermosetting polymer, is one of the most widely used monomers in microencapsulation due to its superior mechanical strength and thermal stability. Tung oil contains unsaturated double bonds that can be oxidized to form a film in air. Tung oil is fast drying and biodegradable, besides it is low cost and does not pollute the environment. Most importantly, tung oil is a versatile substance in industry. Therefore, tung oil is a good choice as core material. The chemical structure of microcapsules were characterized by Fourier Transform Infrared (FTIR) spectroscopy. The surface morphology and particle size and distribution were evaluated by Scanning Electron Microscopy (SEM). The thermal behavior of microcapsules and tung oil were studied by thermogravimetric analysis (TGA). The results showed that the spherical microcapsules (particle size of mostly 4-5 µm) were produced with a filling content of 15.64 wt.%, and a yield of 49.78 wt.%. The microcapsules exhibit a good thermal stability.

Keywords: Microencapsulation, Tung oil, Melamine formaldehyde, In-situ polymerization.

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Introduction

Microencapsulation is a method in which the solid, liquid or gaseous active core material is covered with the coating material in micro sizes [1]. In recent years, the microencapsulation technique has been used for a wide variety of purposes. It is mainly used to protect the core material from adverse environmental factors (pH, temperature, humidity and, microorganisms) and extend the shelf life [2,3]. In some cases, it can be used to mask undesirable flavor and aroma substances especially in food and cosmetic industries [4-6]. Nano and microcapsules are also interesting and promising option in controlled drug delivery technologies [7,8]. Apart from these, there are studies in areas such as energy storage [9-11], wood modification [12], medicine [13] and agriculture [14]. In the self-healing mechanism with the microencapsulation system, the healing agent is encapsulated with a protective layer (shell). With the formation of scratches or cracks, the capsule breaks and the healing agent emerges and repairs the surface.

In microencapsulation, techniques such as spray-drying [15], spray-chilling and spray-cooling [16], extrusion [17], lyophilisation [18], in-situ polymerization [19] and supercritical fluid technology [20] are used for coating the active substances with the coating material. In this project, in-situ polymerization technique was used in the synthesis of microcapsules. The most commonly used monomers in this technique are urea-formaldehyde, melamine-formaldehyde and urea-melamine formaldehyde resins. According to this technique, an oil-in-water emulsion is formed first. For this purpose, the filling material to be encapsulated (water-insoluble, oil-phase core material) is emulsified in the water phase, which is mixed at high speed in the presence of surfactant (emulsifier). Prepolymers (e.g. melamine-formaldehyde) are then added to the emulsion. Finally, the polymerization reaction is initiated between the prepolymers by increasing the temperature and/or adjusting the pH. Instead of the prepolymer, melamine and formaldehyde or monomers such as urea and formaldehyde can be used directly.

Chung et al. [21] prepared mechanically and thermally stable polyurea formaldehyde-coated microcapsules containing curing agents and added them to the urea formaldehyde matrix to improve the self-healing surface layers of instrument panels in automobiles. During the synthesis of microcapsules by in-situ emulsion polymerization method, platinum was used as a catalyst. The self-healing efficiency of the material was examined with the help of an optical microscope and it was observed that there was an improvement of 82%. In another study, microcapsules containing linseed oil coated with urea-formaldehyde were synthesized by in-situ polymerization technique to prevent corrosion in metals. 1%, 3% and 5% microcapsule impregnated epoxy resins were coated on the scratched metal surfaces and immersed in NaCl solutions. SEM images of metals showed that metal

containing 3% microcapsule had a great improvement [22]. Jeong et al. [23] stated that an adhesive with energy storage properties can be obtained for wooden flooring application with micro-encapsulated phase change material and epoxy glue.

In this study the tung oil was encapsulated with melamine formaldehyde (MF) as a shell material. In-situ polymerization method was preferred because of its advantages such as high efficiency encapsulation, low cost, and ease of processing. Tung oil used as core material. Tung oil is a triglyceride and used in many areas such as paint, varnish, and printing ink due to its ability to polymerize into a film when in contact with air. Pretzl et al. [24] and Pan et al. [25] stated that the most commonly used coating material in microencapsulation is melamine formaldehyde resin, due to its resistance to water, acids and alkalis, and its price is also very low in industrial applications. Mustapha and his colleagues [26] encapsulated tung oil with a urea-formaldehyde shell using a one-step in situ polymerization technique for use in extrinsic self-healing applications.

Materials and Methods

Materials

Tung oil, used as core material, and melamine and formaldehyde (37 wt.% aqueous solution) which were used as wall material, were obtained from Sigma Aldrich. Tween 80 utilized as surfactant, was purchased from Merck. Acetone which was used for rinsing the microcapsules was obtained from Tekkim. Ammonium chloride used to remove unreacted formaldehyde was purchased from Merck Millipore. Sodium hydroxide and hydrochloric acid, which were used as pH controllers were supplied from Sigma Aldrich. All materials were used without additional purification. Deionized water was used in all experiments.

Synthesis of Microcapsules

In this study, the method proposed by Hwang et al. [27] was used for the synthesis of melamine formaldehyde microcapsules (Figure 1). In the first step, melamine formaldehyde prepolymer was synthesized. For this purpose fifty milliliters of water and 5 g of melamine were taken into a 100 mL reaction flask. After the resulting solution was stirred for a while, 11.4 g of 37% formaldehyde solution was added. Then the pH was adjusted to 9 by adding 10% NaOH solution. The temperature was increased to 70 °C and stirred at 300 rpm under reflux for a certain time. At the end of the reaction period, the pH was reduced to 6.5 and cooled to room temperature. The obtained melamine formaldehyde prepolymer was characterized by FTIR spectroscopy.

In the second step, tung oil loaded melamine formaldehyde microcapsules were synthesized by in-situ polymerization method. Fifty milliliters of water and 0.5 g of Tween 80 were added in a three-necked round-bottomed flask and stirred for 20 minutes at 300 rpm. At the end of this period, 10 g of tung oil was added and the pH value was adjusted to the range of 4-5.

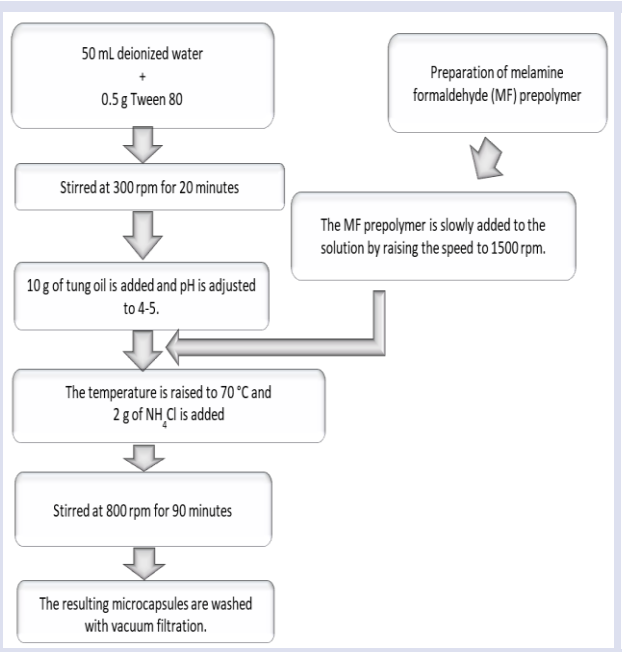

Figure 1. Schematic illustration of the preparation of tung oil loaded MF microcapsules

The stirring rate was increased to 1500 rpm and the previously prepared MF prepolymer was added slowly. After the temperature was increased to 70 °C, 2 g of NH_4Cl was added in order to remove the unreacted formaldehyde and it was mixed for 90 minutes at a stirring speed of 800 rpm. The resulting microcapsules were separated under vacuum using Suction filtration. The microcapsules were washed with deionized water and then air dried. The encapsulation yield calculation for the synthesis made is based on the equation (1) below [28,29].

$$\text{Encapsulation yield}\% = \frac{W_{\text{microcapsule}}}{W_{\text{MF prepolymer}} + W_{\text{tung oil}}} \times 100 \qquad (1)$$

$W_{\text{Microcapsules}}$, $W_{\text{MF prepolymer}}$ and $W_{\text{tung oil}}$ stand for weight of microcapsules, MF prepolymer and tung oil, respectively.

FTIR Analysis

FTIR measurements were performed with a Bruker-Alpha II model FTIR spectrometer in the range of 4000-400 cm^{-1} waveform and 4 cm^{-1} resolution and used to obtain information about interactions within the MF prepolymer and microcapsule formulations.

SEM

SEM analyses were conducted using a ZEISS-LEO 1430 scanning electron microscope available at Akdeniz University Electron Microscope Image Analysis Unit (TEMGA). Before the analysis, the microcapsules were coated with gold-palladium under high vacuum using a Polaron brand, SC7620 model coating device in order to impart conductivity to the microcapsules. Images were taken at a magnification between 200x and 10000x. Image-Pro Plus 2D Image Analysis Software was applied to measure constituent microcapsule particles by using SEM images.

TGA

Thermal behavior of microcapsules was carried out by heating from 30 °C to 800 °C at a nitrogen flow of 20 mL/min, with a heating rate of 10 °C/min, using the Perkin Elmer STA-8000 model thermal analyzer. Samples tested were previously dried in a vacuum oven during 24 h at 40 °C to remove the water moisture absorbed. Sample mass was about 8-10 mg.

Tung Oil Content in Microcapsules

A quantity of microcapsules was taken, ground and weighed (m_1). After grinding, they were immersed in acetone and filtered under vacuum. This process was repeated three times to ensure that all core material was washed. The collected microcapsule walls were dried at room temperature and weighed (m_2). The following equation was used to calculate the core content.

$$\text{Tung oil content } (\%) = \frac{m_1 - m_2}{m_1} \times 100 \quad (2)$$

Results and Discussion

Structure Elucidation of Microcapsules

In this study, in situ polymerization technique was used in the synthesis of microcapsules. In the first step, melamine-formaldehyde prepolymer was synthesized. In the second step, microcapsules were obtained by adding melamine-formaldehyde prepolymer to the oil-in-water emulsion. Schematic representation is given in Figure 2.

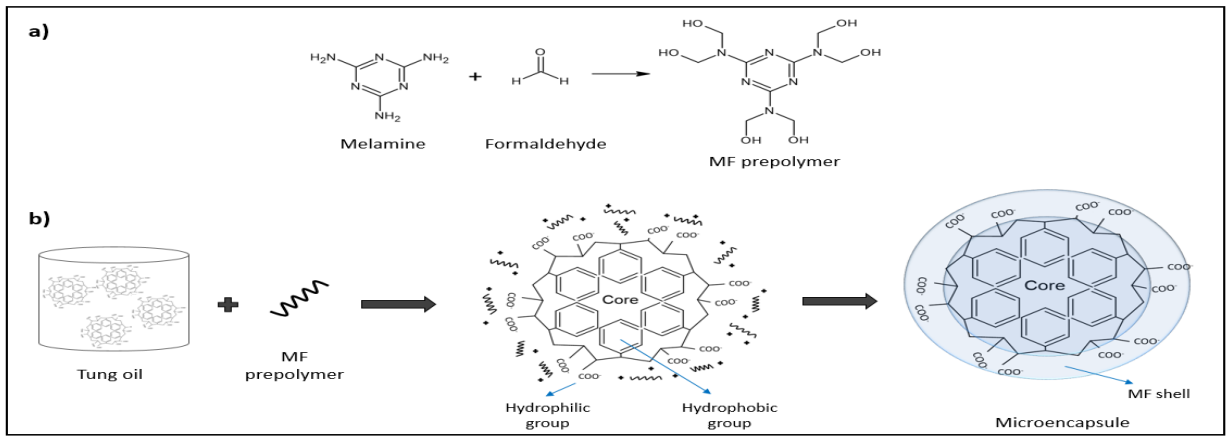

Figure 2. a) MF prepolymer formation mechanism, b) Schematic illustration of the synthesis of microencapsulation of tung oil.

For chemical characterization of prepolymers and microcapsules, FTIR spectroscopy was utilized (Figure 3 and Figure 4). Figure 3a represents characteristic IR absorption bands appear due to melamine. The peaks of $-NH_2$ stretching vibration occur at 3466, 3415, 3321 and 3119 cm^{-1}. In addition, the absorption peaks at 1631, 1529 and 809 cm^{-1} are assigned to the triazine ring [30,31]. FTIR spectra of formaldehyde is presented in Figure 3b. As can be seen from the Figure 3b, the -CH stretching peak is observed in the 2900-3300 cm^{-1} region. Absorption peak of –C=O group of aldehyde was recorded at 1636 cm^{-1} and 1429 cm^{-1}. Symmetric stretching vibrations of C–O and =C–O–C are seen at 1272 cm^{-1} and 986 cm^{-1}, respectively [32]. In the FTIR spectra of MF prepolymer (Figure 3c), the absorption peak appeared between 3300 and 3500 cm^{-1} is attributed to the -NH and -OH stretching. The stretching frequency at 1564 cm^{-1} corresponding to the N-H banding, 1376 cm^{-1} corresponding to C-H bending, 994 cm^{-1} corresponding to C-O stretching vibration in CH_2-OH and peak at 807 cm^{-1} represents the triazine ring [33,34].

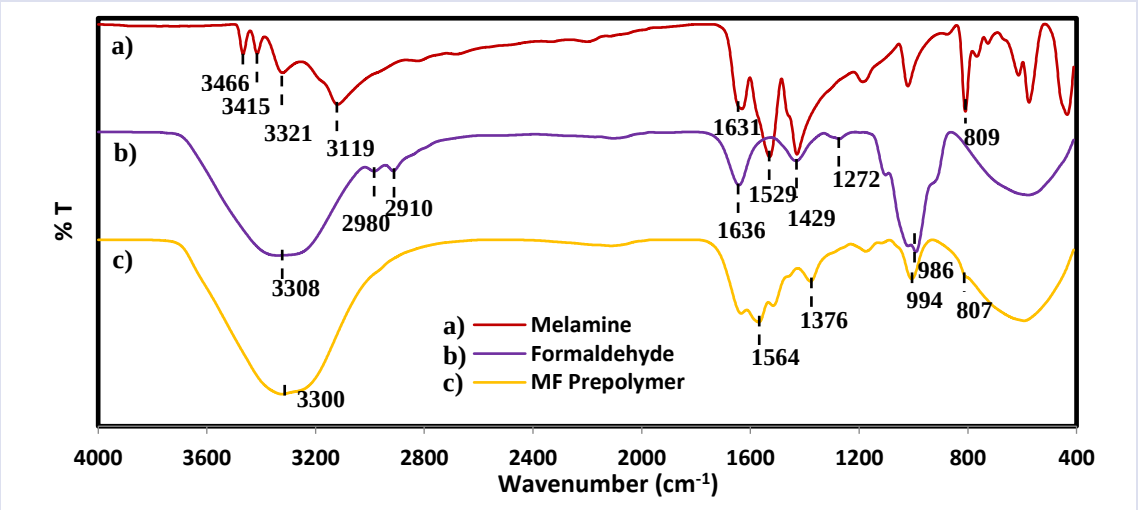

Figure 3. FTIR spectra of a) melamine, b) formaldehyde and c) melamine formaldehyde (MF) prepolymer.

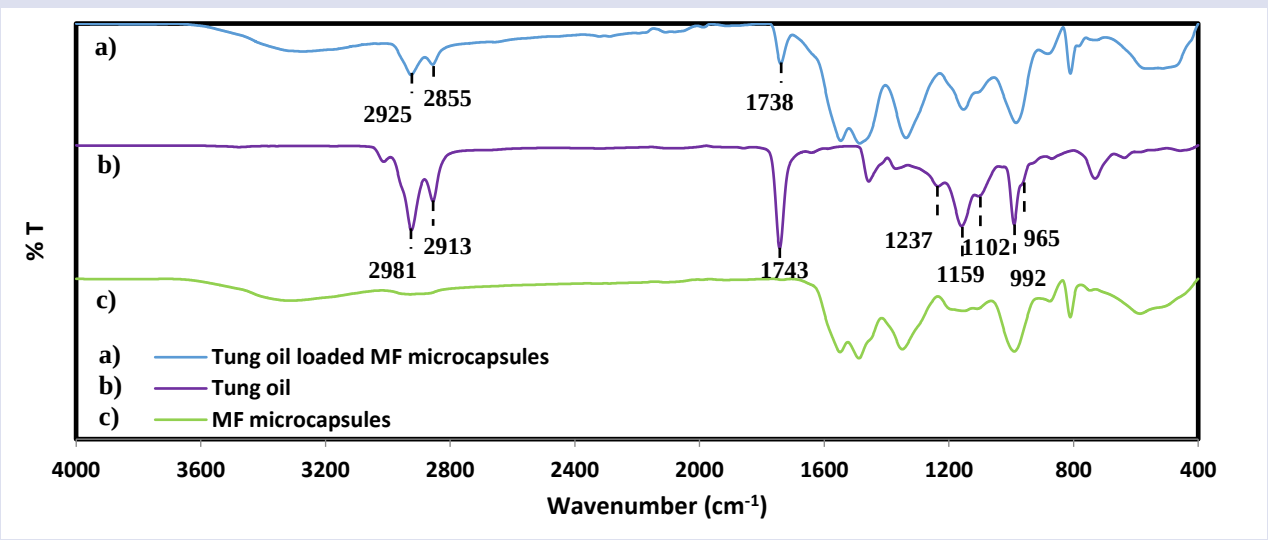

Figure 4. FTIR spectra of a) tung oil loaded MF microcapsules, b) tung oil and c) MF microcapsules.

In the FTIR spectra of tung oil given in Figure 4b, absorption peaks arised from symmetrical and asymmetrical -CH stretching vibrations of methyl and methylene groups are seen at 2981 and 2913 cm^{-1} [35, 36]. These vibrations have also occurred in tung oil loaded microcapsules (Figure 4a). While the C=O stretching vibration of tung oil at 1743 cm^{-1} was not observed in the tung oil free microcapsule (Figure 4c), its occurrence at 1738 cm^{-1} in the tung oil loaded microcapsule confirms that tung oil is chemically bonded with the MF shell structure. The strong absorption band at 1159 cm^{-1} and the bands on both sides (1237 and 1102 cm^{-1}) correspond to the asymmetric stretching vibration of the C-O bond of the C-CO-O fragment of aliphatic triglyceride esters. Besides, there are two absorptions at 992 and 965 cm^{-1} attributed to the C–H swinging vibrations of trans, trans and cis, trans conjugated double bonds.

Morphologies and Particle Size Distribution

The morphology and diameter of microcapsules were observed by scanning electron microscopy (SEM). SEM micrographs taken at different magnifications (3.00 KX, 5.00 KX and 10.00 KX) of MF microcapsules without tung oil and loaded with tung oil are illustrated in Figure 5a-c and Figure 6a-c, respectively. The microcapsules presented compact, regular, smooth outer surface and spherical structures. It appears that MF microcapsules containing tung oil tend to be relatively agglomerated compared to empty microcapsules.

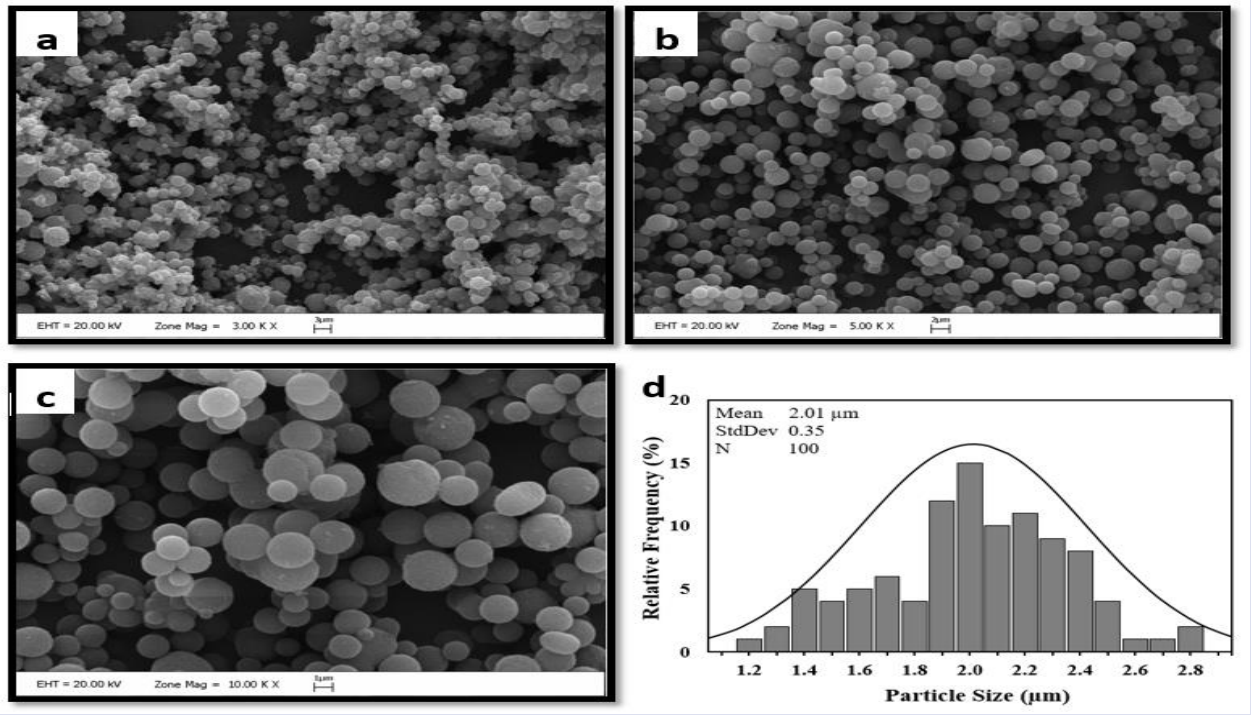

Figure 5. SEM micrographs and size distribution of MF microcapsules (tung oil-free) a) microcapsules magnification: 3.00 KX, b) microcapsules magnification: 5.00 KX, c) microcapsules magnification: 10.00 KX and d) size distribution

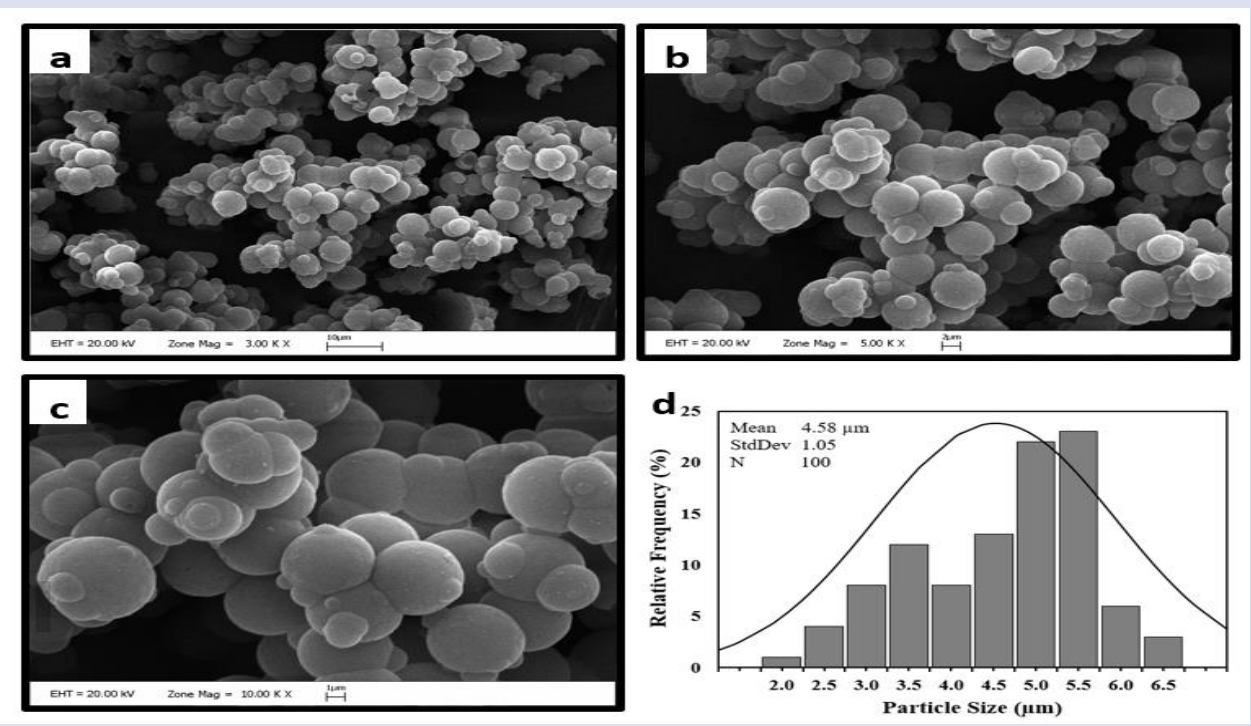

Figure 6. SEM micrographs and size distribution of tung oil loaded microcapsules a) microcapsules magnification: 3.00 KX, b) microcapsules magnification: 5.00 KX, c) microcapsules magnification: 10.00 KX and d) size distribution.

Particle size distribution of the microcapsules are shown in Fig. 5d for MF microcapsules (tung oil-free) and Fig. 6d for tung oil loaded microcapsules. The size of the microcapsules was calculated by measuring 100 individual microcapsules by SEM and the average diameter of the particles was determined as 2.01 ± 0.35 µm and 4.58 ± 1.05 µm for tung oil-free and tung oil loaded microcapsules, respectively. In addition, the microcapsules core content determined as 15.64 wt.% calculated by the acetone extraction method and its yield is approximately 49.78%. In a similar study conducted by Pan et al. [37], it was reported that tung oil-filled urea formaldehyde microcapsules prepared using Tween 80 as a surfactant were obtained with a particle size of 6-15 µm and a spherical morphology.

Thermal Properties of Microcapsules

The thermal behavior of tung oil and microcapsules were studied by TG curves. Figure 7 plotted the weight loss curves of tung oil, MF microcapsules (empty) and tung oil filled MF microcapsules. It was observed that the degradation of tung oil begins at approximately 350 °C. The high decomposition temperature of tung oil is due to its thermally stable structure [38]. MF microcapsules (empty) and tung oil filled MF microcapsules demonstrated almost similar thermal behaviour. Slight loss of both microcapsule systems in the region starting from 100°C and up to 220°C is related to the removal of chemically absorbed water molecules.

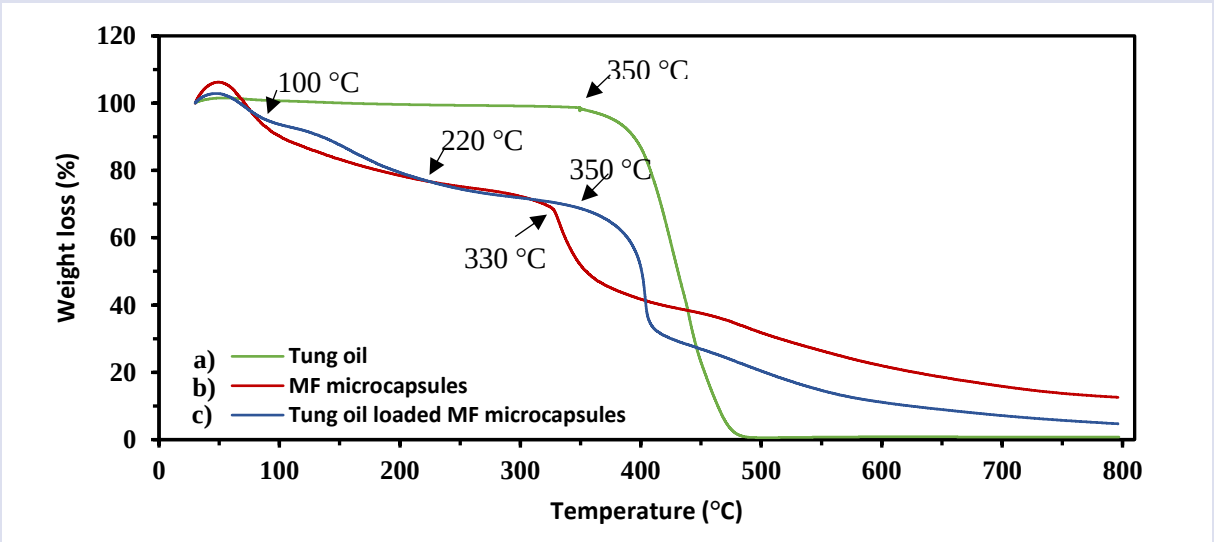

Figure 7. TGA thermograms of a) tung oil, b) MF microcapsules, and c) tung oil loaded MF microcapsules.

The decomposition temperature of MF microcapsules was recorded as 330 °C, while the decomposition temperature of MF microcapsules loaded with tung oil was recorded as 350 C. The residual weight of the MF and tung oil loaded microcapsules at 800 °C was 12.5 and 5.0 wt.%, respectively. Feng et al. [39] prepared tung oil-loaded PU (polyurethane)/PANI (polyaniline) microcapsules by two-step polymerization (interfacial polymerization and in-situ polymerization). In this study TGA thermogram *showed* that the initial *decomposition temperature* of the tung oil was about ~350 °C. They reported that tung oil loaded PU/PANI microcapsules have good thermal stability and can be used in the field of anti-corrosion coatings.

Conclusion

Melamine-formaldehyde microcapsules containing tung oil were prepared with in-situ polymerization technique. The obtained microcapsules were evaluated with regard to chemical structure, morphologies, size distribution and thermal properties. It was determined that the prepared microcapsules contained approximately 15.64 wt.% of tung oil and the encapsulation efficiency was 49.78 wt.%. The successful formation of tung oil-loaded microcapsules was confirmed by FTIR spectroscopy. SEM images proved that both tung oil-free and tung oil-loaded MF microcapsules have regular and smooth surface morphologies with diameters of 2.01 ± 0.35 µm and 4.58 ± 1.05 µm, respectively. These microcapsules can be used as self-healing anti-corrosion coatings due to their high good thermal stability and the ability to form films on exposure to air of the tung oil they contain.

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Conflicts of Interest

The authors stated that did not have conflict of interests.

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