Investigating the effect of synthesis conditions on the formation of urea–formaldehyde microcapsules

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In the current study, a set of urea–formaldehyde microcapsules (UFMs) were synthesized at different conditions via the in situ polymerization method. Encapsulation ability of the UFMs was studied by altering the synthesis parameters, such as formaldehyde to urea molar ratio (0.94, 1.88, 2.81), time (1, 4, 7 h), temperature (25, 55, 85 °C) and pH (3, 7, 11). The capsules were characterized by optical and electron microscopy (OM, SEM and TEM), particle size analysis (PSA), Fourier transform infrared spectroscopy (FTIR) and thermogravimetric/differential thermal analysis (TG/DTA). According to the results, for successful formation of UFMs, the pH value of the synthesis solution must be below 7 and the F/U molar ratio value must exceed 0.94. Effects of temperature and the pH value of the prepared solution were interdependent. To conclude, the results led to determination of the optimum UFM synthesis condition which presented the most effective formation of UFMs. The higher F/U molar ratio as well as higher curing temperatures in UFM-9, increased the UFMs degradation temperature. In order to further investigate the results, the synthesis of the optimized UFM (UFM-Opt.) was conducted, presenting the most effective development of UFMs.

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1. Introduction

In the recent years, new smart materials based on the microencapsulation technology were introduced for different applications including intelligent structures or self-healing composites [1,2]. The microcapsules containing healing agent are dispersed into a polymeric matrix to form a self-healing composite. Additionally, the microcapsules might be incorporated into paint for coating applications. The main purpose is to design smart polymeric self-healing systems with an inherent ability of self-repair. Different kinds of healing triggering mechanisms have been proposed in thermosetting polymer applications [3]. Microcapsules loaded with a variety of functional materials have been used for different application fields such as biology [4,5], flavors protection [6–8], drug release [9], electro-rheological fluids [10], pigments [11,12], and fire resistance powders [2,5,13]. Commonly, the capsules walls comprised from organic polymers, such as polyurethane, melamine formaldehyde and urea–formaldehyde [14,15]. Amino resin microcapsules which mainly consist of urea and formaldehyde polymers provide adequate chemical and mechanical stability, long shelf-life, good adhesion strength to polymeric matrixes and higher

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compatibility with most matrixes [16–18]. Different techniques are available for encapsulation of reactive materials, which can be categorized based on the mechanism of the wall formation [19]. Additionally, microencapsulation processes can be classified as chemical, physico-chemical and physico-mechanical processes [20]. The chemical encapsulation process is directed by the reactions at the interfaces or by the precipitation at the interface to produce the polymeric shell. Different encapsulation mechanisms include in situ polymerization [21], layer by layer assembly [22], coacervation [23,24] and phase separation [25]. In situ encapsulation method is widely used for the encapsulation of oils in polymeric capsules [26]. Polymerization occurs exclusively on the interface of dispersed core material. Polymerization of the reagents produces a rather low molecular weight pre-polymer. As the size of this pre-polymer grows, it further deposits on the surface of the dispersed core material. The polymerization process continues to occur with crosslinking which finally leads to formation of a solid capsule shell. The core material can be liquid or solid with different compositions which may be incorporated as dispersed or dissolved components. Active constituents, stabilizers, diluents, and accelerators or retardants can be added to the core mixture. The ability to vary the core material composition provides utilization of this characteristics and development of the desired microcapsule properties [27,28]. Drying oils as the core material has a significant ability to get tough by oxidative drying [3–31]. Drying oils are natural triglycerides containing high percentage of polyunsaturated fatty acids. These polyunsaturated fatty acids readily oxidize to form a three-dimensional network. Thus, microcapsules containing linseed oil are attractive for the preparation of anticorrosive paints and coatings [32,33].

Urea-formaldehyde (UF) resins are the most important type of thermosetting polymers and consist of linear or branched oligomers as well as polymers with some amounts of monomers. They are formed as a sequence of the following reactions of urea and formaldehyde [34,35]. After hardening, UF resins consist of three-dimensional networks which are insoluble and cannot be melted again. The basic characteristics of UF resins as the shell of the capsules include their fast curing, high reactivity, water solubility, non-flammability, hardness and good thermal properties [36]. They are also relatively cheap for production. This is one of their greatest advantages, and the main reason for using them in such a large quantity. Fundamentally, the reaction of urea with formaldehyde is a two-step process, and it consists of an alkaline methylolation step and an acid condensation step [37]. The alkaline methylolation consists of a substitution reaction in which formaldehyde reacts with urea to form methyl ureas. The acid condensation step involves the formation of UF di-, trimers and oligomers condensation reactions of methyl ureas [38]. The two different linkages between the UF monomers are methylene linkages and dimethylene ether linkages. If one methylol group reacts with an amino group, a methylene linkage would be formed, and water is released. The cross-linking between two methylol groups provides ether linkages (−CH₂−O−CH₂) to which −NH is attached on both sides, and yet again water is a by-product [39]. Schematic drawings of the two reactions can be seen in Fig. 1.

Noticeably, the reaction parameters can be altered in order to control which molecules are formed and using different conditions of reaction and preparation a variety of condensed structures is probable. Parameters which can be altered to investigate the outcome may include formaldehyde/urea molar ratio, pH, reaction time and temperature. In fact, a literature review shows an accelerating number of studies about encapsulation processes in recent years. Thus, a strong need was felt to state a general knowledge for the synergistic effect of different parameters during the synthesis of UF microcapsules. Indeed, few examinations have been reported on the role of all synthesis parameters simultaneously, i.e., formaldehyde/urea molar ratio, pH, reaction time and temperature on the formation of the microcapsules. In particular, the main aim of the present study was to assess a better understanding of the influence of the reaction parameters on the microencapsulation ability of the core material. The UF wall material was selected in order to avoid diffusion of the encapsulated drying oil for a considerable time. Moreover, high bond strength to the host polymer combined with a moderate strength microcapsule shell was required to remain intact during processing of the polymeric matrix [40,41]. Since the presence of free and/or leaked oil from the thin-wall microcapsules may aggregate the microcapsules, hence the optimization of the microencapsulation process has

Fig. 1 – Schematic drawings of the reaction of UF dimers to form: (a) methylene linkage and (b) dimethylene ether linkage.
a great importance. Furthermore, the inexpensive chemicals make them potentially suitable for use in high-performance anticorrosive coatings and a subsequent potential scale-up of production.

Accordingly, in order to evaluate the experimental conditions, a set of urea–formaldehyde microcapsules containing Linseed drying oil was prepared in the present study, and the effects of formaldehyde/urea molar ratio, pH, reaction time and temperature were investigated. Encapsulations were conducted via two steps: preparation of stable oil emulsions and in situ polymerization using urea–formaldehyde. After the preparation of microcapsules, morphology, particle size and thermal properties of UFM-2 were studied to explore the effect of synthesis conditions on the encapsulation process. The obtained results led to determination of the optimal UFM synthesis conditions.

2. Experimental

2.1. Materials

Urea (NH₂CONH₂), formaldehyde (37 wt% formaldehyde in water) (CH₂O), ammonium chloride (NH₄Cl), sodium hydroxide (NaOH), resorcinol (C₆H₄,1,3-OH₂) and poly vinyl alcohol (PVA) (C₇H₁₄O₃) were procured from Merck Co, and Linseed oil (with boiling point of 316 °C) was purchased from Sigma Aldrich. All chemical materials were used as received.

2.2. Preparation of the microcapsules

Microcapsules containing Linseed oil were prepared by in situ polymerization of urea and formaldehyde. PVA powder was mixed with deionized water to obtain a 5 wt.% aqueous surfactant solution. For encapsulation of Linseed oil, 130 ml of deionized H₂O at room temperature was retained in a 400 ml beaker, along with 5 ml of 5 wt.% PVA as a surfactant. Under agitation, the solid wall forming materials consisting of 2.5 g urea as a monomer, 0.25 g ammonium chloride as an initiator, and 0.25 g resorcinol as a cross-linking agent were added to the aqueous solution. Afterwards, the pH of solution was adjusted by addition of diluted HCl solution or NaOH salt to achieve different values (i.e., 3, 7, 11). Next, 30 ml of Linseed oil was added slowly to form an emulsion which equilibrated under stirring for 10 min. Formalin (37% formaldehyde) was then added at different F/U molar ratios (i.e., 0.94, 1.88, 2.81). The prepared solution was slowly heated under stirring at three temperatures (i.e., 25, 55, 85 °C) and held constant for the specified reaction times (i.e., 1, 4, 7 h). The polymerization of urea with formaldehyde started in the presence of already formed and stabilized core material emulsion. From a practical point of view, this means that urea, ammonium and resorcinol are first dissolved in the surfactant solution, and then core material is added and stabilized under vigorous agitation. After emulsion stabilization, microcapsules formation starts by addition of formaldehyde. Once the reaction was completed, the agitation and heating were stopped, and let to cool to the room temperature. Then, the microcapsules from the suspension were recovered by filtration under vacuum. The filtered microcapsules were rinsed with water repeatedly to remove the suspended oil and were dried under vacuum. To ensure complete removal of extra oil and water, the product was kept in an oven at 35 °C for 2 days. The detail of performed synthesis conditions for the formation of UFM and their identification codes are given in Table 1.

| Table 1 – Synthesis conditions for the formation of UFM and their identification codes. |
|----------------------------------|-----------|---------|------|------|
| Sample code | F/U | Temp. (°C) | pH | Time (h) |
| UFM-1 | 0.94 | 25 | 3 | 1 |
| UFM-2 | 0.94 | 55 | 7 | 4 |
| UFM-3 | 0.94 | 85 | 11 | 7 |
| UFM-4 | 1.88 | 25 | 7 | 7 |
| UFM-5 | 1.88 | 55 | 11 | 1 |
| UFM-6 | 1.88 | 85 | 3 | 4 |
| UFM-7 | 2.81 | 25 | 11 | 4 |
| UFM-8 | 2.81 | 55 | 3 | 7 |
| UFM-9 | 2.81 | 85 | 7 | 1 |

2.3. Characterization

A preliminary investigation of structure of the synthesized microcapsules was accomplished by an optical microscope (OM) (Leitz, Laborlux 12ME). Right after the microcapsule synthesis, a drop of the prepared solution was spread over a glass lane and observed under the microscope. A more detailed examination of microcapsule surface morphology was carried out by means of a scanning electron microscope (SEM) (Leica Cambridge Ltd, S360) and transmission electron microscope (TEM) (PHILIPS, CM-10). The filtered dry powders were placed on a glass lane and were coated by gold sputtering (Polaron sputter coater, SC7640) at low pressure of about 10⁻³ MPa to avoid charge build up. Fourier transform infrared spectrometer (FTIR) (Perkin Elmer, RXI) was used to identify the chemical structure of the prepared UFM. Size distribution of microcapsules was determined with laser particle size analyzer (PSA) (Fritsch Particle Sizer, analysette 22). To do so, solutions were diluted by water and then were sonicated for 10 min before PSA. To characterize the UFM’s wall thickness, and their core/shell geometry, the microcapsules were crushed at low temperature, rinsed repeatedly, dried, coated with gold, and finally were observed by SEM. Thermal stability of the produced microcapsules was measured by thermogravimetric/differential thermal analyzer (TG/DTA) (Perkin Elmer, Pyris Diamond) in nitrogen atmosphere by heating rate of 10 °C/min from room temperature to 700 °C.

3. Result and discussion

3.1. Morphology of UFM

Characterization tests were carried out on the UFM to understand the capsules’ morphology, as well as, to investigate the capsules’ shell formation at different synthesis conditions. Fig. 2 shows all the synthesized solutions introduced in Table 1. Due to the difference in density between linseed oil (0.92 g/cm³) and UF resin (1.15–1.19 g/cm³), once the final suspension was allowed to rest, phase separation might occur. The uncapsulated oil (UFM-3, UFM-5, and UFM-7) or oil-filled...
microcapsules (UFM-1, UFM-2, and UFM-4) appeared on the top surface while UF particles settled to the bottom (UFM-6 and UFM-8). In UFM-9, oil-filled microcapsules appeared on the surface, hence less UF particles were settled down. The color of the synthesized solutions at the pH value of 11 was red, while others were milky.

**Fig. 3** is an optical micrograph of UFM-9, prepared at F/U molar ratio of 2.81, pH value of 7, temperature of 85 °C, and agitation time of 1 h, showing the presence of the spherical UFMs particles.

**Fig. 4** shows the synthesized UFMs after filtration under vacuum. To look closer, in some of them such as UFM-3, UFM-5, and UFM-7, there is no evidence of particles or microcapsules formation under the indicated synthesis condition. But to investigate more precisely, electron microscopic studies are presented in the following. UFMs morphology, size and wall integrity were observed by scanning electron microscope (SEM), as shown in Figs. 5–7. Accordingly, investigations of the effect of urea-formaldehyde molar ratio, time, temperature and pH of the medium on encapsulation process are described in detail as follows.

### 3.1.1. Effect of pH value
The SEM results of the prepared samples at different pH values are shown in **Fig. 5**. The results show that UFMs were not formed at high pH values, especially for UFM-5 and UFM-7.

To investigate the reason of this issue, as described in the introduction section, methylation reaction is favored at higher pH values. The condensation stages at acidic media are divided to different stages, which are paused by increasing the pH. In fact, the condensation is started by adding acid, and this is essential to initiate the reaction. Different types of UF dimers are formed by varying the pH values. Obviously, the formed dimers have an impact on the properties of the formed product. Additionally, it was also shown that methylene linkages were favored by a decrease in pH. It was described that the formation of UF dimers with ether linkages had a minimum yield point at pH 8 [42]. Hence, the methylation of the urea is slower at higher pH values. As a consequence, a great extent of the unsubstituted amino groups remains which results in the formation of methylene linkages. In fact, at higher pH values, fewer ether linkages were formed. Furthermore, the amount of ether groups was also decreased if the reaction conditions were acidic. It was inferred to be a result of hydrolyzation of the ether linkages in an acidic environment, instead of methylene linkages [39]. At high pH values the condensation reactions do not occur. Sequentially, this led to the conclusion that by altering the pH value during the condensation that the amount of ether linkages formed can be controlled.

### 3.1.2. Effect of formaldehyde to urea ratio (F/U)
The SEM results of the samples with different F/U molar ratios during synthesis revealed that F/U molar ratio had an important effect on the formation of UFMs, as shown in **Fig. 6**. This is due to the fact that cross linking during curing of low F/U mole ratios resins is lower compared to high mole ratio resins [43]. Two coinciding processes occur during the development of the microcapsules. First, the UF resin reacts on the interface of the Linseed oil to form the capsule shell, and second, the UF reactions in the solution produce UF colloidal particles [44,45]. Less urea or higher F/U molar ratio results to the formation of more dimethyl ether bridges and methylol groups, and the final UF structure is more branched. This is due to further formation of substituted amino groups, at lower urea levels.

It should be noted that the amount of methylol group would affect the tensile strength [46]. As the molecular weight of the pre-polymer increases as F/U ratio changes, the ultimate UF becomes more cross-linked and results in the formation of the
3.1.3. Effect of the reaction time

The most evident effect of reaction time is the size of the formed UFMs, Fig. 7. As mentioned previously, the UFMs formation by polymerization of urea with formaldehyde starts in the presence of a stabilized core material emulsion. From this point of view, the core size in the emulsion can be controlled by adjusting the agitation time during the UFMs formation. As the agitation time is increased, the oil droplets in the emulsion are finer and the UFMs diameter decreases. Besides, the UF particles are precipitated from the higher molecular weight pre-polymers, which form the UFMs shell by deposition on their outer layer. The reaction is allowed to complete at ambient temperature, the emulsion transforms to a gelation solution. As long as the agitation providing the oil droplets is stopped, distinct microcapsules cannot be achieved.

3.1.4. Effect of the reaction temperature

Both UFM-4 and UFM-8 were prepared at the same synthesis time, but different temperatures of 25 and 55°C, respectively. Accordingly, the higher temperature resulted in a decrease in the number of UF particles around the UFMs. Noticeably, the rate of hydrolysis is increased with temperature, so the time held at this temperature is also very effective. In fact, the most pronounced effect of the reaction temperature was displayed at pH value of 7 (UFM-4 and UFM-9). The bonding type between the urea molecules depends on the conditions. Low temperatures and slightly acidic pHs lead to the formation of methylene ether bridges and higher temperatures and lower pHs leads to the formation of methylene bridges [48]. Thus, the effect of the reaction temperature on the UF synthesis depended on the pH value of the reaction mixture. The temperature had no impact on the reactions between urea and formaldehyde at alkaline pH, but an increase in the amount of the substituted urea was observed at pH values bellow 7, as well as, higher time and temperatures [42].

Fig. 4 – The synthesized UFMs over filtering papers.
3.2. Particle size analysis (PSA)

Particle size distributions of UFM-6, UFM-8 and UFM-9 are illustrated in Fig. 8. The results show the bimodal distributions of particles for UFM-6 and UFM-9, and a multimodal distribution for UFM-8. The curves demonstrate high frequency peaks at small sizes (i.e., 16–20 μm) which are attributed to UF particles, and wide size distributions that are related to the formed microcapsules. The size of capsule falls in a wide range of micrometers. The reason for this issue is that during stirring, the fluid flows away from the magnet of the magnetic stirrer. Hence, the large oil droplets exist far from the magnet, and the small droplets exist in the vicinity of the magnet, which results in a wide distribution in size. Finally, UFMs with a diverse range of sizes are present, as described by Dobetti [49]. The cumulative analysis of PSA results is presented in Fig. 9. It should be noted that the sharp peak related to the UF particles has been omitted to avoid any interference between their irrelative data with the reported sizes of the UF microcapsules presented in the SEM images.

Fig. 5 – SEM images of: (a) UFM-3, pH:11, (b) UFM-5, pH:11, (c) UFM-7, pH:11, (d) UFM-4, pH:7, and (e) UFM-8, pH:3.

Fig. 6 – SEM images of: (a) UFM-1, F/U:0.94, (b) UFM-2, F/U:0.94, (c) UFM-4, F/U:1.88, and (d) UFM-8, F/U:2.81.
Statistical analysis has been also conducted on the results to obtain mode, median and mean values. Mode is defined as the peak of the frequency distribution which can be seen as the peak in the distribution diagram. Also, median is the value that half of the data set reside above it and therefore, have below. Moreover, in this calculation mean value presents the weighted average size of the capsules. Values of these parameters are presented in Table 3. The results of capsules size are in good agreement with the SEM analysis. To conclude, UFM-6 with agitation time of 7 h, has the lowest mean particle size of 29.29 μm, in contrast; UFM-9 agitated for 1 h, has the largest mean particle size of 99.05 μm. Thus, the capsule size can be controlled by adjusting the agitation time. As the duration of agitation is increased, the finer UFM-s are obtained.

3.3. Fourier transform infrared spectroscopy (FTIR)

The transmittance FTIR spectra of UFM-4, UFM-6, UFM-8, UFM-9, and the pure Linseed oil are shown in Fig. 10. Moreover, characteristic peaks observed at their FTIR spectra are tabulated in Table 2. In the UF capsules, an absorption peak is seen at 3100–3500 cm\(^{-1}\), which is characteristic of the NH stretching of the bonded —NH group. By altering the pH to more alkaline values, the band at about 3360–3390 cm\(^{-1}\) gets sharper. Thus, the sharpness of these bands may indicate a reduction in the extent of hydrogen bonded interaction, which is expected as the structure becomes more cross-linked due to methenilization reaction [59]. A distinct absorption band appears around 2995 cm\(^{-1}\) which is characteristic of the C–H stretching mode of the —CH\(_2\)—O—CH\(_2\)— group.

![Fig. 7 - SEM images of: (a) UFM-6, agitation for 7 h, (b) UFM-8, agitation for 4 h, and (c) UFM-9, agitation for 1 h.](image)

![Fig. 8 - Particle size distribution of UFM-6, UFM-8, and UFM-9.](image)
absorption band at about 1740 cm\(^{-1}\), is assigned to the C=O stretching of amide I, and the peak at the lower frequency is assigned to the NH\(_2\) deformation mode. A very strong absorption band is observed at 1650 cm\(^{-1}\) in all lab-made prepolymers. Jada [51] reported that if a doublet is seen in this region, the contribution of the NH vibration mode of the free NH group and the C–O stretching of amide I, are very large; UFM-6 and UFM-9 in Fig. 10. But in the case of disubstituted urea derivatives, in which there are no free −NH, groups, contribution of the NH mode of free NH, is minimal. Thus, only a singlet is seen, UFM-4 and UFM-8 in Fig. 10. A weak absorption band at 1470–1460 cm\(^{-1}\) is observed due to the CH\(_2\) bending mode of the −CH\(_2\)–N group. This assignment is in agreement with the reported results in the literature [52–54]. The intensity of this peak varies in all polymers and reflects the amount of −CH\(_2\)–N presents in the prepolymers. An absorption band around 1370 cm\(^{-1}\), is assigned to the CH stretching of the CH\(_2\)OH group and the C–N stretching for all of the UF prepolymers. However, the band around 1400 cm\(^{-1}\) was assigned to the CH vibration mode in CH\(_2\) and CH\(_3\) by Myers [55]. A moderately strong absorption band is appeared from 1150 to 1160 cm\(^{-1}\). In the literature, this peak has been assigned to the C–O stretch of aliphatic ether. It was concluded that the band at 1000–1200 cm\(^{-1}\) in UF polymers was assigned to the amide linkage [55]. Moreover,

a strong peak appears at 1020 cm\(^{-1}\), this band is ascribed to the C–O stretch of CH\(_2\)OH in mono- and dimethylol urea polymers. This assignment was supported by Chabert [56,57]. Besides, Becher indicated that the peaks at 1000–1015 cm\(^{-1}\) were due to the −CH\(_2\)OH group [51]. A medium absorption band is appeared around 800 cm\(^{-1}\). The band was ascribed to symmetric −C–O–C stretch for six-membered cyclic ether [58]. It is inferred that the peaks are highly matched to the characteristic peaks of urea–formaldehyde polymer. The

![Fig. 9 – Cumulative size distribution of UFM-6, UFM-8, and UFM-9.](image1)

Table 2 – Characteristic peaks observed at FTIR spectra of UFM-4, UFM-6, UFM-8, UFM-9.

<table>
<thead>
<tr>
<th>Wavelength (cm(^{-1}))</th>
<th>Mode</th>
<th>Bonding</th>
</tr>
</thead>
<tbody>
<tr>
<td>~3500</td>
<td>N–H stretching</td>
<td>Bonded −NH</td>
</tr>
<tr>
<td>~2995</td>
<td>C–H stretching</td>
<td>−CH(_2)–O–CH(_2)–</td>
</tr>
<tr>
<td>~1740</td>
<td>C=O stretching</td>
<td>Amide I</td>
</tr>
<tr>
<td>~1650</td>
<td>NH vibration; C–O stretching</td>
<td>Free −NH; Amide I</td>
</tr>
<tr>
<td>~1465</td>
<td>CH(_2) bending</td>
<td>−CH(_3)–N group</td>
</tr>
<tr>
<td>~1370</td>
<td>CH(_2) stretching; C–N stretching</td>
<td>UF prepolymer</td>
</tr>
<tr>
<td>~1400</td>
<td>CH vibration</td>
<td>CH(_2) and CH(_3)</td>
</tr>
<tr>
<td>~1250</td>
<td>OH deformation</td>
<td>CH(_2)OH</td>
</tr>
<tr>
<td>~1155</td>
<td>C–O stretching</td>
<td>Aliphatic ether, amide, or the hydroxyl groups Amide linkage</td>
</tr>
<tr>
<td>~1100</td>
<td></td>
<td></td>
</tr>
<tr>
<td>~1020</td>
<td>C–O stretching</td>
<td>CH(_2)OH in mono- and dimethylol urea</td>
</tr>
<tr>
<td>~1015</td>
<td>–</td>
<td>Monomethyl urea due to −CH(_2)OH group</td>
</tr>
<tr>
<td>~1000</td>
<td>–</td>
<td>Dimethyl urea</td>
</tr>
<tr>
<td>~800</td>
<td>Symmetric</td>
<td>−C–O–C stretching</td>
</tr>
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Table 3 – Statistical analysis of the PSA results.

<table>
<thead>
<tr>
<th>Statistical parameter</th>
<th>UFM-6</th>
<th>UFM-8</th>
<th>UFM-9</th>
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<tr>
<td>Mode ((\mu m))</td>
<td>44</td>
<td>74</td>
<td>150</td>
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<tr>
<td>Median ((\mu m))</td>
<td>23.19</td>
<td>65.98</td>
<td>80.22</td>
</tr>
<tr>
<td>Mean ((\mu m))</td>
<td>29.29</td>
<td>78.9</td>
<td>99.05</td>
</tr>
</tbody>
</table>

![Fig. 10 – Transmittance FTIR spectra of UFM-4, UFM-6, UFM-8, UFM-9 and the pure Linseed oil.](image2)

peaks at 1750 cm⁻¹ and between 2800–3000 cm⁻¹ are the typical absorption peaks of Linseed oil, corresponding to carbonyl group vibrations of the triglyceride oil and O–H vibration of the oxirane ring, respectively [59]. The above discussions revealed that microcapsules containing oil have been formed.

3.4. Thermogravimetric/Differential thermal analysis (TG/DTA)

Thermal analysis of microcapsules is useful in finding the right range of application, because different microencapsulate systems are decomposed at different temperatures. Fig. 11 shows TGA diagram of the UFM-4, UFM-8 and UFM-9 samples. The results show that the degradation of UFM consists of three steps. The mass loss near 100 °C, is generally due to the removal of residual water and evaporation of un-reacted formaldehyde in shell. In fact, the curve of all samples almost coincided with each other below 200 °C. The weight loss at the range of 200–400 °C was mainly due to evaporation of formaldehyde from the shell constituents, as well as the core material (boiling point of linseed oil is about 316 °C). According to the TGA data, the weight losses of microcapsules started at a temperature lower than that of linseed oil evaporation. This is mainly attributed to urea–formaldehyde decomposition and the evaporation of formaldehyde. In addition, on the investigation of the decomposition of poly (MUF) microcapsules, it was proposed that the decomposition is caused by a gradual diffusion of the core over the shell [60]. So, it can be concluded that the weight loss at around 300–350 °C may be attributed to the diffusion of the oil core and its decomposition with the degradation of UF shell. In addition, the residual weight at temperatures higher than 450 °C is resulted from the remaining shell components. This is due to the formation of cross-linked polymers which shows the higher thermal stability. Obviously, the thermal degradation of UF microcapsule containing oil is more complicated than the UF walls or resins alone. Through comprehensive analysis of the three curves from different UFMs, it can be understood that the thermal stable temperature of microcapsules containing oil with urea–formaldehyde as shell material is below 250 °C. The weight loss of the UFMs at this temperature is approximately 10 wt%, and basically, the microcapsules are chemically stable below this temperature, indicating that the prepared microcapsules have a good thermal stability. Comparing the different samples in TG analysis, UFM-4, shows the lowest weight loss temperatures. This fact is due to lower F/U molar ratio during the synthesis of UFM-4, and lower dimethyl ether bridges in following. In contrast, UFM-9 remains stable at higher temperatures comparatively. This is because of the formation of more cross links during curing of UFM-9 with respect to the synthesis curing temperature of 85 °C. The increased stability of UFM-9 in the case of higher F/U molar ratio as well as higher curing temperatures, will delay the oil core exposing, and this in turn will increase the temperature of core degradation. Fig. 12 presents the dependence of heat flow on the temperature obtained from differential thermal analysis (DTA). The degradation of UFMs is extended in a wide temperature area. There are several endothermic peaks which are in accordance with the above described stages.

3.5. Morphology of UFM-Opt

As revealed, the formation of UFMs is highly dependent on the synthesis conditions. In order to clarify the results, the synthesis of optimized UFM (UFM-Opt.) was conducted. As a summing up, for successful formation of UFMs, the pH value of the synthesis solution must be below 7 and the F/U molar ratio value must exceed 0.94. As revealed experimentally, the effect of temperature is dependent on the pH value of the reaction mixture, mostly at pH value of 7. Owing to the mentioned facts, the UFM-Opt. was synthesized, by selecting the pH value of 3, F/U molar ratio of 2.81 and reaction temperature of 85 °C. To obtain an average size of UFMs, the solution was agitation for 4 h. SEM images of the synthesized UFM-Opt. are represented in Fig. 13. As it can be seen in Fig. 13a, numerous spherical capsules are formed effectively under the optimized condition. To further explore the nature of the UFMs, the microcapsules synthesized at optimized condition were crushed at low temperature. As shown in Fig. 13b–d, the nature of the particles is evident by means of shell/core constituents, and the thickness of the shell is approximately 1 μm. Moreover, as it can be seen in Fig. 13c, the oil in core is released by the rupture of the capsule’s shell. For more clarification, the core-shell structure of the particles is also confirmed by TEM analysis, as shown in Fig. 13e.

4. Conclusions

A series of urea–formaldehyde microcapsules containing the drying oil have been prepared by in situ polymerization. The influences of experimental parameters such as urea–formaldehyde molar ratio, time, temperature and pH of the medium on encapsulation process were thoroughly investigated. The results showed that the formation of UFMs is highly dependent on the synthesis conditions. Generally, for successful formation of UFMs, the pH value of the synthesis solution must be below 7 and the F/U molar ratio value must exceed 0.94. Effects of temperature and the pH value of the prepared solution were interdependent. Mainly, the UFMs were chemically stable below 250 °C, indicating that the prepared microcapsules have a good thermal stability. UFM-4, showed the lowest weight loss temperatures, due to lower F/U molar ratio during the synthesis of UFM-4, and lower dimethyl ether bridges in following. Comparatively, UFM-9 remained stable at higher temperatures. This was because higher temperatures cause to the formation of more cross links during curing of UFM-9 with respect to its temperature of 85 °C. The increased stability of UFM-9 in the case of higher F/U molar ratio as well as higher curing temperatures, delayed the oil core exposing, and in turn increased the temperature of core degradation.

To conclude, the results led to determination of the optimum UFM synthesis condition, and experiments results confirmed that the synthesis of the UFM-Opt. presents the most effective formation of the UFMs.

Conflicts of interest

The authors declare no conflicts of interest.

REFERENCES


