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Effect of the preparation method on the structure of linseed oil-filled poly(urea-formaldehyde) microcapsules

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ABSTRACT

Linseed oil was satisfactorily encapsulated in urea-formaldehyde (UF) shell by one acid stage polymerization. This was confirmed by thermal analyses (TGA) and FTIR studies. Microcapsules produced by one acid stage were strong enough to bear the preparation circumstances, and were dried into a free flowing powder, which remained stable under storage for 6 months at ambient laboratory conditions. Undesirable formation of UF particles in suspension that do not contribute to the shell growth was inhibited by selecting a proper amount of poly vinyl alcohol (PVA) and sodium dodecyl benzene sulfonate (SDBS), and adjusting the pH of the process.

The surface morphology of the microcapsules was particularly sensitive to the pH of the reaction medium. At low pH values (~1.7) the UF nanoparticles deposited onto the microcapsule surface, thereby producing a strong shell. Conversely, microcapsules prepared at pH 3.5, did not maintain their mechanical integrity after drying because of the weak wall shell. Spherical microcapsules with diameters in the range of 50–200 μm were obtained under mechanical agitation at 600 rpm. The size was reduced to 1–20 μm using an ultrasonic homogenizer. Linseed oil could not be encapsulated by UF resin using the two-stage method. Under basic pH, UF nanoparticles remained in suspension and, consequently, the linseed oil was not completely microencapsulated. Results obtained in this research highlight the role of the pH of the reaction medium on the microencapsulation process of linseed oil by UF resins.

1. Introduction

Polymeric materials are essential to virtually all modern technologies. However, the continuous exposure of polymers to abrasion, and mechanical, chemical or thermal stress can lead to degradation of their physical properties and so, to the mechanical failure of the material. Polymers which can repair themselves when damaged should show significantly enhanced durability and lifetime in applications, and the development of such materials is currently a topic of intense investigation [1]. Ideally the damage should itself trigger a healing response, and materials where this occurs (generally referred to as self-healing materials) include polymers containing embedded microcapsules of liquid monomers. When damage occurs in the material, these monomers are released, and subsequently polymerize to heal the fracture [1]. The microcapsules must possess sufficient strength to remain intact during processing of the host polymer, but rupture when the polymer is damaged.

Paints and coatings are extensively used on various substrates for aesthetics as well as for protection in their service life period. In the case of paints used for protection in corrosive atmospheres, the coating film undergoes changes in surface morphology, leading to the formation of microcracks which subsequently propagate and expose substrate to atmospheric moisture and oxygen. Linseed oil is one of the most widely used drying oils in paints formulation. Drying oils are natural triglycerides containing high percentage of polyunsaturated fatty acids with air-drying property. These polyunsaturated fatty acids readily oxidize to form a three-dimensional network that protects the metal from corrosive species. Thus, microcapsules containing linseed oil are attractive for the preparation of anticorrosive paints and coatings.

Microcapsules containing healing agents are commonly prepared via emulsion polymerization of urea and formaldehyde. During this process, urea and formaldehyde react in water phase to form colloidal cross-linked particles, which deposit at the core material-water interface and form the microcapsule shell wall [2,3]. Polymerization of urea-formaldehyde can be both acid- and base-catalyzed and, conventionally, is carried out in two stages, where the first one is basic and the second acidic [4]. Alternatively, the polymerization of urea-formaldehyde can be carried out in one

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stage under acidic conditions. The two-stage method has been used for encapsulation of epoxy resins [5–8], thiol [9] 5-ethylidene-2-norbornene [10], and linseed oil [11,12]. The one-stage method was developed for encapsulation of dicyclopentadiene [13], oil soluble solvents [14], linseed oil [15–21] and epoxy [22]. The aim of this research was to find the optimal conditions for preparing microcapsules containing linseed oil for use in anticorrosive coatings. Linseed oil was microencapsulated by both one- and two stages and the performance of each method was examined. Microcapsules obtained were characterized by scanning electron microscopy (SEM), thermogravimetric analysis (TGA) and Fourier transform infrared (FTIR).

2. Materials and methods

2.1. Materials

Linseed oil (commercial grade) was purchased from Alba Painting (Buenos Aires, Argentina). Urea (>99 wt.%) and formaldehyde (37 wt.% aqueous solution) were from Biopack (Buenos Aires, Argentina). Resorcinol (99 wt.%), poly vinyl alcohol (PVA) (Mw 61,000 g/mol), sodium dodecylbenzene sulfonate (SDBS) (>98.5 wt.%), 1-octanol (99+ wt.%) and thriethanolamine (TEA) (≥99 wt.%) were from Sigma Aldrich (USA). Ammonium chloride (NH_4Cl) (>99.5 wt.%), hydrochloric acid (37 wt.%) (HCl) and sodium hydroxide (Na(OH)) (≥99 wt.%) were purchased from Fluka (USA). All materials were used without additional purification.

2.2. Microencapsulation by a two-stage synthesis

Firstly, 2.5 g urea and 6.75 g 37 wt.% aqueous solution formaldehyde were added to 10 ml deionized water and the pH of the solution was adjusted to 8–9 with TEA. After 1 h reaction at 70 °C under magnetic agitation at 300 rpm, a transparent water-soluble methylol urea prepolymer was obtained. Meanwhile, 110 ml of deionized water, 0.1–1 g PVA and 0.1–0.5 g SDBS were mixed at room temperature (22–24 °C) in a 500 ml beaker. Two drops of 1-octanol were added to eliminate surface bubbles. A slow stream of either 25 or 12.5 g linseed oil was added to form oil in water emulsion and allowed to stabilize for 20–30 min. After stabilization, the UF prepolymer prepared in the previous step was added. The beaker was suspended in a temperature-controlled water bath on a programmable hot plate (Cole Palmer) with external temperature probe. The emulsion was agitated at 600 rpm with a digital mixer driving a three-bladed, 60 mm diameter glass propeller placed just above the bottom of the beaker. Subsequently, 10 ml water containing 0.28 ammonium chloride and 0.28 g resorcinol were added to the solution. The pH was reduced to 3.5 by drop-wise addition of HCl aqueous solution and the solution was heated at 1 °C/min until the target temperature (variable: 50, 55, 60 and 65 °C). The pH value of the emulsion was maintained at 3.5 during the process by addition of NaOH and HCl aqueous solution. After 4 h of agitation the mixer and hot plate were switched off and the system was neutralized to pH 7 by the addition of NaOH aqueous solution. Microcapsules were separated as described in Section 2.4.

2.3. Microencapsulation by a one-stage synthesis

At room temperature, 140 ml of deionized water, 0.1–1 g PVA, and 0.1–0.5 g SDBS were mixed at room temperature (22–24 °C) in a 500 ml beaker. The beaker was suspended in a temperature-controlled water bath on a programmable hot plate (Cole Palmer) with external temperature probe. The solution was agitated at 600 rpm with a digital mixer driving a three-bladed, 60 mm diameter glass propeller placed just above the bottom of the beaker. Under agitation 2.5 g urea, 0.28 g ammonium chloride and 0.28 g resorcinol were dissolved in solution. Two drops of 1-octanol were added to eliminate surface bubbles. Then, 12.5 g of linseed oil were added slowly to form an emulsion and was allowed to stabilize for 20–30 min under agitation. After stabilization, 6.75 g of 37 wt.% aqueous solution of formaldehyde was added. The emulsion was covered and slowly heated and maintained at 55 °C under stirring at 600 rpm for 4 h. At the completion of the reaction, the mechanical agitation and heating were stopped, and the pH was adjusted to 7 with NaOH aqueous solution. Microcapsules were separated as described in Section 2.4. The synthesis was also carried out in the absence of linseed oil in order to examine the structure of the neat UF polymer.

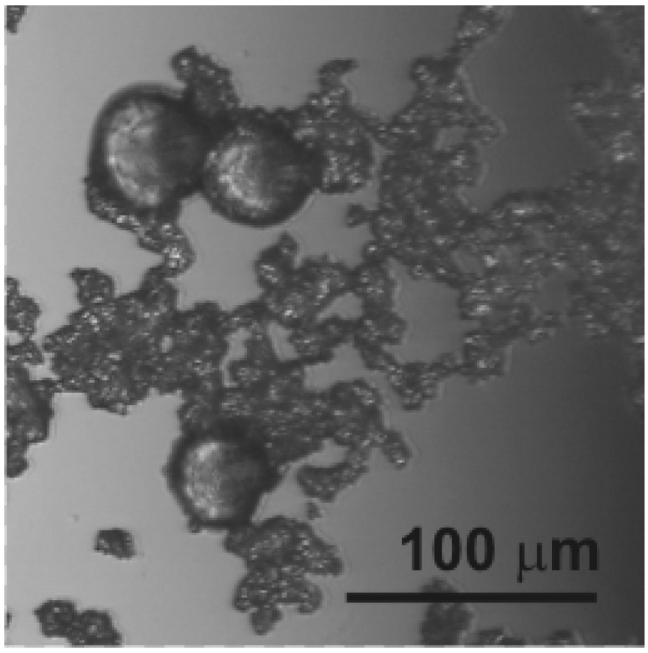

Fig. 1. OM image of microcapsules of linseed oil prepared by a two-stage procedure under mechanical agitation at 600 rpm. The prepolymer was prepared at 70 °C, the core: shell mass ratio was 4.

For some capsule batches high-performance dispersing devices were used to enhance the dispersion of linseed oil in the water phase. A T18-basic Ultra-turrax IKA was used for 10 min at 11000 rpm after addition of linseed oil. Some emulsions were prepared using an ultrasonic homogenizer (Cole-Parmer 750-W). The tapered 3.2 mm tip sonication horn of the homogenizer was placed in the linseed oil-water solution for 4 min at 40% intensity.

2.4. Separation of microcapsules

Due to the density difference between linseed oil (0.92 g/cm^3) and UF resin (~1.15–1.19 g/cm^3), once the final suspension was allowed to rest the linseed oil-filled microcapsules were at the top of the reactor together with UF nanoparticles while UF particles settled to the bottom of the reactor. Thus, the microcapsules were easily decanted from the suspension after the synthesis. The upper layer was first withdrawn whereas the sediment was withdrawn after removing the intermediate phase. After separation, the solids were rinsed with deionized water, vacuum-filtered and air-dried for 24–36 h at ~22 °C. On the other hand, when high-performance dispersing devices (Ultra-turrax and ultrasonic homogenizer) were used to prepare the linseed oil-water emulsions, decantation of microcapsules was very slow. Thus, phase separation was performed by centrifugation [16]. The suspensions were centrifuged at 500–2000 rpm during 1 h using a Rolco CM 36R centrifuge, and

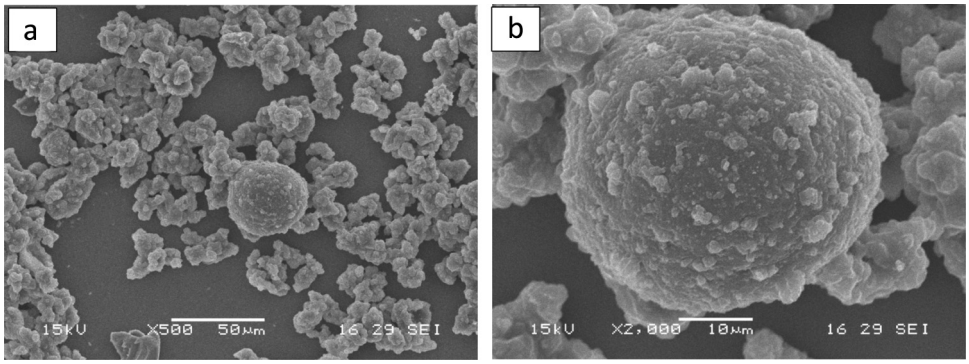

Fig. 2. SEM micrograph of (a) a ~40 μm microcapsule surrounded by agglomerated UF particles. (b) picture taken at higher magnification showing the surface morphology. Microcapsules were prepared by a two-stage procedure under mechanical agitation at 600 rpm. The prepolymer was prepared at 70 °C, the core: shell mass ratio was 4.

then the solids were rinsed with deionized water, vacuum-filtered and air-dried for 24–36 h at ~22 °C.

2.5. Optical and scanning electron microscopy

Optical microscopy (OM) was performed on a Leica DMLB. Every 30 min samples were taken from the reactor to analyze the morphology of the microcapsules. Small portions of each sample resin were placed, uncovered, on a glass slide, and then observed. Magnifications of up to 500 times were used.

2.6. Scanning electron microscopy

The supernatant and sediment resulting from the synthesis were stored in closed vials at 5 °C for future analysis. Morphology of the microcapsules was examined by scanning electron microscopy (SEM) using a JEOL JSM 35 microscope at 5 kV. The samples were vacuum dried and then mounted on aluminum stubs with double-stick tape. Then a layer of gold was evaporated onto the sample surface in a vacuum metallizing unit. In addition, some selected microcapsules were examined by field emission scanning electron microscopy (FESEM) using a Zeiss-Supra 40 instrument at 5 kV. The surfaces of the samples were coated with a thin Au–Pt layer.

2.7. Fourier transform infrared (FTIR) analysis

FTIR spectra were acquired with a Nicolet 6700 Thermo Scientific equipped with a diamond crystal. Attenuated total reflectance (ATR) spectra (4 cm^{-1}, 64 scans) of neat UF resin, linseed oil and microcapsules were analyzed in order to confirm that the microcapsules were filled with linseed oil.

2.8. Thermogravimetric analysis (TGA)

TGA analysis of microcapsules, linseed oil and UF resin was performed using a TGA-50 Shimadzu Thermogravimetric Analyzer at a heating rate of 10 °C/ min under nitrogen atmosphere (35 ml/min) from room temperature (~20 °C) to 900 °C. 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 3–6 mg.

3. Results and discussion

3.1. Microencapsulation by a two-stage synthesis

Microencapsulation of linseed oil was carried out by a two-step procedure that includes (a) dispersion of linseed oil in a surfactant aqueous solution to form an oil-in-water emulsion and (b) preparation of urea-formaldehyde prepolymer under basic conditions. As soon as the prepolymer solution is added to the stabilized emulsion of linseed oil and the medium is acidified, the polycondensation reactions start rapidly. The UF prepolymer was prepared at 70 °C under magnetic stirring at 300 rpm during 1 h and then added to an aqueous solution of linseed oil containing PVA and SDBS. In the initial stage of this study, microcapsules of linseed oil were prepared by the method reported by Brown et al. [13] for encapsulation of dicyclopentadiene using ethylene maleic anhydride copolymer (EMA) as surfactant. Unfortunately, the droplets of linseed oil were not stabilized by EMA and, therefore, after testing different surfactants we decided to use PVA in combination with SDBS. The amount of linseed oil was 25 g (core-shell mass ratio = 4). The process proceeded at 60 °C and acidic pH under mechanical stirring at 600 rpm during 3 h. During microencapsulation, two simultaneous processes occur: (1) the reaction of the UF resin at the linseed oil-water interface to form the capsule shell and (2) the reaction of UF in solution to produce UF colloidal particles [23,24]. Fig. 1 is a typical OM image showing the presence of diffraction rings, which appear when core and shell materials in a microcapsule have different refractive indexes. Thus, from OM studies it emerges that linseed oil was successfully microencapsulated. Fig. 1 also shows that the formation of linseed oil-filled capsules was accompanied by the formation of UF particles that remained in solution. SEM micrographs are presented in Fig. 2a shows a ~40 μm capsule surrounded by agglomerated UF particles. At higher magnification (Fig. 2b) it is seen that the surface of the microcapsule is rough and it is covered with granular deposits. The rough porous surface results from the deposition and agglomeration of UF particles, which precipitate from solution as molecular weight increases [23,24]. The resultant suspension was difficult to filter probably because of the presence of UF nanoparticles. Moreover, the filtered solid was a wet paste turning yellow and waxy after 1–2 days indicating that the linseed oil was not completely microencapsulated during the process.

In order to reduce excessive formation of UF particles, thereby avoiding incomplete microencapsulation of linseed oil, some changes were made in the two-stage procedure. The temperature of the first alkaline stage was reduced from 70 °C to 60 °C and the core/shell ratio was reduced from 4 to 2.5. Fig. 3 are OM and SEM images of capsules prepared under these conditions. Fig. 3a is an OM image showing that the amount of UF particles formed in the aqueous phase was markedly reduced. A typical ~90 μm spherical microcapsule containing some aggregated UF nanoparticles attached to its surface is presented Fig. 3b. The use of dispersing devices to enhance the dispersion of linseed oil in the water phase (Ultra-turrax, 10 min at 11000 rpm) resulted in a reduction of the size of the microcapsules. Fig. 3c is a SEM image showing spherical microcapsules with average diameter in the range of ~10–45 μm surrounded by agglomerated UF particles. Although the development of UF particles was markedly reduced, SEM studies revealed

Table 1
methods used for encapsulating linseed oil by a one-stage synthesis. All batches had 140 ml water, 2.5 g urea, 6.75 g of 37 wt.% aqueous solution of formaldehyde, 0.28 resorcinol, and 0.28 g ammonium chloride. Values of the last column show that initially the pH of the emulsion was adjusted to 3.5 and it reduced to 1.6–1.7 during the course of the synthesis.

Method	Agitation	PVA (g)	SDBS (g)	Linseed oil (g)	Core/shell	pH
I	Mechanical	0.5	0.5	12.5	2.5	3.5–1.7
II	Mechanical	0	0	12.5	2.5	3.5–1.6
III	Ultraturrax	0.2	0.1	12.5	2.5	3.5–1.6
IV	Ultraturrax	0.2	0.1	12.5	2.5	3.5
V	Sonication	0.2	0.1	5	1	3.5–1.6

the presence of significant amounts of UF particles that do not contribute to the shell growth, affecting its strength and stability. A ~40 μm broken capsule showing that a compact wall shell was not formed is clearly seen in Fig. 3d. Despite the amount of UF particles that remained in solution was markedly reduced the quality of the final product was below expectations. Again, the filtered suspension was yellow and sticky after drying because of the rupture of microcapsules and release of linseed oil. Several changes in the process temperature, stirring rate, amount of surfactant and core/shell ratio were introduced in order to improve the performance of the two-stage microencapsulation procedure. Unfortunately, attempts to obtain a dry, free flowing powder were unsuccessful. For that reason, the following modified procedure of microencapsulation was investigated.

3.2. Microencapsulation by a one-stage synthesis

In order to avoid the undesirable formation of UF particles in suspension, thereby promoting the UF polymerization at the interface linseed oil-water, the alkaline stage was omitted from the synthesis. The microencapsulation procedure was carried out by a one-stage polymerization under acidic conditions. Urea was first dissolved in surfactant solution, and then linseed oil was added under agitation and stabilized. Table 1 summarizes the methods used for encapsulating linseed oil by a one-stage synthesis. After screening different concentrations of PVA-SDBS we decided to use the amounts of stabilizers shown in Table 1. Differently from the two-stage procedure used previously, in this approach the UF polymerization starts after the linseed oil emulsion was formed and stabilized. The synthesis was also carried out in the absence of linseed oil in order to examine the structure of the neat UF polymer. Although the polymerization reaction of neat UF resins by the two-stage process has been widely studied [22,23], the cure in one acid stage has not received the same interest. SEM image in Fig. 4 shows that the morphology of the neat UF is characterized by clusters of ~50–200 nm colloidal particles formed by precipitation of high-molecular weight oligomers. No evidence of micro-sized particles was observed.

The microencapsulation of linseed oil was carried out at 50 °C under mechanical stirring at 600 rpm during 3 h at a core-shell mass ratio equal to 2.5 (Method I in Table 1). Initially, the pH of the emulsion was adjusted to 3.5 and it reduced to ~1.6 during the course of the synthesis. Fig. 5 shows that after agitation is stopped the solid phase separates into two layers, which were separated as described in Section 2.4. Fig. 6a is an OM image of an aliquot taken from the upper layer showing that it consists of linseed oil microcapsules. Consistent with OM studies, 50–200 μm spherical microcapsules were observed by SEM microscopy (Fig. 6b). These images show that the microcapsules had a smooth surface morphology, free of nanoparticles agglomeration. SEM images of the bottom layer (not shown here) confirmed that it consisted of sediment of polymer particles. Unfortunately, changes introduced in order to prevent the formation of excessive amount of UF particles were unsuccessful. The upper layer containing linseed oil-filled microcapsules was easily filtered although it appeared a bit sticky. Moreover, yellow traces of linseed oil appeared during storage, indicating that either the linseed oil diffused through the shell or the microcapsules had broken because of its low mechanical strength.

A modified procedure aimed at avoiding excessive particle formation, thereby improving the mechanical strength of the microcapsules was carried out. It was shown by Nesterova et al. that the presence of PVA and SDBS significantly increases nanoparticle formation [16]. In addition, the results of pioneer studies by Dietrich et al. [2,3] indicate that UF resins have tensoactive properties, which promote enrichment of UF molecules at the oil/water interface. Because of the high UF concentration at the interface, the condensation reaction proceeds there much faster than in the volume phase, thus contributing to the formation of the capsule walls. Based on the results reported by Nesterova et al. [16] and Dietrich et al. [2,3], we prepared microcapsules in the absence of PVA/SDBS surfactant (Method II in Table 1). The synthesis was carried out under the same experimental conditions as those in the previous procedure. After 3 h reaction at 50 °C the microcapsules were separated from the UF particles by decantation. OM and SEM micrographs in Fig. 7a and b shows that when no surfactant was used, microcapsules had irregular shapes. This indicates that the surface activity of UF resins is relatively low and cannot stabilize the core droplets in solution even with the aid of mechanical agitation. Although microcapsules were formed, the results were not satisfactory. The filtered product was a white powder that turned oily and sticky during storage indicating that the modified procedure did not improve the strength of the microcapsules.

In light of results shown previously, an alternative method of encapsulation was adopted in order to improve stability of the microcapsules (Method III in Table 1). The linseed oil-in-water emulsion was prepared using a dispersing device (Ultra-turrax, 30 min at 11000 rpm), and then the emulsion was slowly heated and maintained at 50 °C under stirring at 600 rpm. The core-shell mass ratio was equal to 2.5 and the formation of UF particles in suspension was prevented by reducing the amount of PVA y SDBS surfactants as shown in Table 1. SEM micrographs of the upper layer (not shown here) showed that the average microcapsule diameter decreased to ~10–50 μm. In Fig. 8, it is seen that the surface of microcapsules was rough and composed of UF nanoparticles protruding from the surface. In addition, the use of ultra-turax reduced the amount of UF particles formed in solution. This can be explained by the fact that as the size of the linseed oil droplets decreases the linseed oil-water interfacial area increases, therefore, the amount of UF particles deposited onto the microcapsule surface increases. Microcapsules produced by this method were strong enough to bear the preparation circumstances, and were dried into a free flowing powder, which remained stable under storage for 6 months at ambient laboratory conditions.

To further investigate the effect of the pH on the microencapsulation of linseed oil the synthesis was carried out at constant pH (Method IV in Table 1). In the previous on-stage processes the pH of the emulsion was first adjusted to 3.5 and it reduced to ~1.6 during the course of the reaction. A batch of microcapsules was prepared at pH 3.5 by drop-wise addition of NaOH and HCl aqueous solution while the other processing parameters were kept constant. Fig. 9a is a SEM micrograph showing that the microcapsules prepared under constant pH had a smooth surface. Obviously, the shell of the microcapsules was not compact, so the microcapsules were easily fractured during the washing process (Fig. 9a). As a result, the filtered product was a dense sticky mass and not a free flowing powder. SEM image presented in Fig. 9b demonstrates that after the reaction, a large proportion of UF remained in suspension and did not deposit onto the microcapsule surface. This is in

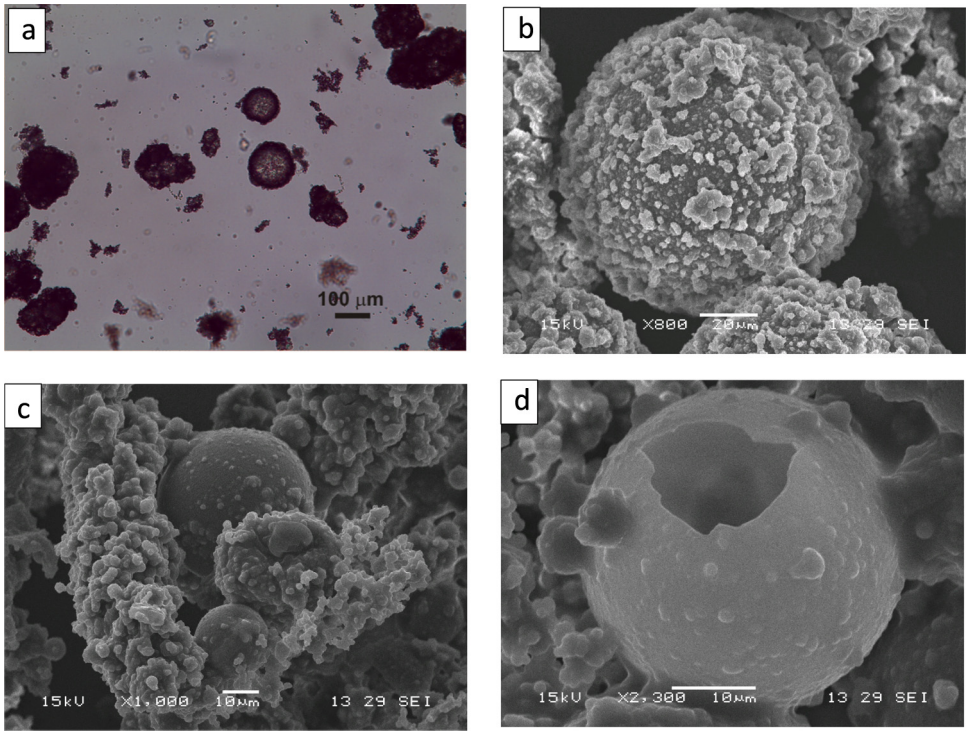

Fig. 3. (a) OM and (b) SEM images of capsules prepared by a two-step procedure under mechanical agitation at 600 rpm. The prepolymer was prepared at 60 °C, the core: shell mass ratio was 2.5. (c)–(d) the emulsion was prepared using a dispersing device Ultra-turrax while the other processing parameters were kept constant.

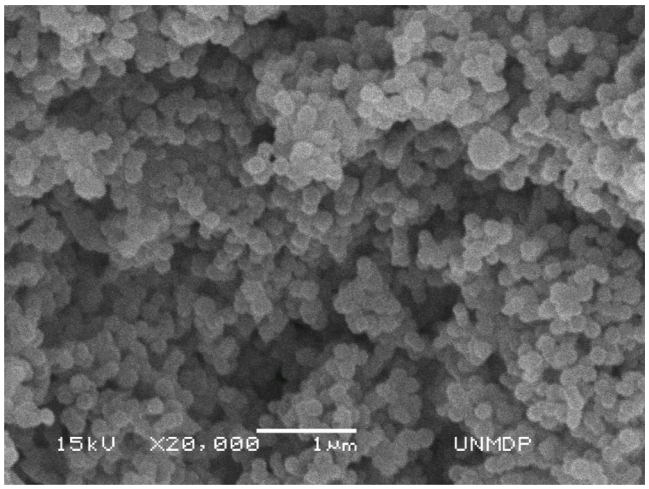

Fig. 4. SEM image showing the morphology of the neat UF resin prepared by a one-stage procedure at 50 °C under mechanical agitation at 600 rpm.

Fig. 5. Final product of reaction. The upper layer consists of microcapsules and nanoparticles while the bottom layer consists of sediment of polymer particles.

agreement with results reported by Zhou et al. [25,26], who studied the influence of the pH value on the formation of UF microcapsules. The authors found that the final pH value can substantially affect the surface morphology of the microcapsule. A high final pH value (>3.0) prevents the deposition of UF nanoparticles onto the surface of the microcapsule. Conversely, a low pH enhances the deposition of UF nanoparticles onto the surface of microcapsules thereby increasing the shell thickness and strength.

A series of microcapsule batches were prepared using an ultrasonic homogenizer for preparing the linseed oil-water emulsion (Method V in Table 1). The emulsions were sonicated for 4 min at 40% intensity, and then they were slowly heated and maintained at 50 °C under stirring at 600 rpm. Studies carried out in order to minimize the amount of UF particles that remain in suspension demonstrated that the optimal weight ratio of linseed oil-UF is 1. Fig. 10a and b are SEM images showing that spherical microcapsules with diameters in the range ~1–20 µm were obtained using sonication techniques. Magnified images presented in Fig. 10c and d

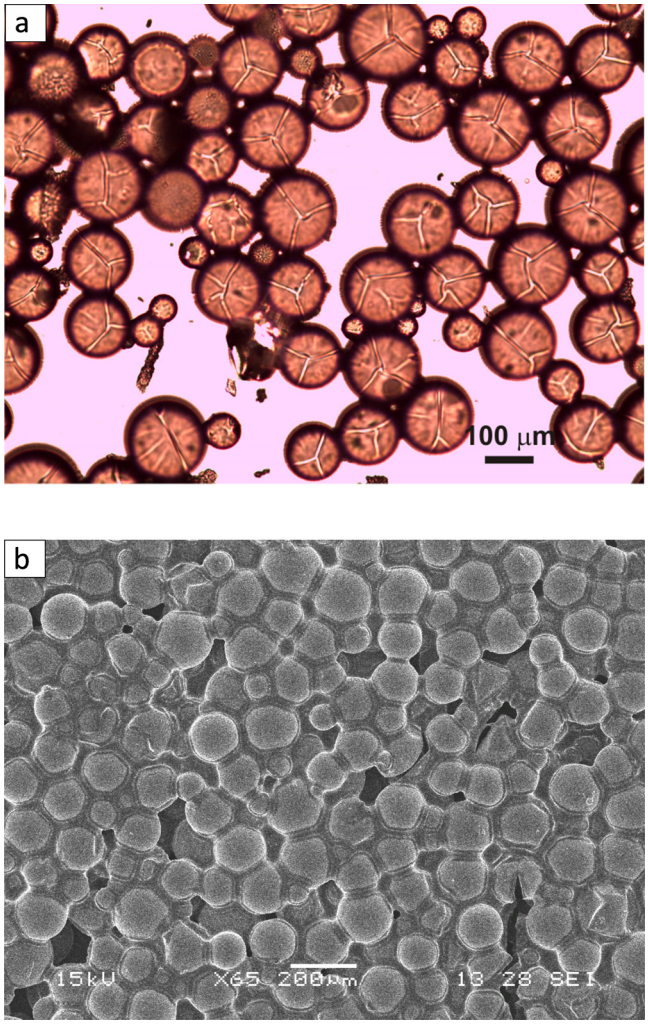

Fig. 6. (a) OM and (b) SEM images of microcapsules prepared by a one-stage procedure at 50 °C under mechanical agitation at 600 rpm. The core: shell mass ratio was 2.5.

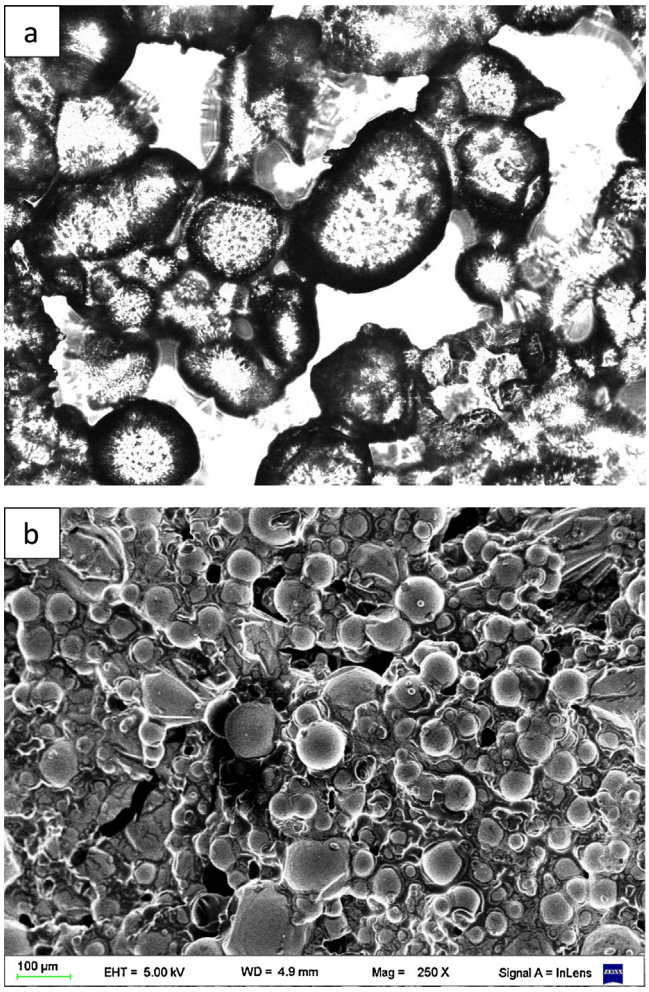

Fig. 7. (a) OM and (b) SEM images of microcapsules prepared by a one-stage procedure at 50 °C under mechanical agitation at 600 rpm. The core: shell mass ratio was 2.5. The synthesis was carried out in absence of surfactant.

shows that the surface of the microcapsules is rough and composed of UF nanoparticles protruding from the surface. It seems that after the reaction, the shell forming UF was deposited at the linseed oil-water interface and, consequently, the surfaces of microcapsules are rough and compact. SEM micrograph in Fig. 10e reveals the presence of spherical microcapsules with smooth surface morphology. The smooth non-porous microcapsule wall is believed to be the result of deposition of low molecular weight pre-polymer at the linseed oil-water interface, while the pre-polymer remains soluble [13]. However, comparison of Fig. 10e with SEM micrographs of UF particles in Fig. 5 demonstrates that UF nanoparticles formed in solution and smooth-surfaced microcapsules are indistinguishable. The microcapsules produced by this method, were strong enough to bear the preparation circumstances, and could be dried into a free flowing powder. The powder remained white and no evidence of leaching of linseed oil was observed after 7 months storage at ambient laboratory conditions.

From results presented, it emerges that surface morphology of linseed oil-filled UF microcapsules is particularly sensitive to the pH of the reaction medium. During the one-step process the pH of the reaction medium decreases from 3.5 to ~1.6. It is believed that the chemical reactions that reduce the pH value are [25]:

$$4NH_4Cl + 6HCHO \Leftrightarrow (CH_2)_6N_4 + 4HCl + 6H_2O \quad (1)$$

and the hydrolysis of ammonium chloride:

$$NH_4Cl + H_2O \Leftrightarrow NH_4OH + HCl \quad (2)$$

Fan et al. [26] proposed that in addition to reducing the pH of the system, the reaction between ammonium chloride and hydroxymethyl urea, can generate surface active substances, which drive UF nanoparticles that precipitated from the emulsion to enrich the oil-water interface. In that way, microcapsules with rough surface and high mechanical strength are formed.

3.3. FTIR studies

FTIR spectra of synthesized UF resin and microcapsules are presented in Fig. 11. The spectra were acquired in microcapsules shown in Fig. 10. In Fig. 11 it is seen that both spectra are closely matching at characteristic peaks such as the N—H stretching vibration at 1545 cm^{-1}, the C=O stretching vibration at 1631 cm^{-1}, and the C—H stretching vibration at 1460 cm^{-1}. The O—H groups appear as a broad absorption band in the region 3600–3200 cm^{-1}. A close matching between spectra of linseed oil and microcapsules was also found at characteristic peaks for C=O and C=C stretching vibrations. In view of these observations it is established that linseed oil was successfully encapsulated by UF resin.

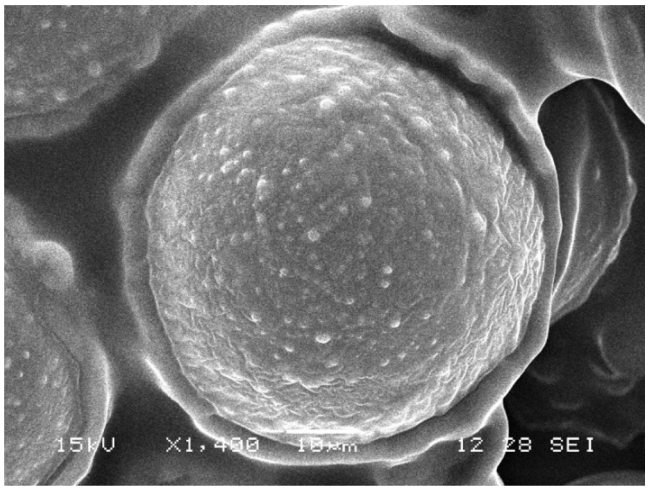

Fig. 8. SEM image of a typical microcapsule prepared by a one-stage procedure. The linseed oil-in-water emulsion was prepared with an Ultra-turrax, and then the emulsion was heated and maintained at 50 °C under stirring at 600 rpm.

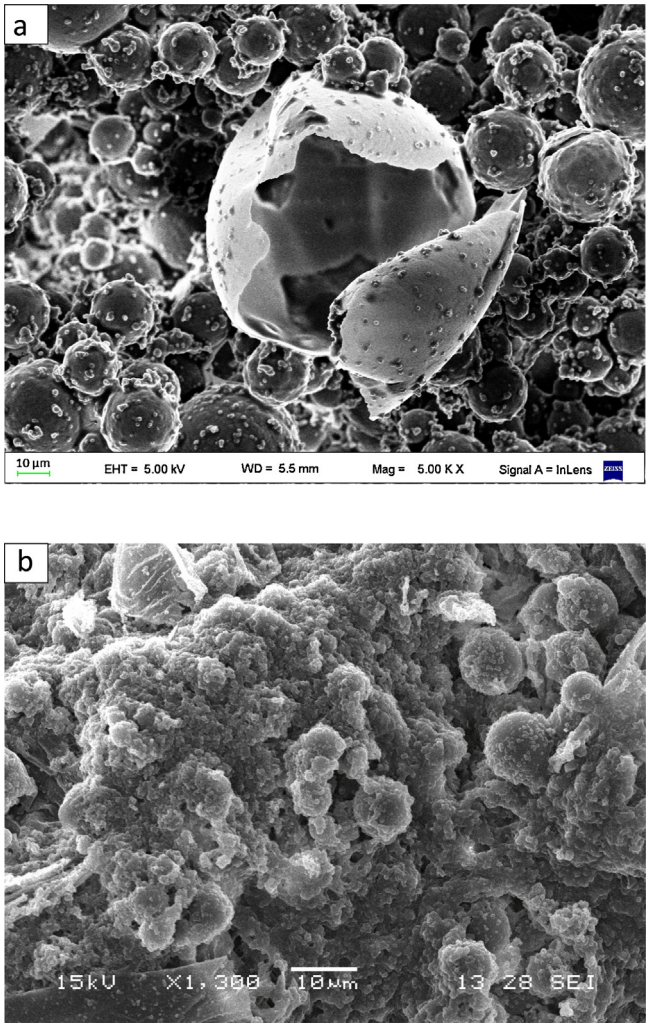

Fig. 9. SEM micrographs of microcapsules prepared under constant pH 3.5 while the other processing parameters were the same as those in Fig. 8. (a) A capsule showing that the UF shell was not compact, so the microcapsule was easily fractured. (b) It is seen that a large proportion of UF remained in suspension and did not contribute to shell growth.

3.4. Thermogravimetric analysis TGA

Thermal analyses were carried out for further characterization of the microcapsules. Fig. 12 shows the TGA curves of microcapsules as well as the neat UF resin and linseed oil. The studies were performed in microcapsules shown in Fig. 10. Degradation of linseed oil commences at about 300 °C as shown in TGA curve. From comparison of degradation curves in Fig. 12 it is further confirmed that microcapsules are filled with linseed oil.

The results obtained in this study show that linseed oil can not be encapsulated by UF resins using the two-stage method. Under basic pH, the produced UF nanoparticles remain in suspension rather than forming a strong wall shell. Conversely, linseed oil was satisfactorily encapsulated using one acid stage. The microcapsules were easily filtered and no traces of oil appeared during the process. The mechanical strength of the wall shell was optimized through the proper selection of pH of the medium, core-shell mass ratio, amount of surfactant, and agitation rate. The product obtained was a dry white free flowing powder, with adequate mechanical strength. It is worth mentioning that undesirable formation of polymeric UF nano-particles in suspension, which prevents shell formation, was difficult to control. This effect has been described in previous reports. Brown et al. [13] encapsulated dicyclopentadiene by the one-stage synthesis. The formation of UF nanoparticles in solution was prevented by carrying out the reaction under reduced pH (∼2.2). Fan and Zhou [25] they prepared microcapsules by in situ polymerization of UF as the shell material and glass beads as the core material. Glass beads were selected as the core material because their size distribution is narrow and their surface hydrophobicity can be easily controlled. Similarly to Brown et al. [13], the authors found that at high final pH value (∼3.6) and high surfactant concentration prevent the deposition of UF nanoparticles onto the microcapsule surface and results in excessive formation of UF nanoparticles in solution. Nesterova et al. [16] prepared linseed-oil microcapsules to be used in self-healing anticorrosive coatings. After a deep screening of the process variables they found that the presence of surfactant results in excessive UF nanoparticle formation and, consequently, they encapsulated linseed oil in absence of surfactants. Yuan et al. [7] studied the microencapsulation of epoxy resins by the two-stage synthesis. The authors reduced the excessive formation of UF nanoparticles by selecting optimal core/shell (epoxy/UF) weight ratios. In this study, the development of UF particles in suspension was inhibited by reducing the amount of PVA and SDBS surfactants (Table 1) and using high-performance dispersing devices. At low concentration of surfactant, most of it is adsorbed on the linseed oil-water interface. As the concentration of surfactant increases, in addition to adsorption on the linseed oil-water interface, part of the surfactant dissolves in the aqueous phase. Therefore, the formed UF nanoparticles are stabilized in emulsion and can not deposit onto the linseed oil-water interface. Conversely, at the proper concentration of surfactant the deposition of UF particles on the microcapsule surface is not inhibited. In agreement with results reported by Zhou et al. [25], the accumulation of UF nanoparticles onto the microcapsule surface under the one-stage process was markedly affected by the pH of the medium. When the pH of the medium was adjusted at 3.5, the UF nanoparticles remained in suspension and did not deposit onto the microcapsule surface. Conversely at low pH values (∼1.7) the UF nanoparticles accumulate onto the microcapsule surface, thereby contributing to the shell growth. At this point, it is worth noting that the strength and stability of microcapsules is very dependent on the core material. The synthesis by one-stage results in satisfactory linseed-oil filled microcapsules, but encapsulation of alkyldiglycidyl ether by the same method did not result in a free-flowing powder [11]. On the other hand, the synthesis by two-stage provided stable capsules with alkylglycidyl ether as

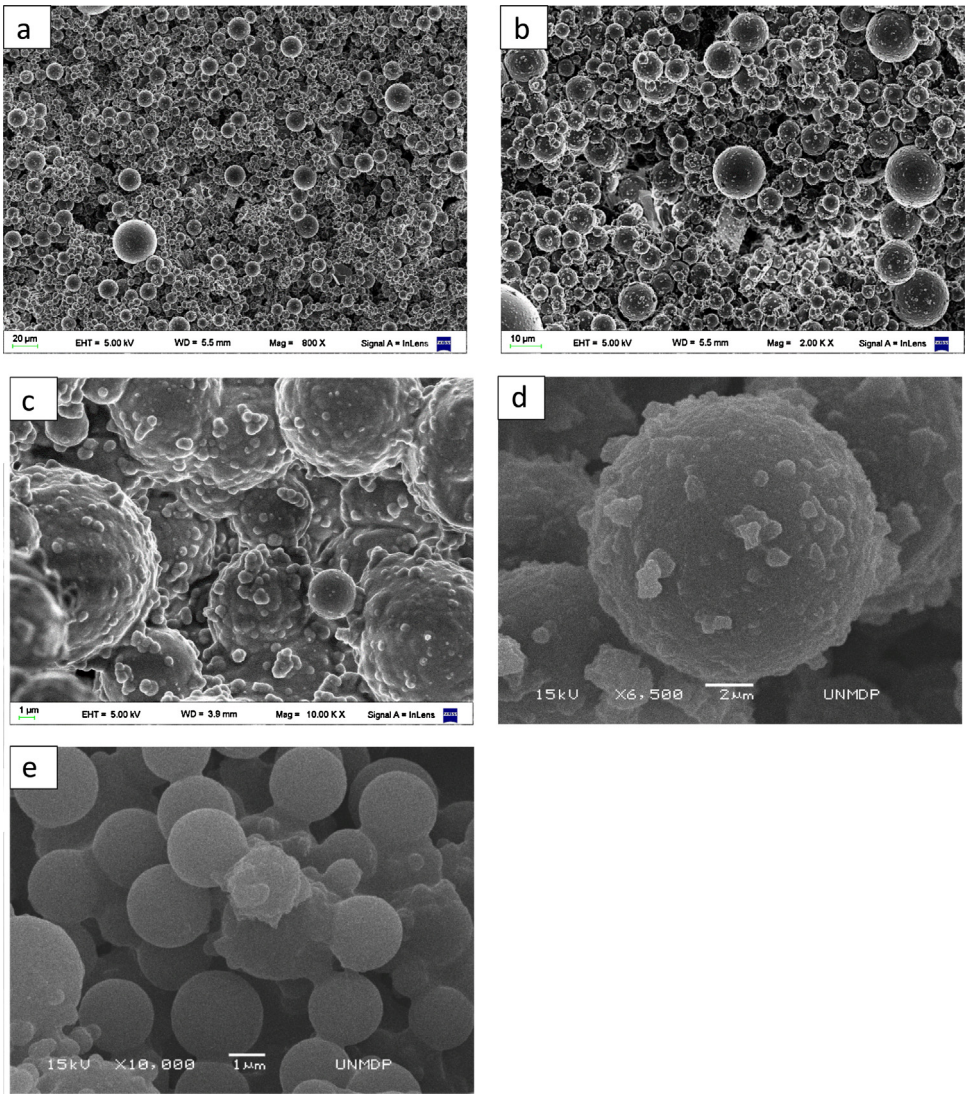

Fig. 10. FE-SEM (a)–(c) and SEM (d)–(e) micrographs taken at different magnification of microcapsules prepared by a one-stage procedure at 50 °C at a core shell: ratio = 1. The linseed oil-in-water emulsion was prepared using an ultrasonic homogenizer and then the reaction was carried out under stirring at 600 rpm.

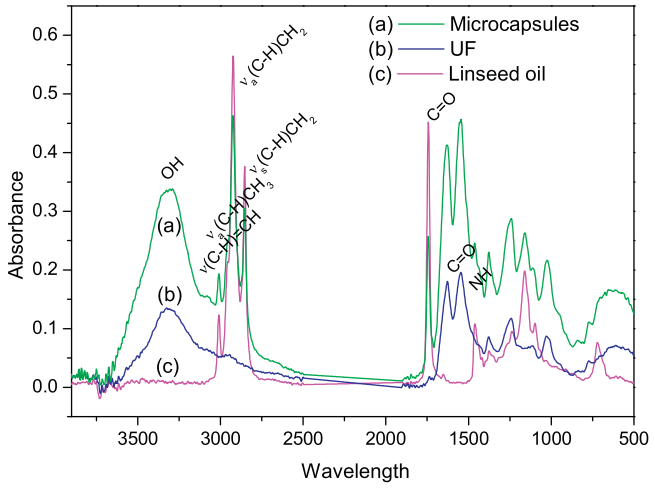

Fig. 11. FTIR spectra of linseed oil, neat UF resin and linseed oil-filled microcapsules.

a core material [11], whereas capsules filled with linseed oil were instable.

4. Conclusion

The performance of different methods of microencapsulation of linseed oil was examined. Linseed oil could not be encapsulated by UF resin using the two-stage method. Under basic pH UF nanoparticles remained in suspension and, therefore, a strong wall shell was not formed. Conversely, linseed oil was satisfactorily encapsulated in urea-formaldehyde (UF) shell by one acid stage polymerization using poly vinyl alcohol and sodium dodecyl benzene sulfonate as stabilizers. This was confirmed by thermal analyses and FTIR studies. Microcapsules produced by one acid stage were strong enough to bear the preparation and drying circumstances and were dried into a free flowing powder, which remained stable under storage for 6 months at ambient laboratory conditions.

The amount of UF particles formed in solution was prevented by adjusting the amount of surfactant, the core/shell ratio and using high-performance dispersing devices.

Spherical microcapsules with diameters in the range of 50–200 μm can be obtained under mechanical agitation at 600 rpm. The size is reduced to 1–20 μm using an ultrasonic homogenizer.

Microcapsules prepared in the absence of surfactant had irregular shapes. The surface activity of UF resins is relatively low and cannot stabilize the core droplets in solution even with the aid

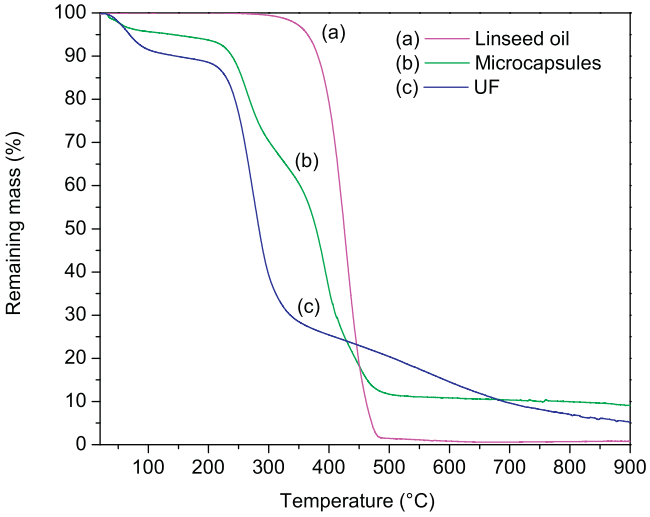

Fig. 12. TGA curves of linseed oil, neat UF resin and linseed oil-filled microcapsules.

of mechanical agitation. Although microcapsules were formed, the results were not satisfactory. The filtered product was a white powder that turned oily and sticky during storage.

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References

[1] J. Syrett, C. Becer, D. Haddleton, Self-healing and self-mendable polymers, Polym. Chem. 1 (2010) 978–987.
[2] K. Dietrich, E. Bonatz, H. Geistlinqer, H. Herma, R. Nastk, Amino resin microcapsules II. Preparation and morphology, Acta Polym. 40 (1989) 325–331.
[3] K. Dietrich, E. Bonatz, R. Nastk, Amino resin microcapsules IV-surface tension ofthe resins and mechanism of capsule formation, Acta Polym. 41 (1990) 91–95.
[4] A.H. Conner, Urea-formaldehyde adhesive resins, in: J.C. Salamone (Ed.), Polymeric Materials Encyclopedia, vol. 11, CRCUSA, 1996, pp. 8497–8501.
[5] T. Yin, M.Z. Rong, M.Q. Zhang, G.C. Yang, Self-healing epoxy composites-preparation and effect of the healant consisting of microencapsulated epoxy and latent curing agent, Compos. Sci. Technol. 67 (2007) 201–212.
[6] L. Yuan, A. Gu, G. Liang, Preparation and properties of poly(urea-formaldehyde). microcapsules filled with epoxy resins, Mater. Chem. Phys. 110 (2008) 417–425.
[7] L. Yuan, G. Liang, J. Xie, L. Li, J. Guo, Preparation and characterization of poly(urea-formaldehyde) microcapsules filled with epoxy resin, Polymer 47 (2006) 5338–5349.
[8] X. Tong, T. Zhang, M. Yang, Q. Zhang, Preparation and characterization of novel melamine modified poly(urea-formaldehyde) self-repairing microcapsules, Coll. Surf. A: Physicochem. Eng. Asp. 371 (2010) 91–97.
[9] Y.C. Yuan, M.Z. Rong, M.Q. Zhang, Preparation and characterization of micro-encapsulated polythiol, Polymer 49 (2008) 2531–2541.
[10] X. Liu, X. Sheng, J.K. Lee, M.R. Kessler, Synthesis and characterization of melamine-urea-formaldehyde microcapsules containing ENB-based self-healing agents, Macromol. Mater. Eng. 294 (2009) 389–395.
[11] T. Nesterova, K. Dam-Johansen, S. Kiil, Synthesis of durable microcapsules for self-healing anticorrosive coatings: a comparison of selected methods, Prog. Org. Coat. 70 (2011) 342–352.
[12] T. Siva, S. Sathiyanarayanan, Self healing coatings containing dual active agent loaded urea formaldehyde (UF) microcapsules, Prog. Org. Coat. 82 (2015) 57–67.
[13] N. Brown, M.R. Kessler, N.R. Sottos, S.R. White, In situ poly(urea formaldehyde) microencapsulation of dicyclopentadiene, J. Microencapsul. 20 (6) (2003) 719–730.
[14] B.J. Blaiszik, M.M. Caruso, D.A. McIlroy, J.S. Moore, S.R. White, N.R. Sottos, Microcapsules filled with reactive solutions for self-healing materials, Polymer 50 (2009) 990–997.
[15] C. Suryanarayana, K. Chowdoji Rao, D. Kumar, Preparation and characterization of microcapsules containing linseed oil and its use in self-healing coatings, Prog. Org. Coat. 63 (2008) 72–78.
[16] T. Nesterova, K. Dam-Johansen, L.T. Pedersen, S. Kiil, Microcapsule-based self-healing anticorrosive coatings: capsule size coating formulation, and exposure testing, Prog. Org. Coat. 75 (2012) 309–318.
[17] S. Hatami Boura, M. Peikari, A. Ashrafi, M. Samadzadeh, Self-healing ability and adhesion strength of capsule embedded coatings-micro and nano sized capsules containing linseed oil, Prog. Org. Coat. 75 (2012) 292–300.
[18] H. Es-haghi, S.M. Mirabedini, M. Imani, R.R. Farnood, Preparation and characterization of pre-silane modified ethylcellulose-based microcapsules containing linseed oil, Coll. Surf. A: Physicochem. Eng. Asp. 447 (2014) 71–80.
[19] T. Szabó, J. Telegdi, L. Nyikos, Linseed oil-filled microcapsules containing drier and corrosion inhibitor-their effects on self-healing capability of paints, Prog. Org. Coat. 84 (2015) 136–142.
[20] M. Behzadnasab, M. Esfandeh, S.M. Mirabedini, M.J. Zohuriaan-Mehr, R.R. Farnood, Preparation and characterization of linseed oil-filled urea-formaldehyde microcapsules and their effect on mechanicalproperties of an epoxy-based coating, Coll. Surf. A: Physicochem. Eng. Asp. 457 (2014) 16–26.
[21] T. Szabó, J.- Telegdi, L. Nyikos, Linseed oil-filled microcapsules containing drier and corrosion inhibitor-their effects on self-healing capability of paints, Prog. Org. Coat. 84 (2015) 136–142.
[22] S. Cosco, V. Ambrogi, Properties of poly(urea-formaldehyde) microcapsules containing an epoxy resin, J. Appl. Polym. Sci. 105 (2007) 1400–1411.
[23] A. Despres, A. Pizzi, Colloidal aggregation of aminoplastic polycondensation resins: urea-formaldehyde versus melamine-formaldehyde and melamine-urea-formaldehyde resins, J. App. Polym. Sci. 100 (2006) 1406–1412.
[24] J.M. Ferra, A.M. Mendes, M.R. Costa, L.H. Carvalho, F. Magalhães, A study on the colloidal nature of urea-formaldehyde resins and its relation with adhesive performance, J. Appl. Polym. Sci. 118 (2010) 1956–1968.
[25] C.J. Fan, X.D. Zhou, Influence of operating conditions on the surface morphology of microcapsules prepared by in situ polymerization, Colloids Surf. A 363 (2010) 49–55.
[26] C.J. Fan, J.T. Tang, X.D. Zhou, Role of ammonium chloride in preparing poly(urea-formaldehyde) microcapsules using one-step method, J. Appl. Polym. Sci. 129 (2013) 2848–2856.