



## Preparation and Evaluation of Paint One and Two Shells Micro-capsules



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THERE are two basic forms of micro-capsules, 1<sup>st</sup> form is covered by one shell made of urea-formaldehyde, while the 2<sup>nd</sup> one is covered by two shells (first one is urea-formaldehyde and the second one made of poly-urethane).

Both forms are filled with two types of corrosion inhibitor (corr A and the other is corr B). Many tests are performed; Optical microscope scanning was applied to the micro-capsules in order to confirm the formation of capsules. Micro-capsules were weighed in order to measure the shrinking rate under heating of the micro-capsules. Infra-red spectroscopy was applied to make sure of the formation of shells of the micro-capsules. Physical properties were monitored weekly to confirm the stability of the micro-capsules. The purpose of preparing these micro-capsules is to install a system of self-healing paints for corrosion protection.

**Keywords:** Micro-capsules, Self-healing, One shell, Two shells, Surfactant, Shrinking time.

### Introduction

Encapsulation of functionally active materials in hollow microspheres is an attractive way of storing, as well as protecting these from environment. Microencapsulated substances have been utilized for sustained drug release [1,2], electro rheological fluids [3], intumescent fire retarding powders [4,5], preservation of flavors [6,7] electro phoretic display applications [8], textiles [9], biotechnology [10,11] and inorganic metal salt catalyst [12],

etc. Recently, there has been growing interest in use of microencapsulated materials for healing of cracks generated during service of a polymer based composite materials [13,14]. Microcapsules containing dicyclopentadiene were incorporated in the composite matrix. These capsules rupture and release dicyclopentadiene during crack formation and react with Grubbs ruthenium catalyst present in the composites leading to crack repair to restore mechanical properties.

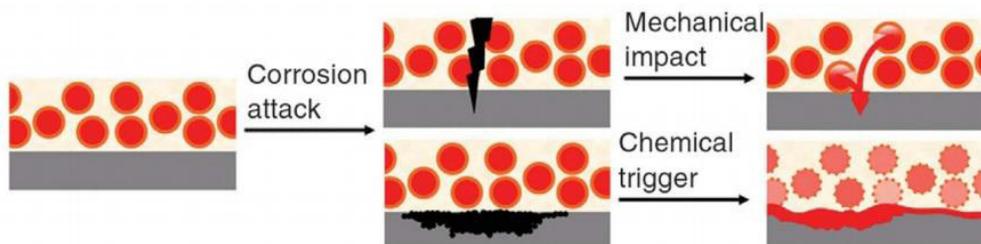


Fig. 1. Mechanism of anti-corrosion micro-capsules working in paints.

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Paints are extensively used for modification of substrates either for aesthetic appearance or for corrosion protection. During its service life, the paint film undergoes changes in mechanical properties leading to formation of micro-cracks which subsequently propagates and exposes substrate to atmospheric moisture and oxygen. This action results in accelerated dis-bonding of the paint and flake formation from the metal coating interface. Paint coatings can be considered as a special class of composite materials, comprising binders and pigments. Hence, the concept of self-healing of cracks, as reported for composites, can be adopted for coatings to provide longer durability. An attempt for healing of scratches on automotive coating using temperature dependent elastic properties of polymer has been reported [15].

Here, we report our work on development of self-healing coatings with microencapsulated drying oil. In this study, linseed oil along with driers has been selected as a healing agent due to its film forming ability by atmospheric oxidation. Microcapsules with

urea-formaldehyde as a shell and drying oil as a core were synthesized by in situ polymerization [13]. Efficacy of these microcapsules in healing of cracks in an epoxy coating and corrosion protection has been demonstrated in the subsequent part.

#### Materials used

##### One shell formation chemicals

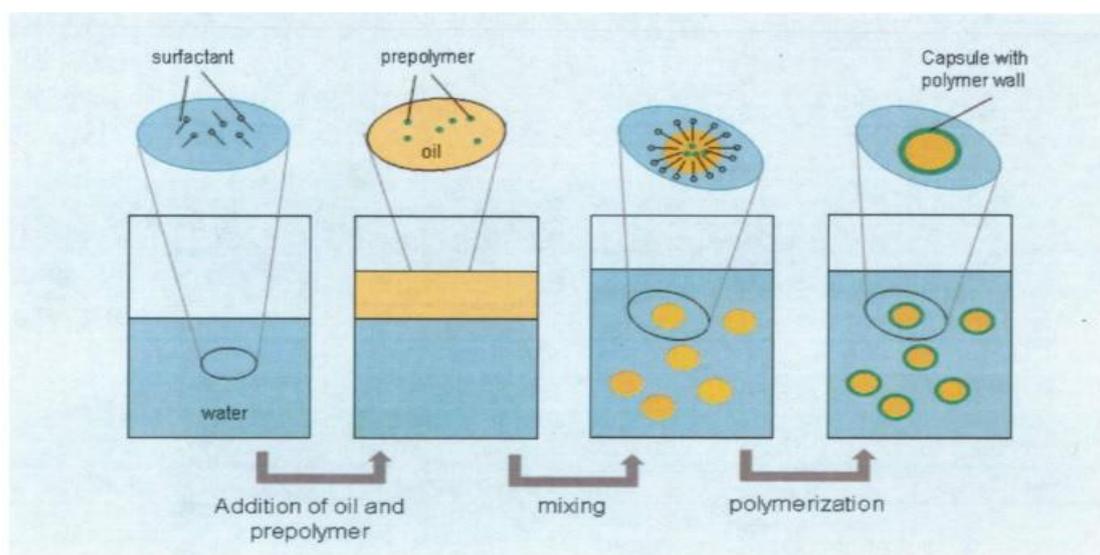
Urea, formaldehyde, ammonium chloride, resorcinol, poly vinyl alcohol (PVA), sodium dodecyl sulphate as stabilizer, nonyl phenol poly ethylene glycol as surfactant and linseed oil.

##### Two shells formation chemicals

Toluene 2,4- di-iso cyanate(TDI), di-ethylene triamine(DETA), micro-capsules obtained from first step would be used as a core material, NP-9 surfactant used as emulsifier added to sodium dodecyl sulphate.

All materials and chemicals are supplied by International trade Co.-Kasr Al-Aini st.-Cairo.

#### Experimental and formation of micro-capsules



**Fig. 2. Mechanism of formation of micro-capsules by oil in water emulsification Experimental synthesis of microcapsules (16).**

#### Experimental synthesis of microcapsules (16)

Microcapsules were prepared by in situ polymerization in oil in- water emulsion. At room temperature, 260 ml of de-ionized water, 10 ml of 5 wt% aqueous solution of polyvinyl alcohol (PVA) and 0.5 gm of sodium dodecyl sulphate were mixed in 1000 ml beaker. Under agitation 5 g urea, 0.5 g ammonium chloride and 0.5 g resorcinol were dissolved in solution. The

pH was adjusted to approximately 3.5 by using 5wt% solution of hydrochloric acid in de-ionized water. One to two drops of octanol was added as an antifoaming agent. 30 ml of linseed oil was added slowly to form an emulsion and allowed to stabilize for 10min under agitation. After stabilization, 12.67 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 200rpm for 4 h.

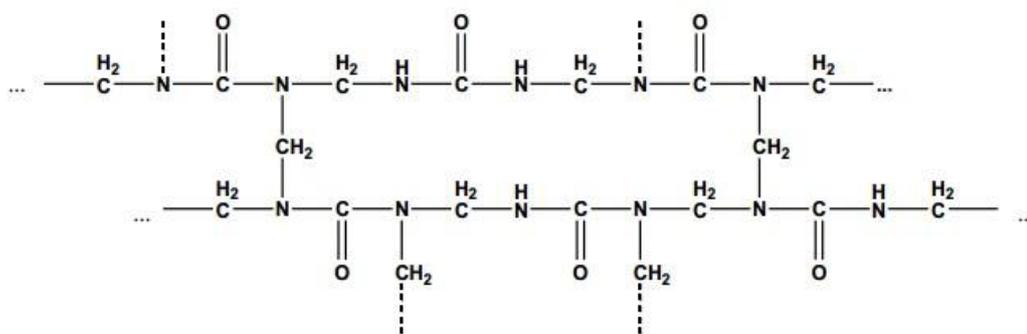
Contents were cooled to ambient temperature. Microcapsules from the suspension were recovered by filtration under vacuum. These were rinsed with water, washed with xylene to remove suspended oil. The capsules were dried under vacuum.

*Preparation of two shells microcapsules (17)*

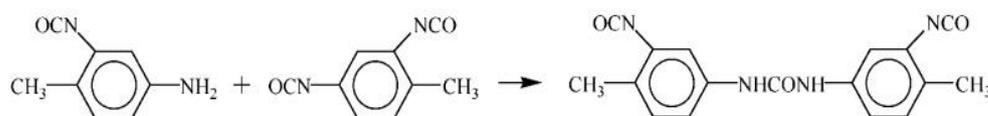
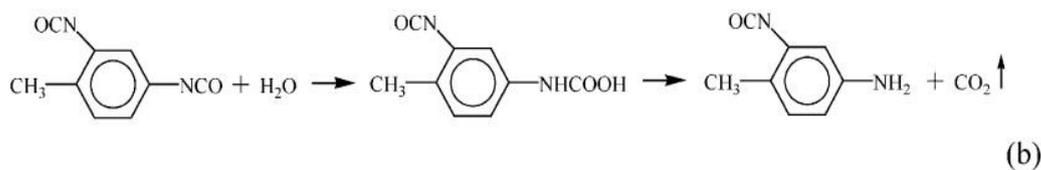
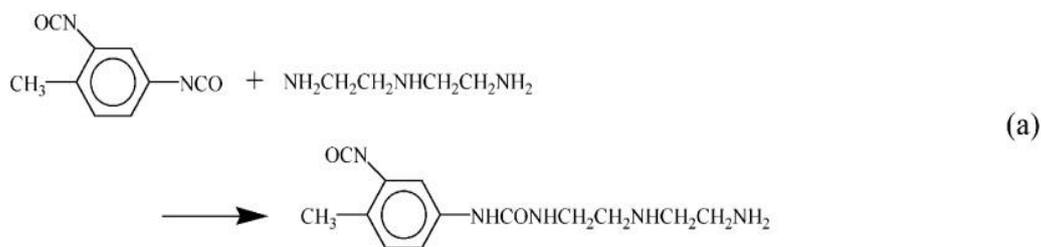
The micro-capsulation was carried out in three necked flask round bottom flask equipped with mechanical stirrer. Prior to encapsulation the surfactant NP-9 (2.5 gm) was added to 80 ml

water. An organic solution of cyclo-hexane (10 ml) added to TDI (3 gm) was prepared. The organic solution was added to the surfactant solution and the mixture was stirred with rate between 400-500 rpm to form oil in water emulsion. After 3 minutes of stirring, DETA was diluted by dis.water (20 ml) and added slowly to start the interfacial condensation reaction continued to 90 minutes at 60 centigrade.

Resultant micro-capsules were filtered and then washed with water to remove the excess of DETA and dried in vacuum oven.



**Fig. 3. Formula of cross-linked poly-urea formaldehyde capsules shell.**



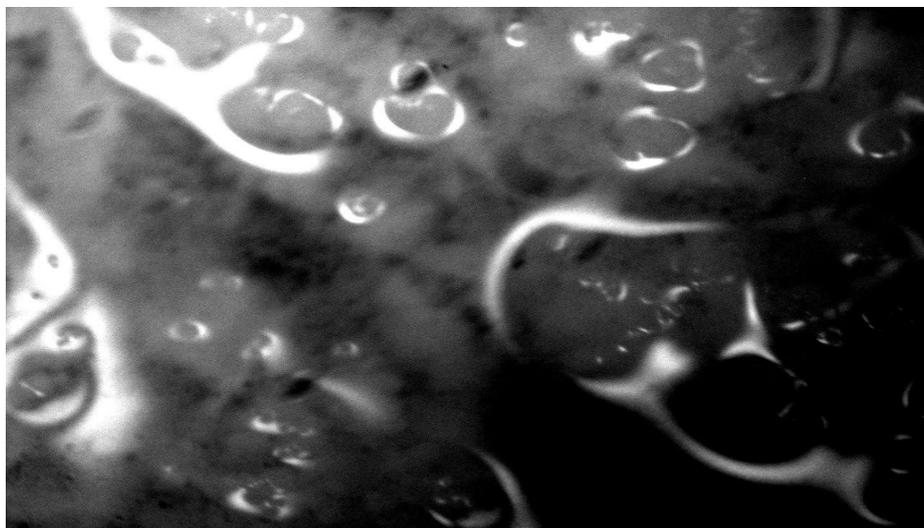
**Fig. 4. Formula of poly-urethane micro-capsules shell .**

*Tests applied on micro-capsules*

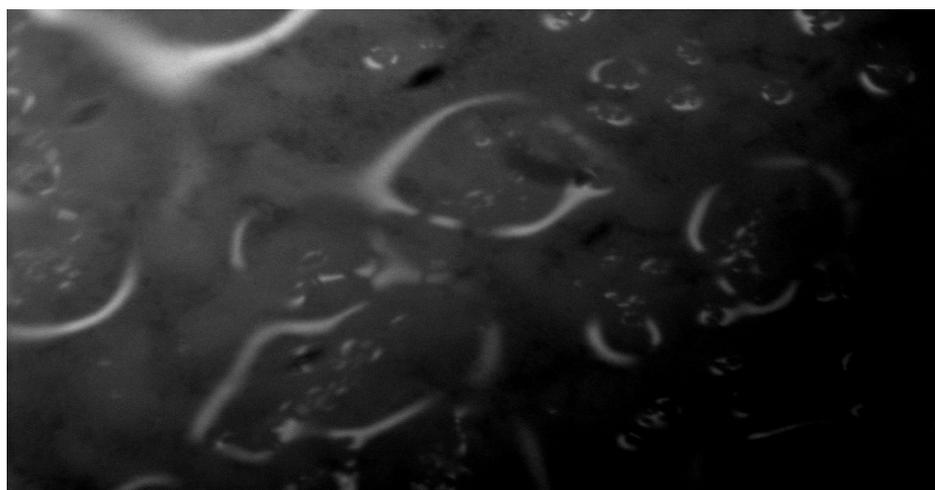
- 1- Optical microscope: applied to confirm the formation of capsules.
- 2- Shrinking time: weighing the micro-capsules weekly in order to notice the change in weight and shrinking rate.
- 3- Thermal gravimetric analysis: Microcapsules, linseed oil and urea-formaldehyde resin were analyzed using thermo gravimetric analyzer (Auto TGA 2950HR, TA instruments) in nitrogen environment with a sample weight of about 3 mg. Heating rate was maintained at 20°C/min in the temperature range of 30–600°C.
- 4- Infra-red spectroscopy: Spectra of shell

and core material extracted from Soxhlet apparatus were recorded on Fourier Transform Infrared spectrophotometer (NICOLET 5700 Thermo Electron Corporation). The solid shell material collected after soxhlet extraction was mixed with KBr and palette was prepared for recording spectra. Infra-red spectra of extract after using Soxhelt apparatus, neat linseed oil and urea-formaldehyde resin were also recorded.

- 5- Physical stability: monitoring the stability of micro-capsules daily, write down any change in the physical appearance.

**Results and Discussion***Optical microscope results*

**Fig. 5.** One shell micro-capsules formation under optical microscope.



**Fig. 6.** Final shot of formation on micro-capsules under optical microscope.

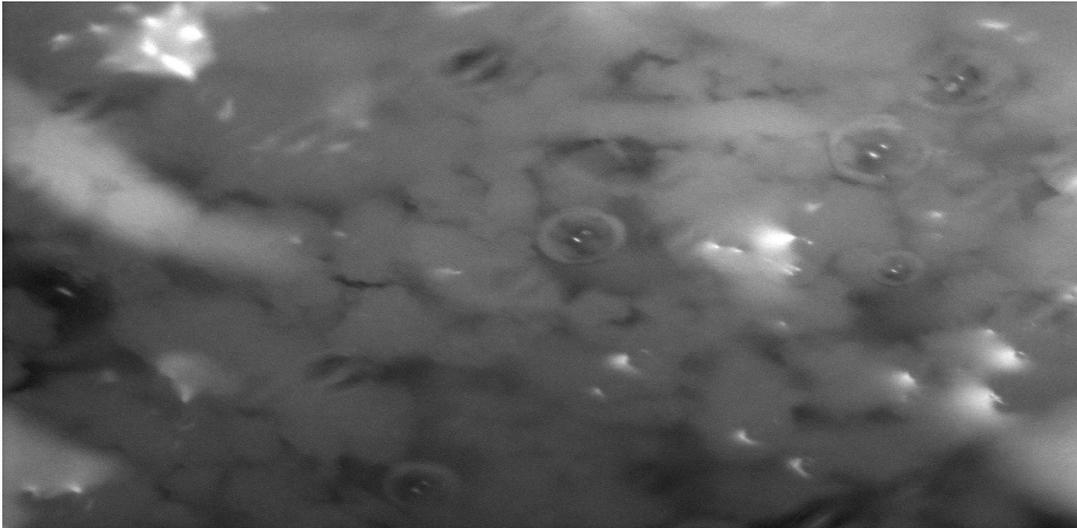


Fig. 7. Formation of two shells micro-capsules under optical microscope.



Fig. 8. Final shot of formation of two shells micro-capsules.

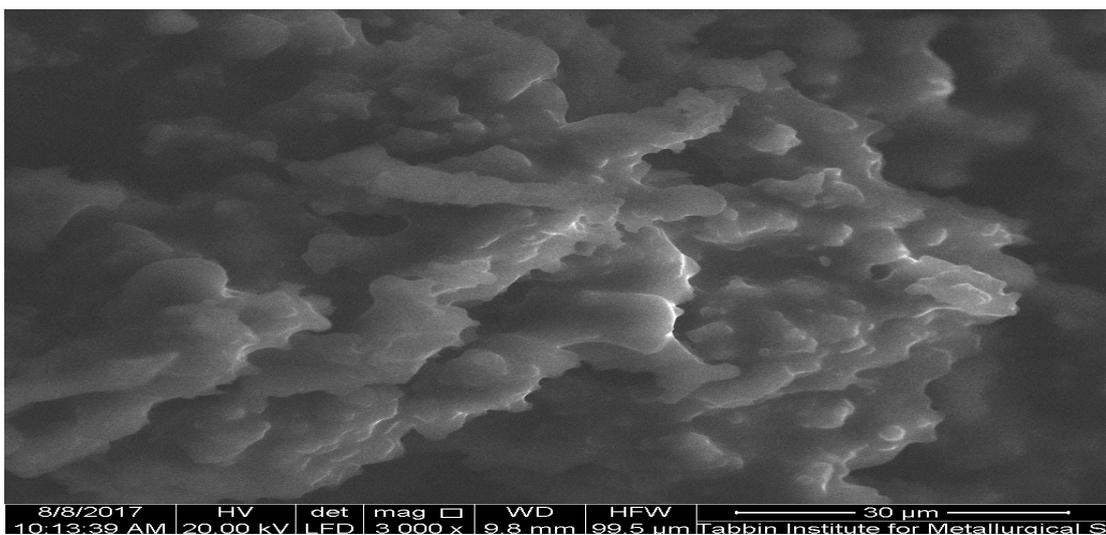


Fig. 9. SEM shot of formation of two shells micro-capsules.

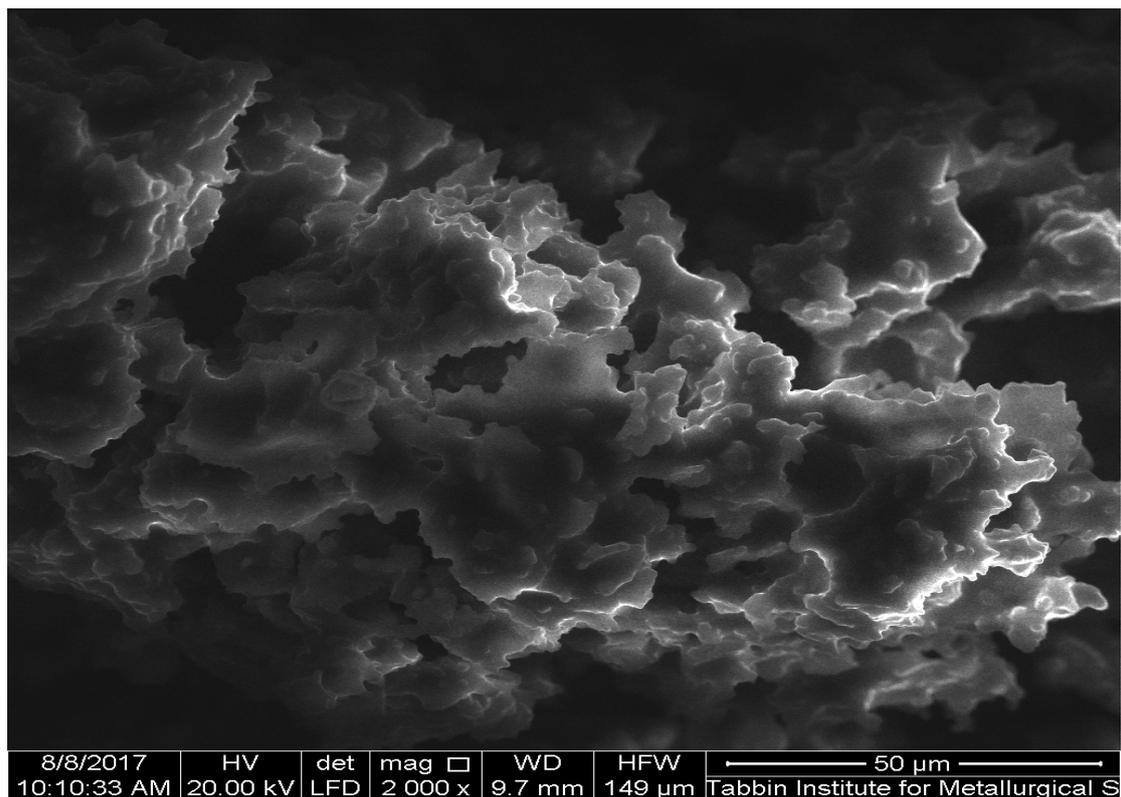


Fig. 10. SEM shot of formation of two shells micro-capsules

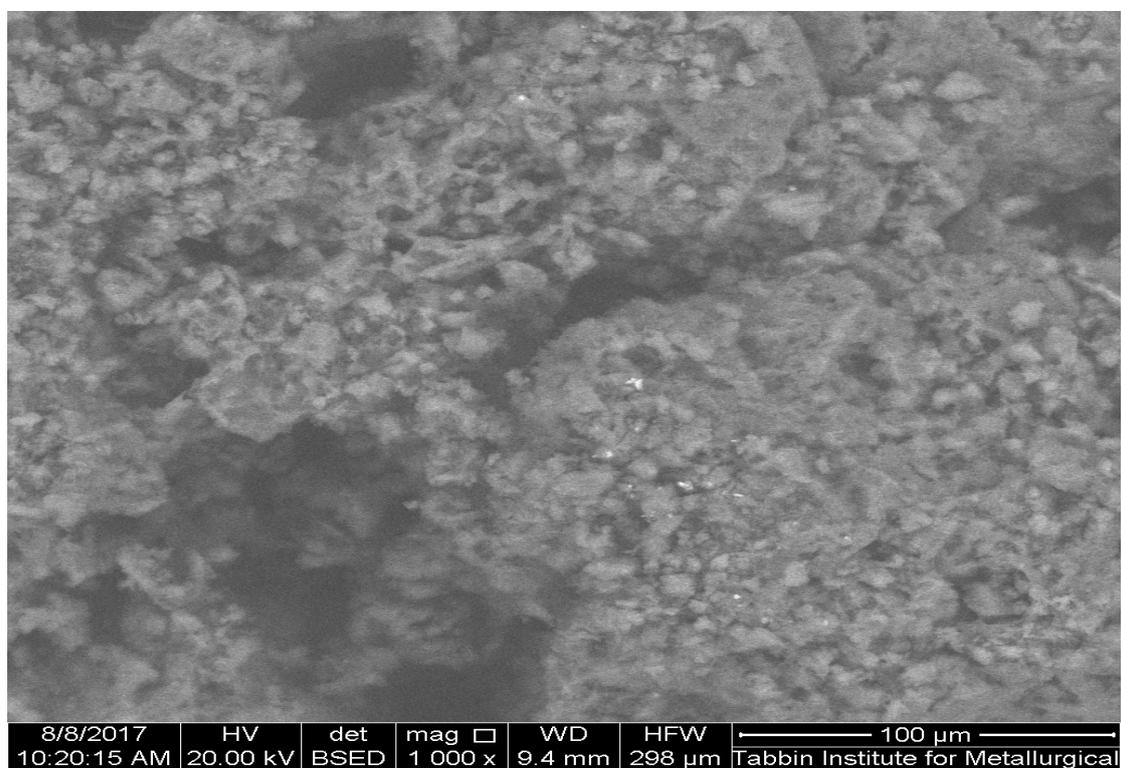


Fig. 11. Final shot of formation of two shells micro-capsules.

*Mechanism of formation of micro-capsules:**Optical and SEM photos analysis*

The formation of urea–formaldehyde capsules has been described by Park et al. [7]. The process comprises reaction of urea and formaldehyde to obtain methylol ureas, which further condenses under acidic conditions to form the shell material.

Encapsulation of linseed oil in the capsules takes place simultaneously during formation of cross-linked urea–formaldehyde polymer. Reactants urea and formaldehyde are soluble in water. When the pH is changed to acidic and heated to 55°C, urea and formaldehyde react to form poly (urea–formaldehyde) as stated above. During the initial stage of polymerization, urea–formaldehyde molecule is rich with polar groups and is water compatible. The number of polar groups will gradually reduce as molecular weight of polymer increases. Finally after attaining

certain molecular weight, hydrophylicity of urea–formaldehyde polymer molecule will reduce leading to separation from aqueous phase and get deposited on the already emulsified oil droplets (hydrophobic organic phase). This process continues and a thin shell is formed over oil droplets. The thickness of the shell has been optimized in such a way that the shell contains maximum amount of core material. A shell thickness of 0.2mm was obtained at rpm of 250 to contain 80% linseed oil.

*Shrinking time:*

It is conducted via weighing the micro-capsules weekly, in order to notice the change in weight and shrinking rate.

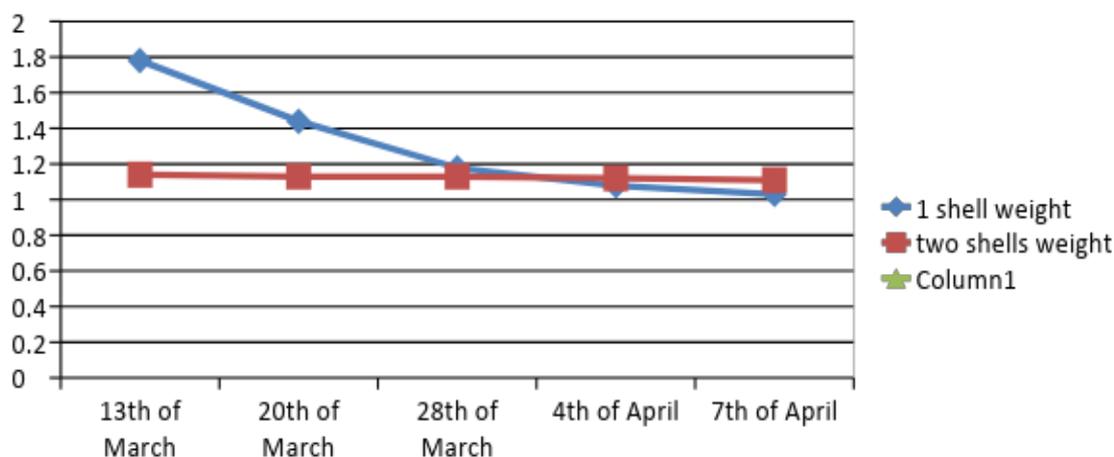
Starting with 1 shell weight of 1.78 grams and 2 shells weight of 1.14 grams and notice the losing in weight weekly.

**TABLE 1. Weight of the one and two shells micro-capsules losing with time.**

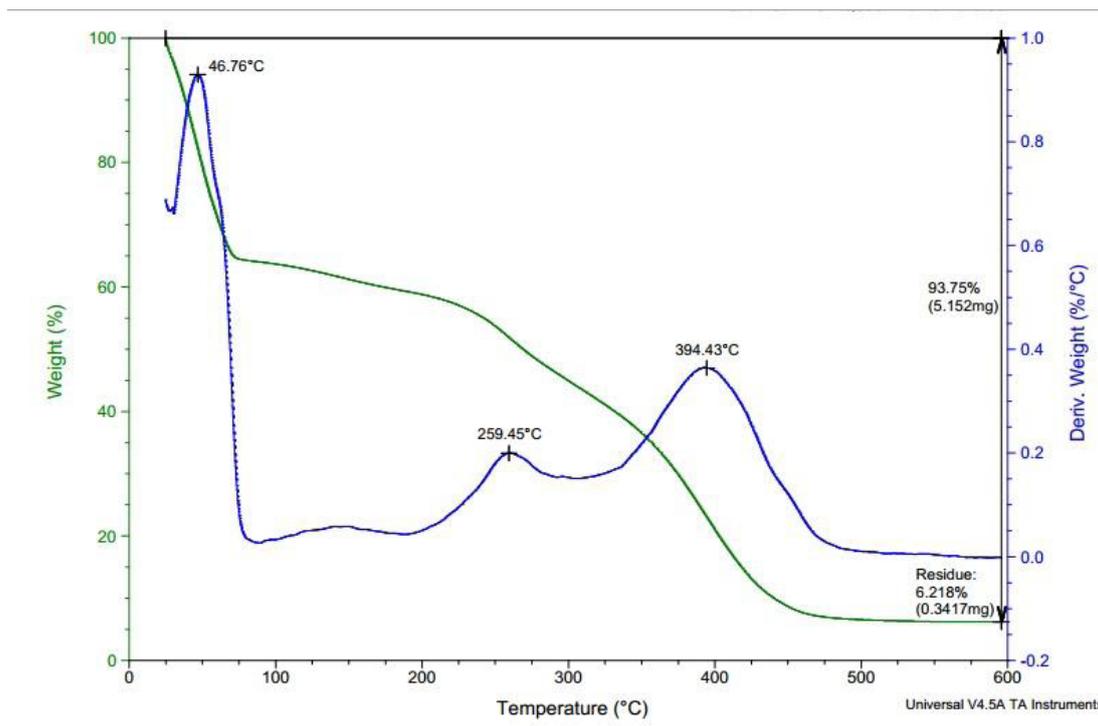
Date / weight	shells micro-capsule <sup>2</sup>	shell micro-capsule <sup>1</sup>
2017/3/13	1.14	1.78
2017/3/20	1.13	1.44
2017/3/28	1.12	1.178
2017/4/11	1.12	1.072
2017/7/11	1.11	1.03

From the results, the two shells micro-capsules show more stability and the losing weight of capsules is slow compared with one shell micro-

capsules which mean the more strength and more life time of capsules.



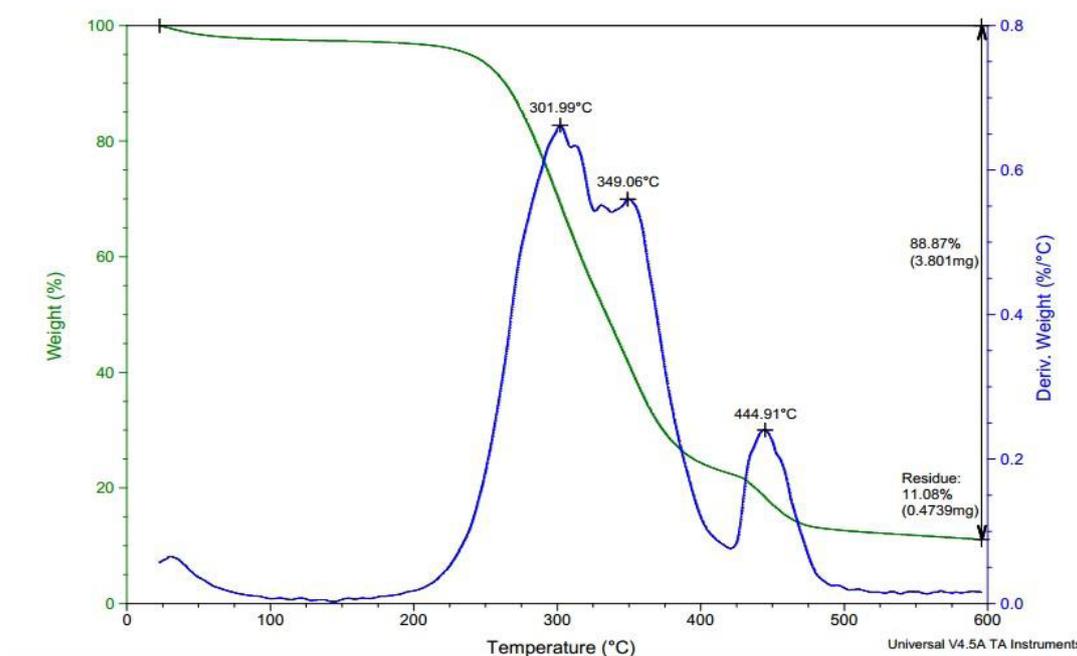
**Fig. 12. Losing weight chart of one and two shells micro-capsules.**

*Thermal gravimetric analysis*

**Fig. 13.** TGA for one shell micro-capsules (urea formaldehyde).

The TGA test is carried out by taking a few amount of the sample and exposed to heat, then recording time and weight till 600 °C. From the results shown in Fig. 5, the destruction starts at

100 °C, then it continues quickly till 375 °C where the remaining residue is about 30%, the slow rate of destruction was shown till 600 °C where the remaining residue is 8 %.



**Fig. 14.** TGA for two shells micro-capsules.

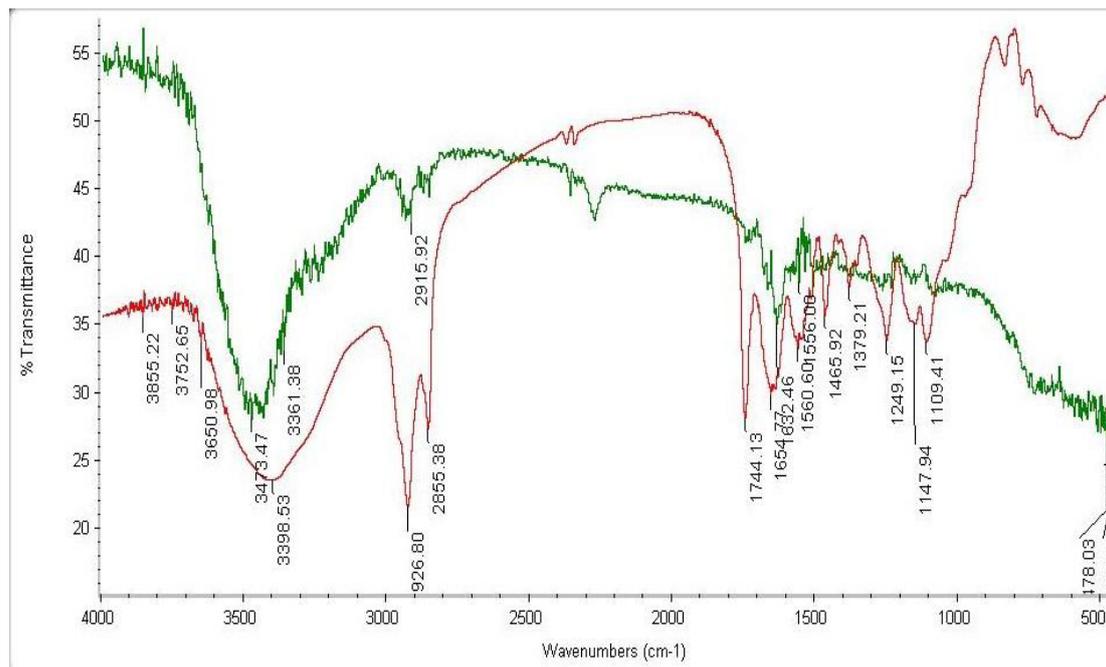


Fig. 15. Comparison between two types of micro-capsules (one and two shells) under IR analysis.

For the composite material, from the results shown in Fig.16, the destruction starts at 230°C with slow rate, showing maximum lose is between 300 °C – 444 °C where about 60% is lost. The rate becomes slow again till 600 °C where the remaining residue 30% of the weight.

#### *Infra-red spectroscopy*

##### *FTIR- analysis for micro-capsules:*

Most of the particles fall in the size range around 50m. This is quite satisfactory for using paints.



Fig. 16. Fresh micro-capsules prepared (one shell micro-capsules).

Microcapsules prepared from urea-formaldehyde resin (shell material) and filled with linseed oil (core material) were characterized using different instrumental techniques. Core and shell of the microcapsules were separated by Soxhlet extraction. FTIR spectra were recorded.

1. red chart: one shell micro-capsules formation of urea formaldehyde.

Peaks of a N-H stretching vibration at  $1560\text{cm}^{-1}$ , a C-O stretching vibration at  $1654\text{cm}^{-1}$ , and a C-H stretching vibration at  $1465\text{cm}^{-1}$ . C-N stretching vibrations

are shown at  $1249$  and  $1147\text{cm}^{-1}$ . The O-H peak is shown as a broad absorption peak at  $3500\text{--}3200\text{cm}^{-1}$ . This spectrum confirms that shell material is made of urea-formaldehyde polymer.

2. green chart: The same peaks of the red chart but with less noise and the peaks of polyurethane are shown in the region of  $1650\text{--}1750\text{cm}^{-1}$ .

*Physical stability:*

By noticing the stability of micro-capsules daily, write down any change in the physical appearance.



**Fig. 17.** The change in micro-capsules color after four months One shell micro-capsules.



**Fig. 18.** Left side shows the fresh micro-capsules while the right side shows the micro-capsules after four months One shell micro-capsules



**Fig. 19.** Left side shows the fresh micro-capsules while the right side shows the micro-capsules after four months two shells micro-capsules

From Fig. 16 - 19, it is noticed the following:

1. The micro-capsules give a white color when freshly prepared.
2. The color starts to change with time and turns to yellow which means the starting of cracking and spreading of inside material. Note that: the capsules are strongly affected by UV.
3. The two shells micro-capsules need more time than the one shell micro-capsules to start cracking, also show more strength and sticky shape and performance.

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### تحضير وتوصيف الكبسولات الميكرونية ذات القشرة والقشرتين

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كلا النوعان مملوء بمادة مضادة للتآكل: الاولى (كورر أ) والثانية (كورر ب).

يتم عمل عدة اختبارات للتأكد من التركيب وهى: الفحص بالميكروسكوب الضوئى، وزن الكبسولات لتقييم مدى الانكماش تحت تأثير الحرارة، اختبار الأشعة تحت الحمراء للتأكد من تركيب الكبسولات. الخواص الفيزيائية يتم فحصها اسبوعيا للتأكد من استقرار الكبسولات الميكرونية. الغرض الاساسى من تحضير الكبسولات الميكرونية هو تجهيز نظام للبيوتات ذاتية الالتئام لمقاومة التآكل.