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# Preparation and characterization of microcapsules containing linseed oil and its use in self-healing coatings

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ABSTRACT

Effectiveness of linseed oil filled microcapsules was investigated for healing of cracks generated in paint/coatings. Microcapsules were prepared by *in situ* polymerization of urea–formaldehyde resin to form shell over linseed oil droplets. Characteristics of these capsules were studied by FTIR, TGA/DSC, scanning electron microscope (SEM) and particle size analyzer. Mechanical stability was determined by stirring microcapsules in different solvents and resin solutions. Cracks in a paint film were successfully healed when linseed oil was released from microcapsules ruptured under simulated mechanical action. Linseed oil healed area was found to prevent corrosion of the substrate.



## 1. Introduction

Encapsulation of functionally active materials in hollow microspheres is an attractive way of storing as well as protecting these from environment till required for fulfilling appropriate applications. Microencapsulated substances have been utilized for sustained drug release [1,2], electro rheological fluids [3], intumescent fire retarding powders [4,5], preservation of flavours [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 reacts with Grubbs ruthenium catalyst present in the composites leading to crack repair to restore mechanical properties.

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 microcracks which subsequently propagates and exposes substrate to atmospheric moisture and oxygen. This action results in accelerated disbonding 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 dependant 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.

## 2. Materials and methods

Urea, formaldehyde, ammonium chloride, resorcinol, poly vinyl alcohol (PVA) and red dye (Disperse red 1) were procured in AR grade from Sigma Aldrich. Epoxy resin (XR-87) was purchased from Atul Limited, India; epoxy hardener (Ancamine 2280) was obtained from Air Products India Limited. Linseed oil (commercial grade) was purchased from Jayant Oil Mils Pvt. Limited, India. All chemicals/materials were used without any purification.

### 2.1. Experimental synthesis of microcapsules

Microcapsules were prepared by *in situ* polymerization in an oil-in-water emulsion. At room temperature, 260 ml of deionised water

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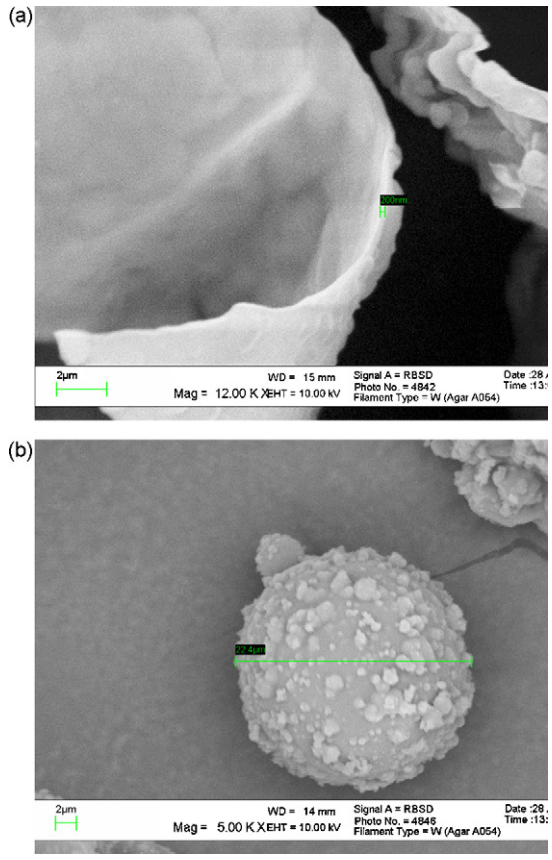


**Fig. 1.** SEM micrographs: (a) shell thickness and (b) shell morphology of microcapsules.

and 10 ml of 5 wt% aqueous solution of polyvinyl alcohol (PVA) 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 5 wt% solution of hydrochloric acid in deionised water. One to two drops of octanol was added as an antifoaming agent. 60 ml of linseed oil containing 0.7 wt% cobalt naphthenate and 2.5 wt% lead octoate driers was added slowly to form an emulsion and allowed to stabilize for 10 min 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 200 rpm 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.

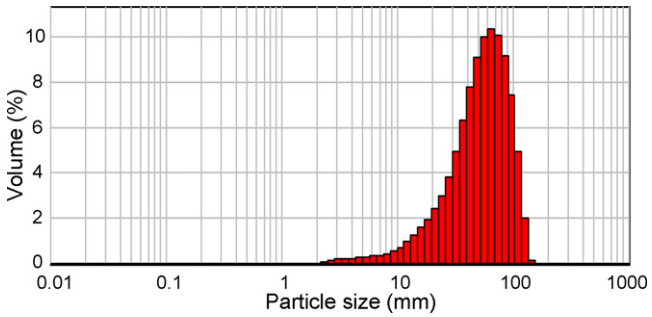


**Fig. 2.** Particle size analysis of microcapsules.

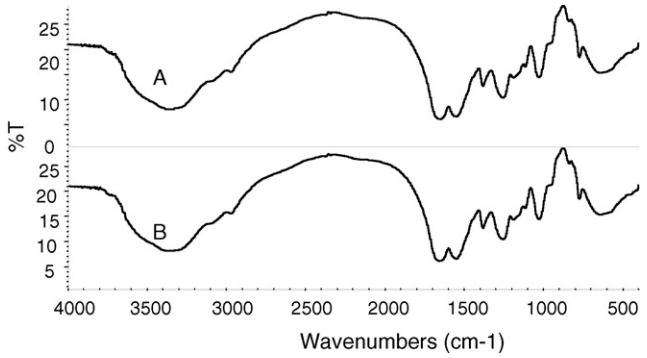


**Fig. 3.** FTIR spectrum: (A) urea–formaldehyde resin and (B) shell material of microcapsule.

### 2.2. Analysis of microcapsule size and shell morphology

Microcapsule size analysis was carried out with a particle size analyzer (Mastersizer 2000, Malvern). Surface morphology and shell thickness of microcapsules were determined by scanning electron microscopy, (LEO1455). Microcapsules were mounted on adhesive tape and ruptured with a razor blade for shell thickness measurement.

### 2.3. Thermal analysis of microcapsules

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 30–800 °C.

Similarly samples were also analyzed by using differential scanning calorimeter (SetsysTG-DSC 16, TA instruments) in oxygen environment with sample weight of about 3 mg at heating rate of 20 °C/min, between 30 and 900 °C.

### 2.4. Linseed oil content in microcapsules

Amount of linseed oil present in microcapsules was determined by extracting oil in a soxhlet apparatus. A known weight of microcapsules ($W_C$) was crushed using pestle and mortar and transferred to a thimble of known weight ($W_{ti}$), pestle and mortar were rinsed with xylene and added to thimble. Extraction was carried out using xylene as a solvent for linseed oil. After 1 h of extraction, thimble was carefully taken out of the soxhlet apparatus and after com-

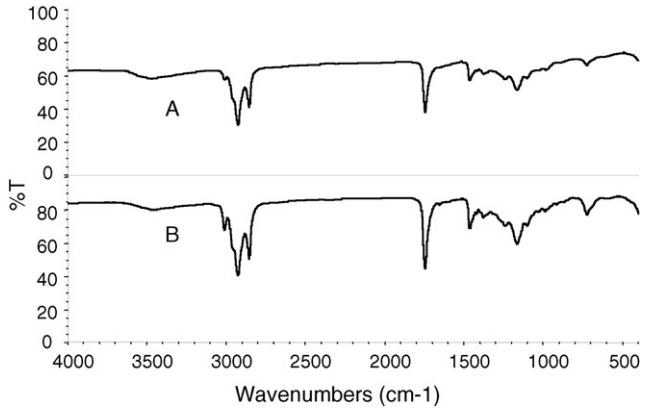


**Fig. 4.** FTIR spectrum: (A) linseed oil and (B) core material of microcapsule.