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FABRICATION AND CHARACTERIZATION OF POLY(UREA-FORMALDEHYDE) MICROCAPSULES FILLED WITH CITRONELLA OIL

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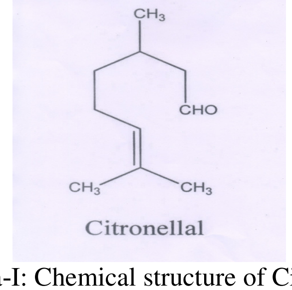
ABSTRACT
These days microencapsulation is finding extensive applications in number of commercial fields.Here we report fabrication & consequent characterization of Poly urea-formaldeyde (UF) microcapsules filled with citronella oil as core material.The chemical structure of the microcapsule was inferred from the FTIR studies.Thermal studies were undertaken to compare the thermal profiles of the fabricated microcapsules with that of poly(U-F) resin.This strongly corroborates the formation of microcapsules filled with citronella oil.Finally SEM studies confirm the formation of microcapsules with entirely different size & morphology compared to that of UF resin and core materials were observed as yolk.
Keywords: polymer,thermochemistry,microencapsulation,citronella oil,urea-formaldehyde resin,FTIR spectra

INTRODUCTION

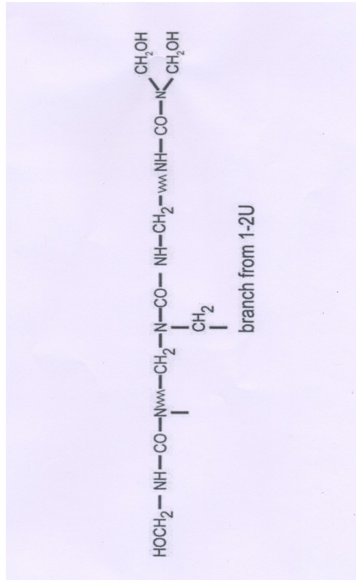
Microcapsules are tiny hollow particles those contain active chemicals as core material protected by the shell[1] . Core materials may be stored or be released under certain conditions.The diameter of the microcapsule are usually in the range of 1-1000μm. The core materials of the capsules may be drugs,fragarant oils,dyes,etc.

Since 1960 microcapsules have been finding applications in a number of commercial fields ranging from chemical[2] and pharmaceuticals[3] to cosmetics[4] and printing ink [5] industries.White et al[6] have demonstrated autonomic healing of structural polymers using microcapsules of poly(urea-formaldehyde) shell filled with dicyclopentadiene .The core materials may be released from the core under the action of surface tension and may polymerize in presence of Grub catalyst and may heal the cracks in structural polymers.Publication of this paper triggered the publication of a few outstanding papers depicting still smarter applications of microencapsulation[7-9].

It may be mentioned in this context that citronella oil is widely used as an insect repellant and also as an anti-bacterial reagent.These microcapsules may find potential application in the field of targeted delivery of the said oil in micro-cracks of a wood substrate to prevent brown rot arising from bacterial attack brought by insects.



Formula-I: Chemical structure of Citronellal



Formula-II: The chemical structure of the fragment of UF resin that statistically occur most frequently.

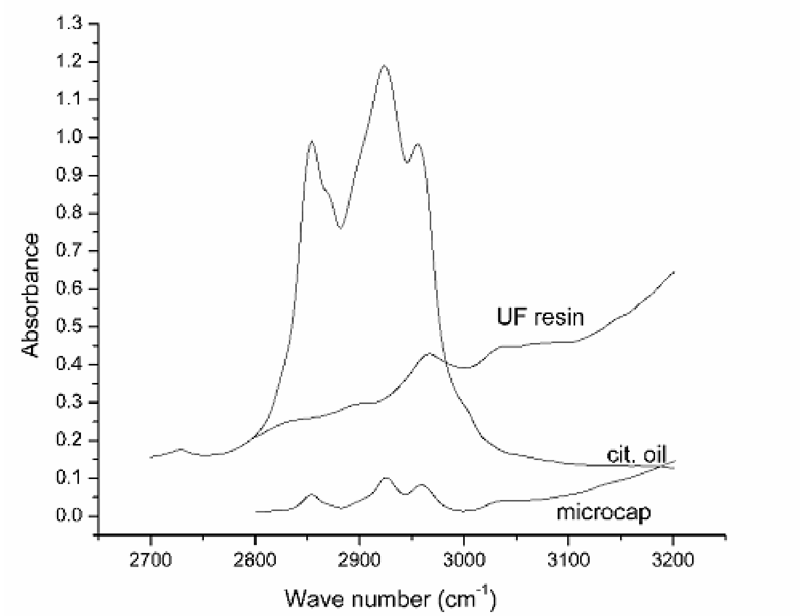


Fig-1: FTIR spectra of UF resin,citronella oil and that of UF resin microcapsules filled with citronella oil in the region of 2800-3200 cm -1

EXPERIMENTAL

Materials necessary

1. Urea,A.R. grade,E-Merk
2. Formalin(37wt% aq. solution of formaldehyde), Loba Chemicals,Mumbai(India)
3. Triethanolamine,E-Merk,India
4. NaDBS(sodium dodecyl benzene sulphonatte),Loba Chemicals,Mumbai(India)
5. Citronella oil(commercial grade),Department of Forestry,Govt. of West Bengal(India)

6. Sulphuric Acid,A.R. grade,E-Merk,India

Fabrication of microcapsules

1. **Preparation of prepolymer:**

81ml(0.5 mole) of formalin(37 wt%) was taken in a 250ml 3-naked round bottom flask. 15g of urea(0.25 mole) was slowly dissolved in it. The pH of this solution was adjusted to 8-9 by dropwise addition of triethanol amine.This mixture was stirred at 70°C for 1 hour.Urea-formaldehyde prepolymer was thus prepared.

2. **Fabrication of microcapsules:**

Under agitation 1% NaDBS solution was added into the prepolymer solution of urea-formaldehyde prepared earlier. Then 5ml of citronella oil was added to it very slowly(0.5ml per two second) with constant stirring to form an oil-in-water emulsion. Dropping rate decides the size of microcapsule[9]. After stirring for 30 minutes the pH value of the solution was slowly adjusted to 2-3 by adding 10 wt% of H_2SO_4 and the emulsion was slowly heated to the target temperature of 60-65ºC.After maintaining this temperature for 3 hours ,another dose of 0.25mole of urea i.e.15g of urea was further added under agitation.This was done to ensure total removal of formaldehyde from the system. Moreover, urea:formaldehyde mole ratio was maintained at 1:1,so that release of formic acid is least [10].

Sometime afterwards a creamy white suspension of microcapsules were obtained.Then the RB flask was cooled down to the ambient temperature. The suspension was rinsed with deionized water and subsequently with acetone.Filtered residue was washed and air dried for 24 hours to obtain UF microcapsules filled with citronella oil.

3. Prior to that UF resin was prepared in a similar fashion without adding citronella oil and surfactant.

FTIR spectra of citronella oil, globules of UF resin and that UF microcapsules filled with citronella oil were recorded in a Nicolet FTIR spectro-photometer(model no:IR Magna 750) with a resolution of 4 cm^{-1} .Prior to that 50 scans were co-added.

TG,DTA and DSC thermograms of the globules of UF resin and that of citronella oil filled UF microcapsules were recorded in a thermal analyzer,T.A Instrument, model No: SDT Q 600 from the ambient temperature to 500ºC with a heating rate of 10°C/min.

The SEM diagram of UF microcapsules containing citronella oil and that UF globules were recorded in a JEOL field emission scanning electron microscope(model no:JSM6700F) .The elemental composition for both the samples were obtained from the energy dispersive spectroscopic (EDS) studies.

Main constituent of citronella oil is citronellal,a biterpinoid whose structure is depicted below(formula I) alongwith that of structural unit of acid catalysed UF resin (formula II).The structure of citronellal shows it contains hydrogen configurations like sp^3CH_3,sp^3CH_2,sp^3CH and sp^2CH(olefinic).Free UF resin essentially contains only one hydrogen configuration ,viz,sp^3CH_2.

The spectra of microcapsule recorded in the range of 2800-3100 cm^{-1} show a band corresponding to sp^3 CH_3(sym) at 2954 cm^{-1} alongwith sp^3CH_2(sym & asym) at 2854 cm^{-1} & 2923 cm^{-1} respectively,shown in fig 1.A broad hump is also observed near 3020 cm^{-1} assigned as sp^2CH(olefinic). All assignment were done according to Dasgupta[11].From the above observations we infer that UF microcapsules filled citronella oil has been fabricated.

Fig 2(a) depicts the TG thermogram of UF resin globules and that of UF microcpsules filled with citronella oil.In case of UF resin globule there is only one endothermic peak upto the range of 100°C , suggesting removal of residual water. Sharp weight loss begins at about 230°C. In case of UF microcapsules filled with citronella oil ,three peaks were observed. The first peak at about 48□C was assigned to the removal of citronella oil(boiling point 47°C).This is followed by a broad exothermic peak ranging from 100ºC to 190ºC assigned as degradation of citronellal/geraniol(geraniol is also present in citronella oil,although in lesser proportion) into isoprene.This is followed by another exothermic peak at about 270°C ,assigned as degradation of other constituents present (in citronella oil) apart from citronellal and geraniol. Less sharper weight loss,compared to that observed in the TG thermogram of UF resin , begins at about 280°C .Weight loss between 270°C to 315°C is due to the degradation of UF resin. The gradient of the thermogram of the UF globules differ considerably from that of microcapsules up to the extent of rapturing of microcapsules(as a sequel to the degradation of UF resin).This suggest their thermal conductivity vary widely as because they are chemically different upto the extent of completion of degradation of UF resin.After the release of core material or their degradation product , the degradation product of the UF resin is similar in both the cases and after 350ºC two thermograms are parallel to each other suggesting that both the materials posseses same thermal conductivity and are chemically identical .

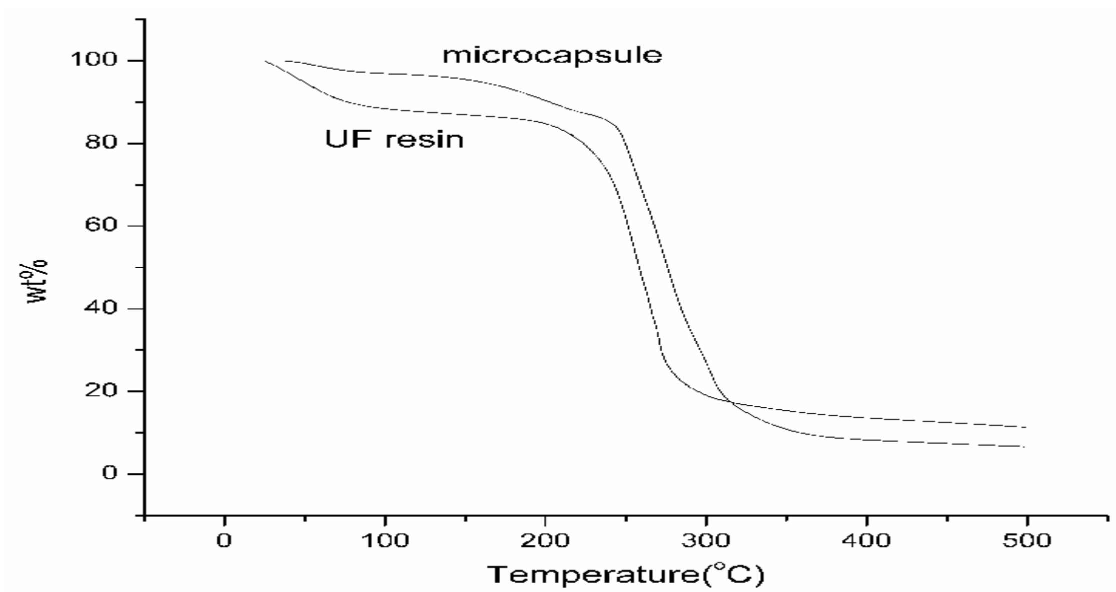


Fig-2(a): TG of UF resin and that of UF resin microcapsules filled with citronella oil.

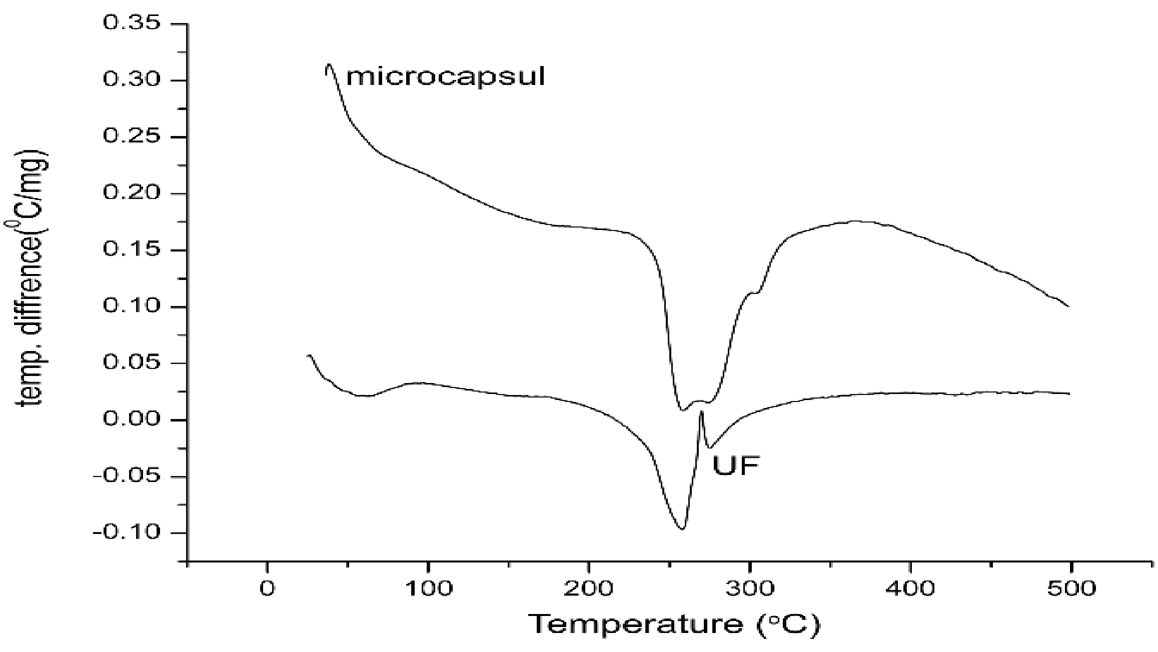


Fig-2(b): DTA of UF resin and that of UF resin microcapsules filled with citronella oil.

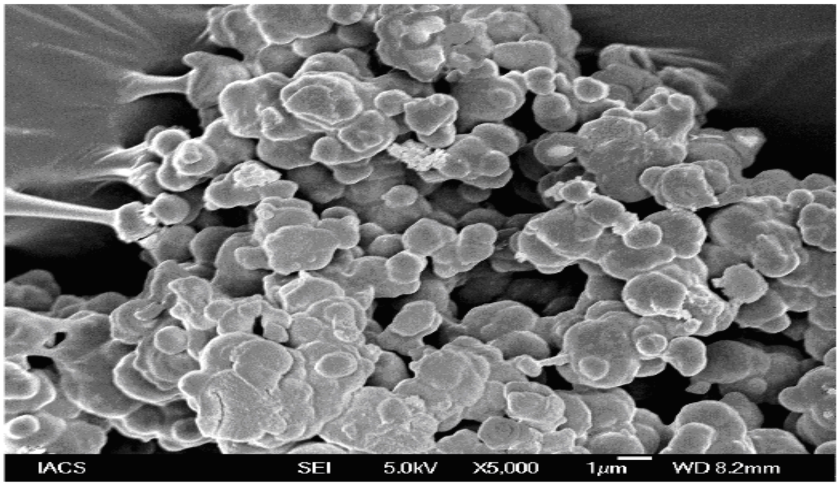


Fig-3(a): SEM diagram of UF resin

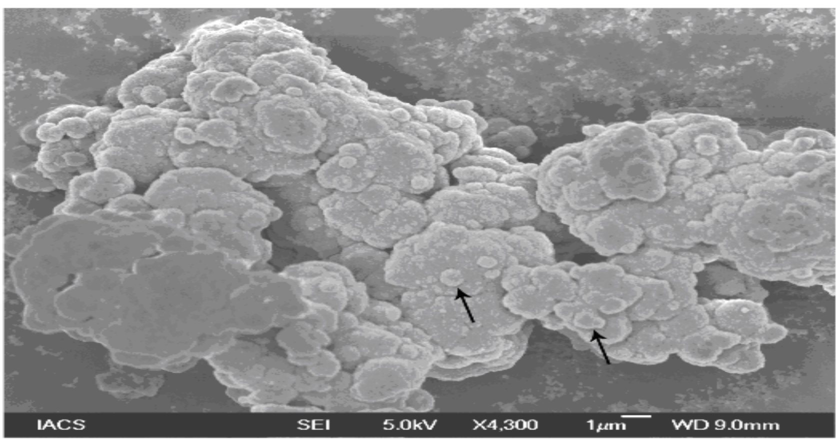


Fig-3(b): SEM diagram of UF resin microcapsules filled with citronella oil

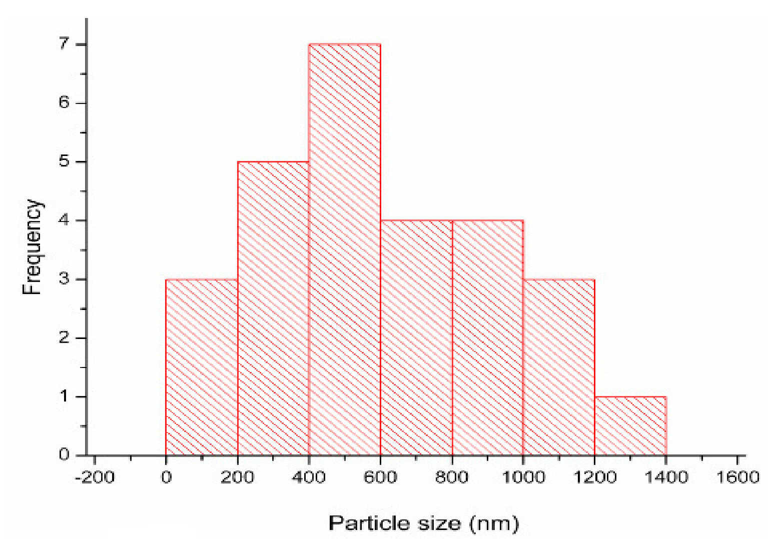


Fig-4: Particle size distribution of UF microcapsules filled with citronella oil.

Fig-2b depicts DTA curves for the UF globules and microcapsule.DTA of UF globule show three endothermic peaks ,the first one in the range of 60°C to 100°C,another at 256.5°C and a very narrow peak at 274.3°C.The first peak is assigned as removal of residual water, the 2nd peak at 256.5°C is associated with the degradation of UF resin and the third at 274.3°C is due to further degradation of UF resin.In case of microcapsule these three endothermic peaks were also observed. In case of microcapsule 2nd and 3rd peaks are by far broader (as a matter of fact they overlap) suggesting considerable change in thermal conductivity in the materials under study.Enthalpy change associated with 2nd peak also differ considerably. ΔH=2.67J/g for UF resin globule and ΔH=230J/g for microcapsule. The 2nd and 3rd peak in case of microcapsule are so broad that they superpose with each other.It impossible to measure the enthalpy change associated with 2nd peak alone.We strongly doubt that at this stage thermal decomposition of citronellal and geraniol takes place with the liberation of isoprene, which consequently breaks down to still smaller fragments and finally to elemental carbon.This explains why we observed a very high enthalpy change at this stage.This is why we also observed a 4th endothermic peak at about 350°C assigned as degradation of other compounds present in citronella oil.Finally there is a very broad exothermic peak at about 400°C.This ,we may well presume,is due to the exothermic degradation of isoprene into elemental carbon.This worth mentioning that Isoprene ,being a petroleum hydrocarbon, has a very high heat of combustion and heat of formation. Above observations clearly corroborates that citronella oil is incorporated within the microcapsules.This was finally confirmed by SEM images.

Fig 3(a) and 3(b) show the SEM micrographs of UF resin globules and that of citronella oil filled microcapsules respectively.Materials under study differ not only in size & shape ,but also in their surface morphology.The UF resin globules measure about 1µm or less in diameter, whereas the microcapsules measure 200µm-1400µm in diameter. Moreover ,the surface of the UF resin globule appear smoother ,while that of the microcapsules are rugged .

Clearly yolk like(slightly darker) core material could be observed in case of microcapsules.Blackening is often observed due to the presence of several lattice defects/dislocations.Material under study ,in this case, is an amorphous material and a liquid and hence no question of lattice defect arises.EDX studies confirms the absence of any heavier metal, which might give rise to such blackening.

Although all possible steps were taken to ensure minimum release of formaldehyde and hence formic acid, which are considered as hazardous for most of the living beings,authors are planning to extend this work with bio-degradable polymers,e.g. poly lactic acid and poly- caprolactone as shell material.

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