

A Comprehensive Review on the Developments in Encapsulation of Various Active Ingredients into Urea Formaldehyde Shell

Sheril Varghese¹, R. Neelakandan¹, Sushma B.S¹, Pasupuleti Sri Sai Tejaswini¹,
Vinutha Moses², V. Naveen³

P.G. Student, Department of Chemical Engineering, Rashtreeya Vidyalaya College of Engineering, Bengaluru,
Karnataka, India ¹

Assistant Professor, Department of Chemical Engineering, Rashtreeya Vidyalaya College of Engineering, Bengaluru,
Karnataka, India ²

Principal Scientist,CCFP Division, CSIR - National Aerospace Laboratories, Bangalore, Karnataka, India³

ABSTRACT:As an evolving method, microencapsulation has offered an effective solution to the challenges faced by the pharmaceutical, cosmetic, food processing, textile, aerospace and structural production industries to deliver elements to target sites in their active forms. Urea-formaldehyde, a high tensile strength thermosetting polymer, flexural modulus, surface stiffness and low water absorption make it useful for the encapsulation of various active ingredients with positive potential applications.

In this review, we discuss the different core material for shell-modified urea formaldehyde and urea formaldehyde, in addition to the process of encapsulation of different active ingredients and their applications in various fields of science and technology.

KEYWORDS: Urea formaldehyde; Encapsulation; Microencapsulation; Shell.

I. INTRODUCTION

The fast-paced topic of self-healing covers a variety of polymers, namely: polymer coatings and composites of polymers [1–3]. Scientists have created these life-long materials as of today according to trends they have found in nature to provide a remedy for unforeseen losses that are likely to occur during their use. It is the embedding of micro / nano-capsule based systems as well as micro / nano-fibre based systems containing healing agents that allows the self-healing materials exude the healing agent in composites and coatings to create this characteristic in them [4,5]. The equal distribution of micro / nano-capsules while trapping the healing agent in the matrix helps to avoid unfavourable reactions between the matrix and the reactive elements which can lead to unpredictable leakage [6].

A microcapsule consists of a core and a shell layer, the core contains an active component while the shell is either a polymeric or a waxy. Microcapsule preparation depends on different parameters such as solubility, viscosity, and the reaction mixture emulsification behaviour. The active ingredients are inclined to release under controlled conditions when applied on a desirable site. The shell acts as a transfer channel to the target where it releases the active ingredients that, in effect, depend on the material used to form the shell including its different end uses [2]. Microencapsulation allows the active ingredient to be released for deposition at the targeted site under specific conditions for performing the functionality required. Any external chemical, physical or mechanical stimulant may be applied on a microcapsule to adjust the active ingredient release controlled.

We have addressed current research on encapsulating various active compounds in urea formaldehyde as well as its derivatives. Several examples of microencapsulation of various active ingredients of specific chemical nature have been studied, demonstrating the wider range of microencapsulation for various applications such as biomedical, tissue

engineering, pharmaceutical, food, fiber, agricultural and environmental applications. Moreover, this review also gives insight into recent advances in encapsulation techniques.

II. UREA FORMALDEHYDE AS SHELL

Liao L P et al., [7] a micro-encapsulated combination of epoxy resin 711 and E-51 into a shell of urea formaldehyde using an in situ encapsulation process that generates capsules 100 μ m in diameter and 4 μ m shell thickness. Self-healing was effectively visible by using salt spray procedure microcapsules were inserted into the paint and tested for corrosion protection properties. A. Yuan et al. [8] successfully encapsulated in a polyurethane urea-formaldehyde shell a mixture of epoxy resins, bisphenol A diglycidyl ether and 1-butyl glycidyl ether The mean size of the capsule was found to be 145 μ m and the thickness of the wall dropped in the 5-82 μ m range. In F. Safaei et al., [9] synthesized microcapsules with epoxy resin (EPL 1012R) as the core material and (urea-formaldehyde) (PUF) as shell, by method of in situ encapsulation. Microcapsules were obtained with an average diameter of 2,13 μ m and a core content of 54 wt %. Excellent corrosion resistance in scratched coatings was assessed by corrosion testing of the salt fog, confirming their self-healing properties. A. Han et al., [10] used nanoindentation on UF microcapsules with epoxy resin E-51 and butyl glycidyl ether as core materials, prepared using an in-situ polymerization process to test viscoelastic properties of microcapsules. Three viscoelastic models such as the 3-parameter Maxwell model, the 5-parameter Maxwell model and the 4-parameter Burgers model based on shell theory have been used to refine experimental nano-micro-material dynamics in the understanding of microcapsule nanoindentation.

Oil phase solvents such as linseed oil can be encapsulated using both one and two phase approaches, and the process has been optimized using M. De la Paz Miguel et al., [11] stated that UF resin cannot be encapsulated with basic pH, but encapsulation was successful encapsulated in the shell of urea-formaldehyde (UF) by one-stage acid polymerisation using polyvinyl alcohol and sodium dodecyl benzene sulfonate as stabilisers. Spherical microcapsules in the range 50–200 μ m with diameters were obtained. . M. Hasanzadeh et al., [12] synthesized two types of urea – formaldehyde microcapsules, one with CeO₂ nanoparticles in the core, along with linseed oil, and the other with linseed oil only. The research optimized the self-healing coating sample containing 15% microcapsules charged with nanoparticles as it displayed comparable scratch sealing performance values to those of samples containing 20% concentration of microcapsules despite its lower concentration of microcapsules.

A strong microcapsule / matrix interface enhances repair efficiency in microcapsule-filled self-healing coatings by steering the crack through the microcapsule and releasing the core material. M.S. Mirabedini, et al., [13] modified the layer of linseed oil filled with 3-aminopropyltrimethoxy silane polyurethane urea-formaldehyde (PUF) microcapsules to strengthen its interface with epoxy coating to a significant degree leading to enhanced microcapsule matrix coupling caused by silane modulation of the microcapsule surface. Microcapsules of urea formaldehyde filled with dual active agent (linseed oil and mercaptobenzothiazole) were synthesized by T. Siva and S. Sathiyarayanan [14]. EIS studies in the area of artificial defects have shown that the coating containing microcapsules can protect steel in neutral media since the impedance values remained at 107cm² even after 15 days of exposure, but while EIS coatings without microcapsules have lost their power to protect. G. Kurt and S. Çömlekçi Ulutan [15] encapsulated linseed oil and alkyd resin based on linseed oil into formaldehyde shells and successfully introduced the use of alkyd resin as a prospective material for corrosion usage in epoxy coating systems through self-healing.

III. MELAMINE-UREA FORMALDEHYDE AS SHELL

Xing Liu et al., [16] synthesized microcapsules with a melamine-urea-formaldehyde polymer shell containing two different elements as healing agents, 5-ethylidene-2-norborne and 5-ethylidene-2-norbornee with 10 wt. % of a norborne-based cross-linking agent (CL), by in situ polymerization in an emulsion of oil in water. The capsules obtained had a mean diameter of 113 mm for filled ENB and 122 mm for microcapsules filled with ENB+CL, and capsule shell thickness ranged from 700 to 900 nm. Tracking healing agent release through invisible cracks from incorporated microcapsules is beneficial for self-healing growth. For visual observations of damage, the addition of tracers such as X-ray dye [17] and UV fluorescent material [18] for hollow fiber reinforced composites and red dye [19] for microcapsules containing coatings in the self-healing agents was recorded. Noh et al., [20] synthesized microcapsules with two separate self-healing chemicals, endo-DCPD and ENB, containing a fluorescent dye surrounded by melamine -urea-formaldehyde shell by a technique of in-situ polymerisation. The microcapsule shell

thicknesses were $\sim 880 \pm 80$ nm for endo-DCPD and $\sim 620 \pm 60$ nm for ENB. The insertion of a fluorescent dye as a tracer into self-healing agents did not affect microcapsule formation. A fluorescence microscopy was used to track the release of self-healing liquid into the induced crack from ruptured microcapsules inside an epoxy coating sheet. Using a fluorescent dye resulted in clear visual images of microcapsules and cracks that filled the self-healing agent from ruptured microcapsules following damage at various excited wavelengths.

Alkyd resin made from coconut oil has been successfully encapsulated by S.N. Khorasani et al., [21] through one step of in situ polymerization in an oil-in - water emulsion, into polymelamine-urea formaldehyde shell content. Free-flowing microcapsules with a diameter range of 1-40 μ m and a core content of 55 % were obtained at an optimized resin / urea melamine (M / U) ratio of 0.08, initial pH 3.6 and agitation rate of 450 rpm. Shenjie Han et al., [22] investigated the effects of processing conditions on the characteristics of paraffin / melamine-urea formaldehyde microcapsules containing phase-change content, paraffin as the core, synthesized by in situ polymerization. When the core-to-shell ratio was 1.5, the styrene / maleic anhydride concentration was 20mg / ml, the reaction temperature was 80 ° C, the reaction time was 2h and the final pH value was 5.5, the latent melting and crystallization values for paraffin / MUF microcapsules were around 134.3 J / g and 133.1 J / g , respectively. Meanwhile, the performance of encapsulation was about 77.1 %.

M. Miguel de la Paz, and C.I. Vallo [23] researched the emulsifying system's role in extracting linseed oil-filled microcapsules with a poly melamine-formaldehyde shell that was synthesized through a two-stage in situ polymerization process. The research concluded that mixing commercial gum arabic in grain solution with sodium dodecyl sulfate solution was the most successful emulsifying combination for the production of linseed oil-filled poly melamine-formaldehyde based microcapsules. In H. Yuan et al., [24] researched on the synthesis of melamine-formaldehyde resin microcapsules suitable for seed treatment to reduce the frequency of application and improve the effectiveness of insecticides by encapsulating a mixture of fipronil and chlorpyrifos through in situ polymerization. Once the suspension of the MF resin microcapsule was used to coat peanut seeds, the continued release of formaldehyde from the degradation of wall resins played an important role in seedling emergence inhibition. Field experiments showed that MF-resin-encapsulated fipronil and chlorpyrifos mixtures have far greater efficiencies against white grubs compared to conventional formulations.

IV. POLYURATHANE AS SHELL

Yang et al., [25] used polymerisation of the interfaces to encapsulate reactive diisocyanate into polyurethane. These healing agents that are free from catalysts can be used in humid or wet environments. Microcapsules with an average diameter of 40-400 μ m and an average wall thickness of the shell ranging from 2-17 μ m have been recorded. F. Alizadegan et al., [26] synthesized polyurethane microcapsules filled with reactive isophorone diisocyanate through polymerisation of the interfaces. The synthesis method developed in this work substitutes toxic solvents which are widely used in the preparation of polyurethane microcapsules, namely cyclohexanone and chlorobenzene, with a more benign solvent, namely n-butyl acetate. Two self-healing agents were encapsulated by Vinicius Henrique de Souza Rodrigues et al., [27] one being toluene diisocyanate and the other isophorone diisocyanate in polyurethane shell through in situ polymerization in an oil-in-water emulsion method. It was validated that toluene diisocyanate as well as isophorone diisocyanate in an epoxy resin matrix demonstrated to be effective core materials for self-healing. The greater rigidity of the matrix led to the rupture of a larger number of microcapsules after surface damage, promoting complete restoration of the original surface material shape. A. Beglarigale et al., [28] encapsulated sodium silicate in polyurethane by polymerizing the shell-forming monomer interfacially, which was optimized by conducting various experiments.

V. CONCLUSION AND FUTURE PERSPECTIVES

Encapsulation includes the creation of tiny capsules containing unique core material surrounded by shell that plays an important role in the slow release of certain chemicals. It has applications in food, agriculture, cosmetics, pharmaceutical aerospace and structural growth industries such as creating new flavours, improving oil ingredients such as omega 3, with sugar beet pectin microencapsulated to substitute milk proteins and gum arabic, self-healing structures, and enhancing oxidative stability; The encapsulation of active ingredients by urea formaldehyde protects them from the external environment for a given time.

Different techniques have been developed to encapsulate drugs and curing agents through methods such as emulsification, interfacial polymerization and in-situ polymerization as core material using urea formaldehyde as shell

material. Encapsulated materials are discharged by various means, including stimulus of temperature, change of UV-light and pH, as well as mechanical rupture. Encapsulation requires an art and science where experience is important to the creation of the capsules needed.

Current stimulant factors such as pH, activity of the enzyme, temperature, osmotic force and mechanical stress-release drug from urea formaldehyde quickly or controllably. For the food industry, heat stable encapsulating polymer consistency will be required in the future, as there is a great challenge to probiotics survival during heat treatment. System costs and the scale of microcapsules must also be taken into account in future.

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