Chapter 3

Self-healing Anticorrosive PU Coatings Embedded with Microcapsules Containing Tung Oil

A convenient method for the preparation of robust polyurea microcapsules containing tung oil as a interior material was developed for self curing anticorrosive application. Well distinct microcapsules with polyurea as a shell material were prepared by reacting hexamethylene diisocyanate (HDI) trimer (isocyanurate) with 0.0 G polyamidoamine (PAMAM) via interfacial polymerization technique. Fourier transform infrared spectroscopic (FTIR) analysis was performed to elucidate the chemical structure of microcapsule and to confirm successful encapsulation of core moiety. Surface morphology, particle size and size distribution, thermal and mechanical properties of prepared PAMAM based polyurea microcapsules were studied against microcapsules prepared with DETA and TETA. The prepared microcapsules were embedded with acrylic based PU coatings to ensure self-healing nature of microcapsules. The immersion study of self-healing polyurethane (PU) coating loaded with different percentages of microcapsules revealed that the composite embedded with 5 % PAMAM based polyurea microcapsules shown satisfactory anticorrosive property under an accelerated corrosion process in 5% NaCl aqueous solution.
1. Introduction

In current years, microcapsules containing healing materials have been drawn immense interest in self-repairing polymer composites [1-5]. Among the different approaches developed for self-healing material such as loading of microcapsule, microvascular network and hollow pipeline embedment (including glass tube and glass fiber), microcapsule loading become more popular and widely used because of simple preparation and easy dispersion in polymer matrix [6,7]. Different chemical methods are reported including in situ polymerization, interfacial polymerization, etc. to prepare microcapsules having desire properties [8, 9]. Different process parameters such as agitation rate, weight core-shell ratio, type and concentration of emulsifier, reaction temperature, etc. have been found to bring the microcapsules with variable properties [10-12]. In the last few decades, researcher’s working in this field has paid more attention to improve the performance of microcapsules to make them more effective tool for self-healing composites. Tong et al. demonstrated melamine modified PUF microcapsules with long storage time, improved heat resistance and water resistance properties [13]. Interfacial interaction between microcapsules and matrix was found to be improved by shell modification of microcapsules through use of coupling agent or grafting of specific functional groups on the surface of microcapsules [14, 15]. In our previous study we reported greater thermal stability of polyurea microcapsules prepared using PAMAM dendrimer with improved interfacial interaction towards the matrix [16].

The membrane strength of microparticles is also one of the most important factors that need to be improved for successful accomplishing microcapsule-based self-healing system. Thus in order to have adequate strength and withstand the
breakage of microcapsules, which otherwise happened during the post treatment and dispersion into polymer matrix, microcapsules must be carefully fabricated [17]. If the membrane is not adequately sturdy, the external impact would trigger the unwanted release of healing agent during handling and processing of microcapsules. Therefore, considering technical and commercial importance, it is of basic requirement to develop and explore a new shell material having high impact resistance.

Out of the several microencapsulation techniques, the interfacial polymerization, due to its simplicity and versatility of structural performance, it is one of the most common processes used to encapsulate wide range of active agents within different polymeric shells [18]. Dicyclopentadiene [19-21] and epoxy resin [22-24] are the most common healing agents which have been used for self-repairing coatings. However, to polymerize both reactive healants released from ruptured microcapsules catalyst is required that must be dispersed into the matrix or in some cases needs to be encapsulated to maintain its activity which would make self-healing mechanism quite complex. But drying oils such as linseed oil [25] and tung oil [26] act as healing agents and do not require the catalyst to polymerize. In such cases oxidative polymerization of drying oils just with air contact heals the crack present in the matrix. Faster drying rate due to high degree of unsaturation and ability to polymerize into a tough, waterproof coating could make tung oil, a good candidate for self-healing mechanism.

Considering afore mentioned points, here attempts were made to fabricate the polyurea microcapsules containing tung oil as a curing agent by interfacial polymerization. Multifunctional HDI trimer and 0.0 G PAMAM dendrimer having several amino groups were reacted to form highly branched crosslinked polyurea shell
wall with the hope to obtain microcapsules possessing improved mechanical and thermal stability. It is noteworthy that heterocyclic isocyanurate ring present in trimer of diisocyanate enhances thermal stability of polymer [27] and trifunctionality of trimer can introduce higher cross linking density in polymer structure which is advantageous for the wall strength of the microcapsules [28]. In first part of the work optimal emulsifier system was investigated to obtain polyurea microcapsules with superior morphology. Further, PAMAM based polyurea microcapsules fabricated at optimized emulsifier system were evaluated in terms of particle size, shell morphology, thermal and mechanical stability against microcapsules prepared with different types of amine. PU coatings embedded with PAMAM based polyurea microcapsules containing tung oil were tested and found with better anticorrosion performance.

2. Materials and Methods

2.1. Materials

Aliphatic polyisocyanate based on hexamethylene diisocyanate trimer [HDI trimer] (Tolonate HDT 90, Perstorp Chemicals, India) was used as oil phase monomer for shell material. Tung oil (Rarco Research Lab, Mumbai) was used as a core material. Zero generation PAMAM dendrimer was used as a water phase monomer for shell material. Poly(vinyl alcohol) (PVA) was procured from Loba Chemicals, Mumbai, India. Acrylic polyol was synthesized as reported in the literature [29]. Sodium dodecyl benzene sulfonate (SDBS) was purchased from Sigma-Aldrich, India. Triethylenetetramine (TETA), diethylenetriamine (DETA) and butyl acetate (s. d. fine - Chem Ltd., Mumbai, India.) were of synthetic grade and used as such for the reaction. Desmodur W was used as received from a Bayer Material Science.
2.2. Experimental Synthesis of Microcapsules

The preparation of polyurea microcapsules containing tung oil was carried out by interfacial polymerization in two steps viz emulsification and polymerization. In first step an organic phase containing HDI trimer (2.0 g) and core material (9.0 g) dissolved in butyl acetate (3.0 g) was mixed with aqueous emulsifier solution. Then the mixture was emulsified at 3000 rpm with homogenizer (ultra turrax®, Ika T25, Germany) at temperature from 15 - 20 °C for 5 min to obtain stable emulsion. Thereafter the emulsion was transferred to 100 mL three necked round bottom flask equipped with a mechanical stirrer and thermometer. Polymerization reaction was started at lower temperature by dropwise addition of a solution containing 1.0 g of PAMAM in 20 mL of 1 wt % emulsifier solution. The reaction mixture was stirred continuously at 300 rpm over a 45 min period at ambient temperature around 25 - 30 °C to complete the formation of the polyurea shell. Formation of microcapsules was checked by observing reaction mixture time to time under a optical microscope. The resulting microcapsule suspension was filtered and rinsed first with ethanol solution (25% v/v in water) and with water for few times to remove the remaining reactants and then dried under reduced pressure at ambient temperature. Scheme 1 illustrates possible reaction mechanism of wall formation for polyurea microcapsules.
2.3. Optical morphology

The microcapsule formation during the fabrication process was preliminary observed by a optical microscope (Labomed Sigma, 2124001, Texas) at magnification 10–100X. About 1-2 mL of capsule suspension was took out and spread on a clean glass slide. Various images were taken by a digital camera (model -Fujifilm Finepix S3300) during the microcapsule forming process.

2.4. Scanning Electron Microscopy

Surface morphologies of microcapsules were recorded in a field emission scanning electron microscope (FE-SEM) (Model S- 4800, Hitachi High Technologies Corp). The dried microcapsules were mounted on a double sided adhesive tape, sputter coated with a thin layer of gold prior to examination and were observed at a
voltage range of 0.5 to 30 kV. Dried microcapsules were ruptured manually with a razor blade for measurement of shell thickness.

2.5. Fourier Transform Infrared Spectroscopy

To identify the constituents of the microcapsules, transmittance analysis of microcapsules, pure capsule shell and pure capsule core material were performed in a shimadzu 8400 FTIR spectrophotometer with resolution of 2 cm\(^{-1}\) and 40 scans per spectrum. Specimens were prepared by homogenizing the samples with a potassium bromide (KBr). To obtain pure capsule shell for FTIR spectrum, small amount of microcapsules were crushed in a Morton piston and washed for a few times by ethanol. After filtration and drying, pure shell was used for analysis.

2.6. Particle size Analysis

The particle size and size distribution of prepared microcapsules were determined on a Malvern Mastersizer 2000 particle size analyzer (Malvern Instrument, UK) by a laser diffraction technique.

2.7 Thermogravimetric Analysis

Thermogravimetric analysis (TGA) was performed to evaluate the thermal stability of microcapsules on a PerkinElmer TGA 4000, operated in the temperature range of 30 \(^0\)C to 600 \(^0\)C at a scanning rate of 10 \(^0\)C min\(^{-1}\) in a flow rate of 20 mL min\(^{-1}\) N\(_2\).

2.8 Viability of Encapsulation and Flexibility of Microcapsules

Elastic strength of newly fabricated cross linked polyurea shell wall and its feasibility to encapsulate the core material was practically judge through visual observation under the optical microscope and video recording by the digital camera.
About 0.1 g of microcapsule powder was mounted on a clean glass slide immediate after filtration and drying. Under the optical microscopic observations, one particular microcapsule from the elected field was dragged by using capillary in order to demonstrate the elasticity and finally squashed it to verify encapsulation of core material by observing it’s come out from ruptured microcapsule.

2.9 Preparation and Analysis of PU coatings

PU composite coatings were prepared by dispersing PAMAM based polyurea microcapsules with different loading from 0 to 5% into the synthesised acrylic polyol dissolved in xylene. Then Desmodur W was mixed with the above polyol solution containing microcapsules at ambient temperature. The mixture was then applied by brush on mild steel panels of 150 mm × 70 mm × 1 mm in dimension with a wet film thickness of 250-300 μm and resultant coatings were allowed to cure at room temperature. Pure PU coating was prepared as a control. Steel panels were polished by sand paper and degreased by acetone before application of coatings.

The prepared PU coatings embedded with different amount of microcapsules along with control sample were then tested for anticorrosion property by immersion study carried out in an aqueous solution of NaCl (5 wt %). For this study artificial cross scratches were made on the coating with razor blade with the aim to break the microcapsules in the path and left at room temperature for 3 days to allow to heal the cracks by tung oil leak out from ruptured microcapsules. After 3 days the specimens were immersed in 5 wt% NaCl solution for a total exposure time of 120 h to evaluate the accelerated corrosion process. The corrosion performance of all the panels coated with neat PU coating and self-healing coatings was examined by a optical photography.
3. **Results and Discussion**

3.1. **Overview of microcapsule formation**

In the synthesis of polyurea microcapsules to encapsulate a tung oil as a healing agent by interfacial polymerization, HDI isocyanurate was dissolved in butyl acetate along with tung oil to obtain oil phase. In order to get stable dispersion, oil phase was then emulsified under higher agitation speed in 1 % emulsifier or stabilizer solution which formed an oil in water emulsion.

Emulsification was carried out at lower temperature (15-20 °C) so as to minimize the chances of reaction between triisocyanate and water. Polymeric shell membrane surrounding the core droplets was formed when reaction between 0.0 G PAMAM having terminal amine groups in water phase and trifunctional HDI isocyanurate in oil phase taken place at the interface of oil and water. To avoid the possibility of gelation due to fast reaction between reactive PAMAM and HDI isocyanurate, dilute PAMAM solution (in 1 wt % emulsifier solution) was added slowly at lower temperature (15 -20 °C) for a period of 15 min. Then temperature was allowed to rise at room temperature and hold the reaction for a period of 45 min.

The **Fig. 1** illustrates schematic diagram for preparation of polyurea microcapsules by interfacial polymerization method. Stable microparticles were observed by optical microscope just after 10 min of PAMAM addition. However to complete the reaction between isocyanate and amine, reaction mixture was stirred continuously for next 45 min. The used functional monomers, PAMAM dendrimer and HDI isocyanurate were with multiple functional sites which contribute to form highly branched cross-linked structure in the interaction region to form the polyurea membrane with good mechanical strength.
3.2 Selection of Emulsifier System

The formation of microcapsules involves two steps i.e. emulsification and actual polymerization. In emulsification step surface active agent and stabilizer play an important role to form stable oil droplets dispersed in the continuous water phase. In a typical experiment, emulsification was carried out by using 1 % PVA solution. It was found that the prepared microcapsules were larger in size with wrinkled shell wall and they get ruptured over the period of time after exposure to surrounding environment. It suggested that for the present system, PVA could not be able to stabilize the droplets formation and tend to coalescence of particles which results into larger microcapsule formed. Further experiment was carried out with 1 % SDBS solution, an anionic surfactant adapted for oil in water emulsion system having
hydrophilic–lipophilic balance value (HLB) suitably matched with used oil, in order to produce stable and uniform size microcapsules. It is clearly seen from the Fig. 2 that prepared microcapsules were coagulated with major abnormality and weaker shell wall which infers that the emulsifier SDBS fails to keep the balance between interfacial tension and stability of the present colloid system.

**Fig. 2:** PU microcapsules obtained at different concentration of SDBS/PVA (a) 1/0 (b) 0.5/0.5 (c) 0.4/0.6 (d) 0.2/0.8 (e) 0/1
Thus in order to provide suitable formulation that can facilitate desired interfacial properties both for droplet formation and subsequent stabilization, series of composite emulsifier (SDBS/PVA- (a) 1/0 (b) 0.5/0.5 (c) 0.4/0.6 (d) 0.2/0.8 (e) 0/1 were used for the present system. It was found that with the composite emulsifier SDBS/PVA-0.2/0.8, spherical, smooth, compact shell walled microcapsules were formed. Hence it was concluded that composite emulsifier system is more effective than individual emulsifier and the ratio of SDBS to PVA of 0.2/0.8 was found the optimal emulsifying system for present study.

Particle size distribution curve for polyurea microcapsules containing tung oil prepared at composite emulsifier SDBS/PVA-0.2/0.8 is represented in the Fig. 3.

![Particle size distribution curve](image)

**Fig. 3:** Particle size distribution of the polyurea microcapsules containing tung oil

The size of microcapsules was found to be distributed in the range of 58–260 μm. It is reported in the literature [30] that during the preparation of microcapsules due to the turbulence fluid flow, higher shear force is produced near the propeller blade which tend to lower the size of microcapsules while comparatively larger microparticles
exist away from the propeller which overall tend to wider size distribution of the microparticles. The mean diameter of the prepared microcapsules was found 133.6 μm that is quite suitable to utilize it for self-healing application.

3.3. Structural Analysis

The Fig. 4a shows the FTIR spectra of the polyurea microcapsules and extracted shell. The spectrum of both polyurea microcapsules as well as shell showed the absorption band at 1685 cm\(^{-1}\), which was assigned to \(>\text{C}=\text{O}\) stretching frequencies for amide. Furthermore N–H stretching was evidenced with a broad absorption band observed in the 3550–3300 cm\(^{-1}\) range. Also absorption band at 1440 cm\(^{-1}\) was corresponded to the –C–N stretching of amide.

![FTIR spectra](image)

**Fig. 4(a):** FTIR spectra of (a) extracted polyurea shell and (b) microcapsules containing core material
Fig. 4(b): FTIR spectra of (a) extracted core and (b) pure core material

The spectrum of core material tung oil (Fig. 4b) revealed strong absorption band at 1745 and 1162 cm\(^{-1}\) that were assigned to >C=O stretching and –C=C=O– stretching vibrations of ester respectively. Moderate to weak absorption peak for –C=C– stretching vibration was observed at 1640 cm\(^{-1}\). The frequencies observed at 2927 cm\(^{-1}\), 2858 cm\(^{-1}\) were corresponded to C–H stretching and at 1457 cm\(^{-1}\) was corresponded to C–H bending of methylene group.

FTIR spectrum of microcapsule (Fig. 4a) discloses whether the core material was successfully encapsulated or not within the polyurea shell wall. The appearance of characteristics signals at 1886 cm\(^{-1}\) for >C=O stretching frequencies of amide group present in shell and >C=O stretching vibration of ester at 1745 cm\(^{-1}\) confirmed the presence of core in the synthesized polyurea microcapsules. Also observing nearly identical spectrum for the individual core and extracted core were confirmed again that by retaining all functional groups, tung oil have been encapsulated by polyurea microcapsules.
3.4. Scanning Electron Microscopy

The Fig. 5 illustrates the surface morphologies of microcapsules synthesised from the different amine monomers viz. 0.0 G PAMAM, DETA and TETA at agitation speed of 3000 rpm and optimized emulsifier system. In case of DETA and TETA, microcapsules observed were spherical in shape having wrinkled wall structure along with shrinkages. On the other hand spherical microcapsules with compact, smooth wall structure was obtained in the case of PAMAM. Among the microcapsules synthesized from DETA and TETA, comparatively less shrinkage was observed in the case of TETA. The different chemical structures and reactivities of amines can significantly determine unusual membrane morphologies of resultant microcapsules. In the PAMAM based microcapsules, it is certain that a rapid reaction occurred on the emulsion globules between PAMAM with several amino groups from the water-soluble phase and HDI isocyanurate from the organic phase, producing a cross linked network structure in wall membrane which tends to healthy, spherical, elastomeric microcapsules as compared to microcapsules based on DETA and TETA. Additionally, shell thickness of the microcapsules were 1.84, 1.68 and 1.60 µm, found higher in the order of PAMAM> TETA >DETA. Thus the things responsible for the shrinkages of microcapsules such as compression and shear forces, shell determined elastic forces, etc. [31] are defeated in the case of PAMAM based system which result into microcapsules with better membrane morphology than in case of DETA and TETA where thinner shell thickness promoting wrinkled formation.
Fig. 5: SEM images of polyurea microcapsules showing (a) capsules prepared from DETA (b) capsules prepared from TETA (c) capsules prepared from PAMAM (d) compressed capsule reflecting elastic nature which is squeezed at first after compress but not ruptured easily (d) core-shell morphology of a capsule and (e) shell thickness of a capsule.
3.5. Microcapsule Size and Size Distribution

The Fig. 6 represents the particle-size distribution of the polyurea microcapsules prepared with different amine monomers. As shown in the figure, mean diameters and particle-size distributions of the microcapsules are affected by the different chemical structure and properties of amines used to prepare wall membranes of microcapsules. The particle size of the samples was found to be decreased in the order of PAMAM > TETA > DETA. The mean volume diameter of the microcapsules prepared from PAMAM, TETA and DETA were 133.58, 54.86 and 48.76 μm respectively.

![Particle size and size distribution of polyurea microcapsules from different amines](image)

**Fig. 6:** Particle size and size distribution of polyurea microcapsules from different amines (a) DETA (b) TETA (c) PAMAM

The molecular weight and reactivity of the monomers combinely affects the mean diameters and particle-size distribution of the microcapsules, as reported in the previous literatures [32, 33]. The sample has many large particles than DETA and TETA, when PAMAM was used as a monomer, which may be due to the higher molecular weight and reactivity among the amines used, while due to not significant
difference in reactivity and molecular weight, slight variation in the mean diameters of the particles from DETA and TETA was observed.

3.6. Thermogravimetric Analysis

Thermal degradation profile of the extracted polyurea shell walls of microcapsules prepared from different amines were investigated using a thermogravimetric analysis (TGA) and result are shown in the Fig. 7.

![TGA thermogram for shell material of microcapsules prepared from (a) PAMAM (b) TETA and (c) DETA](image)

Initial 2-3 % weight loss was observed in all samples from 100–170 °C which may be associated with evaporation of solvent entrapped or trace amount of moisture present in the shell material. The degradation observed between temperature range of 170 - 600 °C attributed to the decomposition of polyurea network and the residual weight of each sample verified the formation of microcapsules wall membrane with different heat resistant properties. As compared to DETA and TETA, thermal stability
of shell in temperature range of 250-450 °C was observed higher in case of PAMAM with 10% of the original mass remaining at 600 °C while only 8% and 5% residual mass was observed for DETA and TETA respectively. As reported in the literature, chemical structure of monomer such as presence of number of reactive groups and linearity play an important role to decide the thermal performance of the material [32]. Thus in the present work, use of PAMAM with more reactive amine groups corresponds to higher intensities of cross linked structure in the resultant membrane that would lead to have higher thermal stability than with other types of amines used.

3.7. Environmental Stability of Microcapsules

In order to observe the elastic strength of the prepared microcapsules, manual compression test of single microcapsule was performed under optical microscopic observation and results are represented in the images (Fig. 8) taken from recorded video. In this test single selected microcapsule was drag up and down under compress pressure. It can be noticed that the microcapsule from PAMAM exhibited good elastic strength against applied force while comparatively the capsules from DETA and TETA were not withstand to applied force and broken easily. Thus it can be conclude that the strength of polymeric membrane obtained from HDI trimer and PAMAM is as good as to make microcapsule survive during the polymer processing. Also nature of compressed capsule reflecting elastic behavior which is squeezed first after compress but not ruptured easily. Further in addition to the FTIR analysis, the leak out of encapsulated fluid from single ruptured capsule during this test validated the entrapped tung oil within the polyurea shell. The core content of the microcapsules was found to be 68% determined by Soxhlet extraction method (as described in previous chapter).
In order to utilize the microcapsules in hot and humid condition, the capsules were analyzed for hot water resistance by examining the morphology under optical microscope. The microcapsules were stirred at 300 rpm in hot water for 3 h at 70-80°C temperature and the result are shown in the Fig. 9.

**Fig. 8**: Optical photographs of PAMAM based Polyurea microcapsules at different stage when mechanically drag

**Fig. 9**: Optical photographs of PUa microcapsules after hot water stability (a) DETA (b) TETA and (c) PAMAM (magnification: 10x)
It was found that the samples from DETA and TETA shown intense deformation with 70-80% microcapsules and ruptured after stirred for 3 h rather in the case of PAMAM based microcapsules, less amount of deformations were observed and only 5-10% microcapsules were found to be failed to withstand surrounding environment. From these results it can be concluded that the PAMAM based polyurea microcapsules exhibit better stability to hot water than the microcapsules prepared from DETA and TETA.

3.8. Immersion Study

The Fig. 10 represents the results obtained from immersion test of the prepared PU coatings embedded with 1 to 5% PAMAM based polyurea microcapsules. The test was performed in a salt solution since a presence of electrolyte is one of the factors affecting on corrosion rate of metal surface [4]. It can be seen that least corrosion was taken place with 5% loading of microcapsules after 120 h immersion in NaCl solution. On the other hand in the control sample severe corrosion was seen in and around the scribed area. This difference in corrosion performance of coated panels could be the result of self-healing of cracks by releasing tung oil from ruptured microcapsules present in the path. The process of corrosion inhibition involve filling of crack by released tung oil which protect the opened metal surface from surrounding environment through protective film formation by oxidative polymerization of tung oil. This newly formed material tends to responsible for sealing of grove and protection of substrate from corrosion by avoiding the diffusion of salt ions. The healing mechanism encompasses autonomous repairing of the crack without providing any external assistance such as catalyst, heat, etc. In contrast, for the sample without microcapsules metal surface was exposed to the
environment and resulted in severe corrosion after 120 h of exposure. Hence from this test it can be revealed that self-healing PU coating composite containing 5% polyurea microcapsules exhibit better anticorrosion property for steel panels tested in a salt solution.

**Fig. 10:** Corrosion test results for steel panels coated with PU coatings with and without microcapsules after 120 h
4. Conclusions

A method for fabrication of PAMAM based polyurea microencapsule containing tung oil via interfacial polymerization between HDI trimer and 0.0 G PAMAM in an oil-in-water emulsion was developed. Well defined and spherical shape microcapsules were obtained at optimal composite emulsifier system with ratio of SDBS to PVA- 0.2/0.8. The particle size of the resultant microcapsules was found in the range of 58-259 μm with the average diameter of 133 μm and shell thickness in the range of 1–1.9 μm were observed. Successful encapsulation of tung oil within polyurea shell wall was confirmed by visual observation as well as FTIR analysis. Difference in chemical structure of amines (DETA, TETA and PAMAM) tends to form microcapsules with different morphology, particle size, thermal and mechanical properties. Spherical, elastomeric and healthy microcapsules with better thermal stability and processing survivability were obtained in the case of PAMAM as compared to microcapsules with DETA and TETA. It was found that the self-healing coating with 5 % loading of PAMAM based microcapsules shown significant corrosion retardancy under an accelerated corrosion test in 5 % NaCl salt solution.

5. References


