# MICROENCAPSULATION OF MERCAPTAN USING POLYCAPROLACTONE AS SHELL MATERIAL TOWARD SELF-HEALING COATING APPLICATIONS

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## ABSTRACT

Polymer materials incorporating microencapsulated self-healing agents have a wide range of application from paint coating, anti-corrosion coatings to automotive and construction materials. In this research, microcapsules containing reactive mercaptan compound for use in self-healing polymers were successfully fabricated via the oil-in-water emulsion method. We employed for the first time the UV-initiated thiol-ene reaction between an alkene-functionalized polycaprolactone and a tetrathiol compound to form the microcapsule shell. To synthesize microcapsules, the tetrathiol was used in large excess, thus maintains inside the microcapsules as the core material. The obtained microcapsules were analyzed by Fourier Transform infrared (FTIR) specroscopy, optical microscopy, scanning electron microscopy (SEM) and laser diffraction particle size analysis. The core was extracted by Soxhlet extraction and analyzed by ^{1}H NMR and FTIR spectroscopy.

*Keywords:* microcapsules, polycaprolactone shell, thiol-ene addition.

## 1. INTRODUCTION

Polymeric coating materials are susceptible to degradation that may lead to the formation of microcracking, thus reduces the mechanical properties and shortens their lifetime. Therefore, self-healing polymers have attracted significant interest [1]. Among many developed self-healing concepts, extrinsic self-healing systems require encapsulated self-healing agent preembedded into polymer matrix that would be released and close the damage upon crack triggering [2,3]. Commonly used are dual microcapsule systems, in which two healing agents that can react with each other, are encapsulated in separate microcapsules [4].

Mercaptans have been used as efficient healing agents to react with a couple of reagents, such as epoxy, isocyanate, acrylate and norbornene for two-part microcapsule containing self-healing composites [5,6]. Microencapsulated mercaptans can also be combined with other encapsulated agents, such as multi-maleimide reagents, to develop fast healing systems [7].

Mercaptan compounds, such as the tetrathiol pentaerythritoltetrakis(3-mercaptopropionate), have only been widely encapsulated in poly(melamine-formaldehyde) and poly(urea-formaldehyde) shells [8,9]. However, care has to be taken in these procedures because of side reactions of tetrathiol during the shell crosslinking condensation reaction [9].

Hence, we explore a new microencapsulation strategy to form a crosslinked polycaprolactone (PCL) shell around the liquid tetrathiol to produce a microencapsulated mercaptan agent for self-healing applications. In this work, we present an innovative methodology for the microencapsulation of tetrathiol by an allyl-functionalized polycaptolactone (PCL) shell material. The PCL shell is cured by application of a fast thiol−ene addition reaction under UV irradiation of the double bond pendant groups of the PCL and thiol groups of tetrathiol. The employment of the thiol−ene "click" reaction [10] led to efficient photo-curing of the shell and hence successful formation of microcapsules. To the best of our knowledge, this is the first report on microcapsules of thiol using a PCL shell.

## 2. MATERIALS AND METHODS

### 2.1. Materials

Pentaerythritol tetra(3-mercaptopropionate) (95% purity) (tetrathiol); methyl benzoate; 2,2-dimethoxy-2-phenylacetophenone (DMPA) and gum arabic from acacia tree were purchased from Sigma-Aldrich. Alkene-functionalized polycaprolactone (PCL) was synthesized according to a previously reported method [11].

### 2.2. Synthesis of PCL shell/tetrathiol core microcapsules

60 g of a well-mixed mixture of tetrathiol, methyl benzoate, DMPA and alkene-PCL (methyl benzoate to tetrathiol weight ratio of 25/75; the feeding weight ratio between the mixture of tetrathiol and methyl benzoate and alkene-PCL was in the range of 3–5) was emulsified in 150 mL of a 13 wt% gum arabic aqueous solution in a double-neck round-bottom flask (250 mL) at the rate of 300 rpm. The obtained emulsion was exposed to UV light (365 nm) in an UV irradiation chamber for 15 min. All microcapsules, with different (tetrathiol + methyl benzoate) to alkene-PCL ratios were synthesized at the same emulsification rate and UV light exposure time. After stopping the reaction, the microcapsules were filtered, washed several times with distilled water and air-dried at room temperature for 48 hours before further analysis.

### 2.3. Characterization

$^1$H NMR spectra were recorded in deuterated chloroform (CDCl$_3$) with TMS as an internal reference, on a Bruker Avance 300 at 300 MHz. Attenuated total reflectance (ATR) FT-IR spectra were collected as the average of 128 scans with a resolution of 4 cm$^{-1}$ on a FT-IR Tensor 27 spectrometer equipped with a Pike MIRacle ATR accessory with a diamond/ZnSe element. Optical microscopic images were recorded on an Olympus GX51F microscope. SEM images were obtained on a TM-3000 Hitachi table topmicroscope. Average particle sizes and dispersities of the microcapsules were measured by laser diffraction particle size analysis using the Beckman Coulter LS 200.

## 3. RESULTS AND DISCUSSION

### 3.1. Synthesis of microcapsules

Alkene-functionalized polycaprolactone (PCL) was synthesized by functionalization of a commercial PCL-diol (Mn = 2112 g mol$^{-1}$) with allyl glycidyl ether, following a previously reported method [11]. The obtained alkene-functionalized PCL has in average 5 pendant alkene groups per polymer chain ($M_n$ = 2683 g mol$^{-1}$) [11].
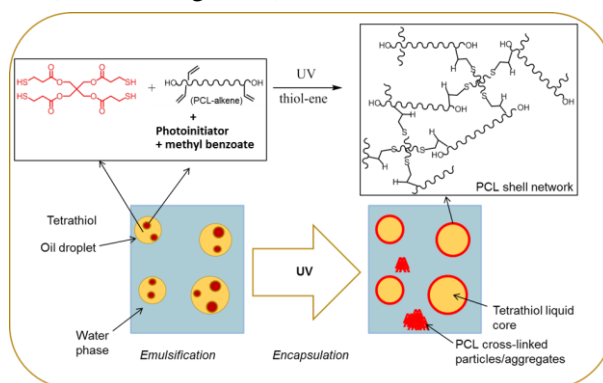


*Scheme 1.* Representation of the formation of microcapsules of tetrathiol core and crosslinked PCL shell.

A demonstration of the microencapsulation concept of tetrathiol is shown in Scheme 1. The alkene-PCL was mixed with an excess amount of tetrathiol and methyl benzoate in the oil phase. Methyl benzoate has a role as a co-encapsulated solvent agent together with the reactive tetrathiol. A methyl benzoate/tetrathiol weight ratio of 25/75 was used in the feeding. The addition of 25 wt% methyl benzoate lowers the viscosity of the core mixture from 500 to 85 cP. Upon storage under air-free conditions, the tetrathiol/methyl benzoate mixture remains stable, as confirmed by $^1$H NMR and FTIR analysis. In the presence of a trace amount of DMPA (1 mol% with respect to the alkene groups) as a radical photoinitiator included in the oil phase, under UV irradiation a thiol−ene addition reaction between allene-PCL and tetrathiol was initiated and a cross-linked PCL network was formed. The excess tetrathiol remained as the encapsulated liquid core.

The core−shell formation is based on phase separation of the material to be encapsulated (liquid core) and the formed PCL shell material. Addition of methyl benzoate, a common solvent for both tetrathiol and alkene-PCL, to the material that is to be dispersed in water allows simultaneous dispersion of both the core-component and the shell material. Addition of the surfactant (gum arabic) to the water phase prevents coalescence and the formation of larger size capsules. Methyl benzoate is hydrophobic and remains in the core as a co-encapsulated component.

UV irradiation of the homogeneous dispersed methyl benzoate/tetrathiol/alkene-PCL droplets in the water phase leads to the formation of crosslinked PCL and simultaneously the phase separation of the core component and the PCL shell, resulting in core−shell capsules.

Figure 1A and B show the SEM images of the obtained microcapsules and broken microcapsules after core removal with a defined shell consisting of PCL cross-linked material and an inner core, suggesting a core−shell structure. It was also noted that the microcapsules had a distinctive "wrinkled" appearance. The formation of the wrinkled morphology could be related to the fast reaction kinetics of the thiol-ene shell curing reaction. Indeed, the combination of

inhomogeneous reaction kinetics, fluid-induced shear forces, and shell-determined elastic forces may cause wrinkles on the microcapsules [12]. In fact, generally the wrinkled shell morphology could possibly serve as an advantage in promoting the binding of microcapsules to a polymer matrix.
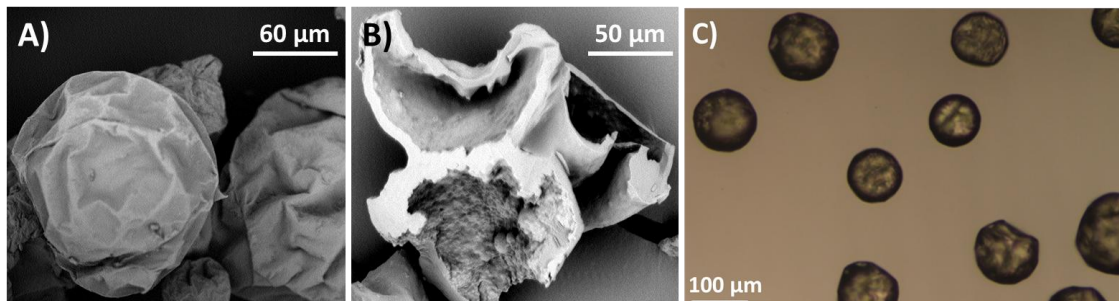


*Figure 1.* (A) SEM image of PCL shell microcapsules containing tetrathiol/methyl benzoate core (prepared with (tetrathiol+methylbenzoate)/alkene-PCL feeding weight ratio of 4/1), (B) SEM image of broken microcapsules after core removal, and (C) optical microscope image of the microcapsules.

## 3.2. Shell and core analysis

ATR FT-IR analysis of the shell material (i.e. microcapsules after core removal by Soxhlet extraction in warm acetone for 24 h) was conducted. A comparison of the spectrum of the shell material with those of tetrathiol and alkene-PCL (Figure 2) shows the absence of the characteristic thiol (S-H) stretch vibration at 2570 cm$^{-1}$ and double bond vibration at 3082 cm$^{-1}$, indicating that the thiol and alkene groups have reacted with each other completely forming the crosslinked shell structure.
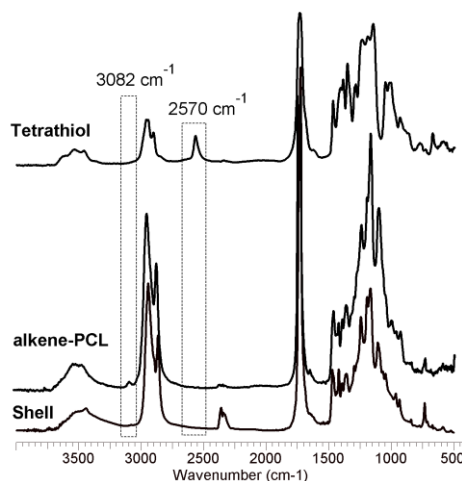


*Figure 2.* A comparison of the ATR FT-IR spectra of tetrathiol, alkene-PCL and capsule-shell after core removal.

In addition, the encapsulated core was extracted from the microcapsules by breaking them via ultrasonication in deuterated acetone-d$_6$, followed by filtration to eliminate the shell material. The extracted core was analyzed by $^1$H NMR. The spectrum showed the presence of the free thiol peak (triplet) at around 1.87 ppm and the methyl protons of methyl benzoate at around 3.82 ppm (Figure 3).

### 3.3. Influence of the feeding weight ratio between tetrathiol-methyl benzoate mixture and alkene-PCL

Figures 4 and 5 show the optical microscopic and SEM images of the microcapsules prepared with (tetrathiol+methylbenzoate)/alkene-PCL feeding weight ratio of 3/1 and 5/1, respectively (for a comparison with Figure 1).
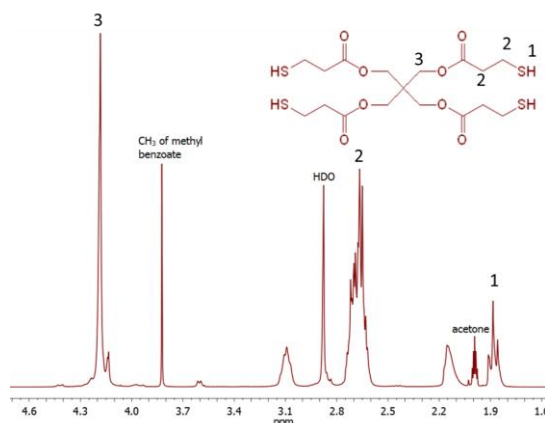


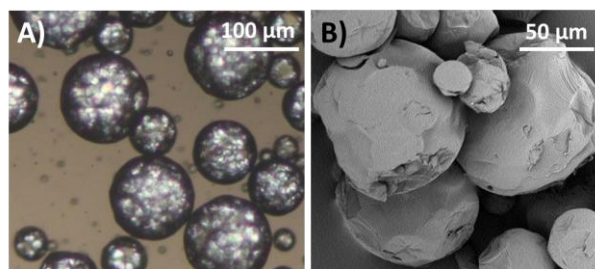*Figure 3*. $^1$H NMR spectrum of the extracted core.



*Figure 4.* (A) Optical microscope and (B) SEM image of microcapsules prepared with (tetrathiol+methylbenzoate)/alkene-PCL feeding weight ratio of 3/1.

It was found that increasing the (tetrathiol+methyl benzoate)/alkene-PCL feeding ratio resulted in increases in the weight content of the encapsulated core. However, a high (tetrathiol+methylbenzoate)/alkene-PCL feeding ratio also led to the formation of microcapsules with thinner shell as well as increasing the amount of un-encapsulated liquid core, which could stick to the outer surface of microcapsules and hence cause agglomeration. With a (tetrathiol+methylbenzoate)/alkene-PCL feeding ratio of 3/1 (g/g), well separated microcapsules with a core content (as determined by Soxhlet extraction) of 50 wt% was obtained (Figure 4). With a tetrathiol/PDMS feeding weight ratio of 4/1, the core content increased to 70 wt%, while microcapsules with well-defined core-shell structures were still received (Figure 1). Further increasing the tetrathiol/PDMS feeding weight ratio to 5/1 provided bad quality microcapsules which were highly agglomerated as a result of ineffient encapsulation of the liquid core (Figure 5). Therefore, the optimal (tetrathiol+methylbenzoate)/alkene-PCL feeding ratio was 4/1.
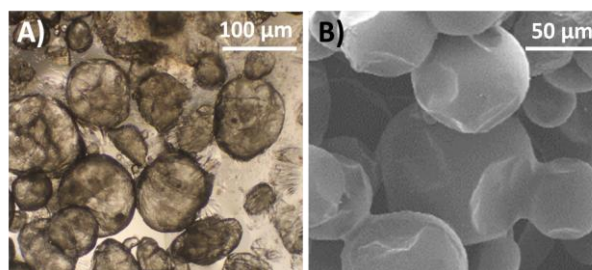
*Figure 5.* (A) Optical microscope and (B) SEM image of microcapsules prepared with (tetrathiol+methylbenzoate)/alkene-PCL feeding weight ratio of 5/1.
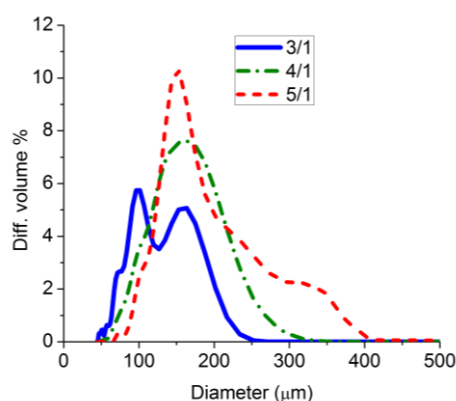


*Figure 6.* Size distributions of microcapsules with (tetrathiol+methylbenzoate)/alkene-PCL feeding weight ratio of 3/1, 4/1 and 5/1.

Figure 6 compares the size distributions of the microcapsules prepared at different feeding ratios. The average microcapsule size was about 160 µm. In addition, broader distributions were observed for the microcapsules prepared with a tetrathiol/PDMS feeding ratio of 5. The fraction of the larger size microcapsules is attributed to the agglomeration, confirming the optical microscopy and SEM results.

## 4. CONCLUSIONS

In conclusion, a one-pot, simple and efficient approach for the synthesis of PCL microcapsules with a high content of an encapsulated reactive liquid tetrathiol core mixed with methyl benzoate using the thiol−ene reaction for UV curing of microcapsule shell has been successfully developed. Our future work will involve in investigating the crack-induced breakage of these microcapsules and the release of the thiol core in the healing process.

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