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Two-Step Synthesis of Poly (urea formaldehyde) Microcapsules

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Abstract:

Self-healing coatings have potential to reduce waste and minimize repair costs in industries where materials need to be protected from harsh environmental conditions and mechanical abrasion. These coatings can be created by embedding healing-agent filled microcapsules which release their contents and fill voids in the event of damage. To synthesize microcapsules that are ideal for self-healing coatings, they must have a diameter less than 100 microns, smooth surface morphology, and have improved dispersibility. Our current one-step method does not produce microcapsules within the desired size distribution, so a two-step route where oligomers of the shell wall material are formed prior to microcapsule formation was investigated. This was done by evaluating the effects of solution viscosity, size of reaction vessel, addition of poly (vinyl alcohol) (PVA), and core/shell ratio on microcapsule properties. Characterization of microcapsule size, morphology, and composition was done using optical microscopy, Fourier-transform infrared spectroscopy (FTIR), and thermogravimetric analysis (TGA). Microcapsules with an average diameter of 78 ± 16 microns were successfully synthesized. Further work must be done to minimize PUF crystallites on the surface of the microcapsules.

1. *Introduction:*

Polymeric coatings are used in the electronics, aerospace, and automotive industries due to their lightweight and processable nature.[1] During normal use, these coatings are subject to harsh environmental conditions (e.g. water, oxygen) and mechanical abrasion leading to formation of microcracks and mechanical degradation.[2] A coating that automatically heals itself would minimize upkeep and extend its lifetime, saving consumers money and reducing waste.[3] These “self-healing” coatings utilize either intrinsic or extrinsic mechanisms.[4] Intrinsic self-healing is driven by chemical bonding of the polymer matrix itself, while extrinsic self-healing involves embedding healing agent-filled containers within the matrix.[5]

The most common method of extrinsic self-healing is through microencapsulation.[6] These microcapsules are comprised of a core healing agent coated in a thin shell material (**Figure 1**). When these capsules are loaded into a coating, they will rupture and release the healing agent when the coating is breached. After sufficient time to cure, the healing agent will solidify and heal the damage.

Microcapsule-based coatings should be evenly dispersed with microcapsules and comparable in properties and performance to the neat coating.[2] As coatings are generally limited to 200 microns or less, ideal microcapsule diameter should be less than 100 microns. To aid in dispersibility, the microcapsules should not aggregate or have excess shell wall material on their surfaces.

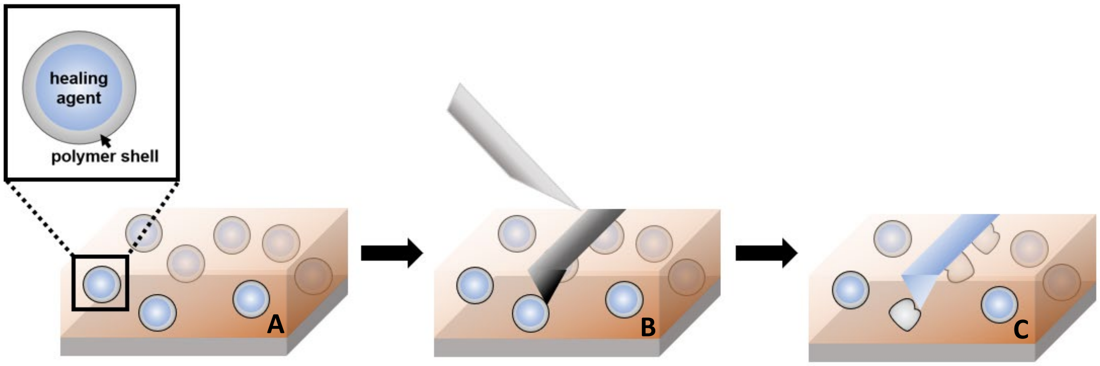

Figure 1. Schematic depicting (A) microcapsule loaded coating, (B) crack formation, and (C) self-healing ability

Microcapsules containing healing agents are commonly prepared via emulsification and in situ polymerization of urea and formaldehyde.[7] During this process, urea and formaldehyde in an aqueous phase react to form colloidal cross-linked particles which deposit at the core material-water interface to form the microcapsule shell wall.[8] The formation of poly(urea formaldehyde) (PUF), can be catalyzed via acid or base to initiate polycondensation. This leads to a two-stage polymerization process where oligomers of PUF are formed under basic conditions and cross-linking of the shell wall is performed under acidic conditions. Alternatively, the polymerization of PUF can be carried out in one stage under acidic conditions.

Using the two-stage method, microcapsules containing epoxy resins[9-11], thiol[12], and linseed oil[13, 14] have been synthesized. The one-stage method was developed to encapsulate dicyclopentadiene[15], linseed oil[16], and epoxy.[17] Comparative studies of one-step and two-step PUF microcapsule syntheses for linseed oil[7] and epoxy resins[13, 18] have been done, but they were unsuccessful in producing viable microcapsules with their selected two step method.

Because of this, our group currently utilizes a one-step method by Yao et. al to fabricate microcapsules.[17] However, the synthesis does not produce microcapsules with the desired size distribution, so an alternative route by Ye et. al. was investigated.[19] It was hypothesized that utilizing a two-step synthesis route will lead to finer tunability of microcapsule size and morphology due to PUF pre-polymer formation aiding in faster polymerization of a robust shell wall.

The main goal of this project was to develop a two-step synthesis route to produce microcapsules containing epoxy resin with the following properties: diameter less than 100 microns, smooth surface morphology, increased dispersibility, and high yielding synthesis. The effects of solution viscosity, size of reaction vessel, adding poly(vinyl alcohol) (PVA), and core/shell ratio on microcapsule properties were investigated. Characterization of microcapsule size, morphology, and composition was done using optical microscopy, Fourier-transform infrared spectroscopy (FTIR), and thermogravimetric analysis (TGA).

2. Experimental:

2.1. Materials

Urea (99.0-100.5%), formaldehyde (37 wt.% aqueous solution), ammonium chloride (NH_4Cl) (≥99.5%), and resorcinol (99%) were purchased from Sigma-Aldrich for the shell wall formation. Bisphenol A Diglycidyl ether epoxy resin (E-51) was purchased from Sigma Aldrich to be the encapsulated material. Butyl glycidyl ether (BGE) (≥98.0%) purchased from TCI was used as a diluent. Sodium dodecylbenzene sulfonate (SDBS) was used as a surfactant/emulsifier from Sigma-Aldrich. Medium molecular weight poly (vinyl alcohol) (PVA) (M_W=56,000-65,000 g/mol) was purchased from Alfa Aesar to use in conjunction with SDBS. Potassium hydroxide (KOH) (90%) and 37 wt.% hydrochloric acid (HCl) purchased from Sigma-Aldrich were used to adjust reaction pH. All materials were used without additional purification.

2.2. Synthesis of PUF Microcapsules

2.2.1. *Method 1:*

This method is an adaptation of the synthesis found in Zhang et. al. and was performed for MAW-01 through MAW-04.[20] Baseline quantities for full-scale and half-scale reactions are located in **Tables 1 and 2**.

In the first step, deionized water, urea, and 37 wt. % formaldehyde were added to a beaker at room temperature. While stirring at 150 rpm with a stir bar, the pH of the solution was gradually adjusted to 9.0 by adding 10 wt.% KOH solution dropwise. The beaker was then slowly heated to 65°C and maintained for an hour to create the prepolymer.

After cooling the prepolymer to room temperature, the surfactant (SDBS or 5 wt.% aqueous PVA), ammonium chloride, and resorcinol were added to the reaction flask while stirring at 800 rpm with an overhead mechanical stirrer. The stirring was done with a four-blade propeller 1 cm from the bottom of the beaker. 60 wt.% E-51/BGE was then added dropwise and emulsified for thirty minutes. During emulsification, 1-octanol was added dropwise as needed to reduce foam levels. The pH of the reaction was lowered to 3.5 by adding 3.75 wt.% HCl, and the reaction was left stirring at 55°C for two hours. Finally, the product was separated via vacuum filtration or centrifuging, rinsing with water three times and acetone once, and left to dry at room temperature overnight. This process did not produce any viable microcapsules.

Table 1. Baseline quantities for pre-polymer formation

Pre-polymer Formation			
Scale	**Urea (g)**	**37 wt.% Formaldehyde (g)**	**DI H_2O (mL)**
1	3.75	10.0	200
1/2	1.875	5.0	100

Table 2. Baseline quantities for microcapsule formation

Microcapsule Formation					
Scale	**5 wt. % PVA (g)**	**SDBS (g)**	**NH_4Cl (g)**	**Resorcinol (g)**	**60 wt.% E-51/BGE (g)**
1	15	-	0.375	0.375	16.6
1	-	0.3	0.375	0.375	16.6
1/2	7.5	-	0.1875	0.1875	8.3

2.2.2. Method 2

The procedure was derived from Ye et. al. and was performed for MAW-05 through MAW-18. Quantities for full-scale, half-scale, and quarter scale baseline reactions with can be found in **Tables 3-4.** Full reaction quantities and reaction parameters for each test can be seen in **SI Tables 1-3**. A schematic of the process can be seen in **Figure 2.**

First, urea and 37 wt. % formaldehyde were added to a flask at room temperature and dissolved while stirring at 200 rpm with a stir bar. While stirring, the pH of the solution was gradually adjusted to 9.0 using 10 wt.% KOH solution. The flask was then placed into a water bath at 65°C for one hour to form the prepolymer.

In a separate beaker (inner diameter = 6.23 or 5.70 cm), the epoxy system (60 or 70 wt.% E-51/BGE), SDBS (0.5, 1, or 2 wt.% aq. SDBS), room temperature prepolymer, and 5 wt. % PVA were combined. This reaction mixture was emulsified at 800 rpm using overhead mechanical stirring with a four-blade propeller at either 0.6 cm or 1 cm from the bottom of the beaker and heated to 50°C for 30 minutes. During emulsion, 1-octanol was added dropwise as needed to decrease foaming. The speed of the propeller was then decreased to 400 rpm and the pH was decreased to either 2.5, 3.0, or 3.5 using 3.75 wt.% HCl. As the temperature was raised to 60°C, 0.5 wt.% aqueous resorcinol was added dropwise to the reaction flask. Once at 60°C, the propeller speed was decreased to 300 rpm and the reaction continued for two hours. When the reaction was completed and cooled to room temperature, the product was obtained via vacuum filtration and washed with water three times and acetone once. The product was dried at room temperature overnight.

Table 3. Baseline quantities for pre-polymer formation

Pre-Polymer Formation		
Scale	**Urea (g)**	**37 wt.% Formaldehyde (g)**
1	5	12.5
1/2	2.5	6.25
1/4	1.25	3.125

Table 4. Baseline quantities for microcapsule formation

Microcapsule Formation							
Scale	**Pre-PUF (g)**	**E-51/BGE (g)**	**aq. SDBS (g)**	**5 wt. % PVA (g)**	**DI H_2O (mL)***	**1-octanol (drops)**	**5 wt.% Resorcinol (g)**
1	12.25	12.17	50	-	0	5	10
1/2	6.125	6.085	25	-	0	5	5
1/4	3.0625	3.0425	12.5	0.375	10	5	2.5

*water required for mixing with 5.70 cm diameter beaker

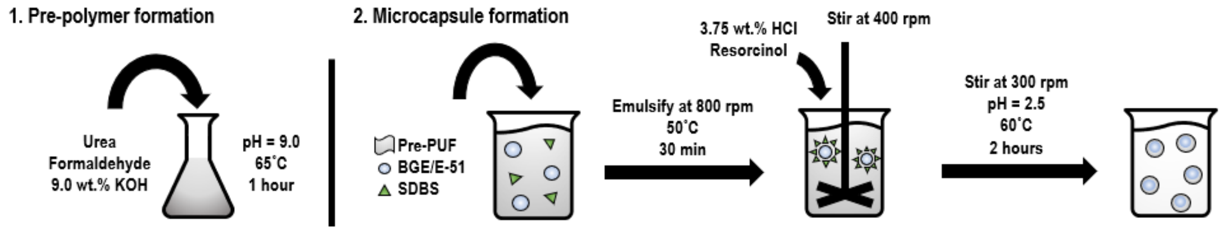

Figure 2. Schematic of Method 2.

2.3. *Microcapsule Characterization*

The surface morphology and diameters of the microcapsules were examined using a Keyence VR-3200 3D Measurement Macroscope during in-situ polymerization and post-filtration. Average diameter and standard deviation of size distribution was calculated by measuring more than 100 microcapsules per sample. Confirmation of epoxy encapsulation was done by crushing dried microcapsules and observing core material.

To determine the mass loss and degradation temperatures, thermogravimetric analysis (TGA) was done using a Netzch TGA-209 Iris instrument. For the PUF and microcapsules, a sample of approximately 10-15 mg was put into aluminum pans weighing approximately 60 mg. The program began at room temperature and was ramped to 500°C at a rate of 10°C/min under nitrogen flow, then allowed to cool to room temperature. Proteus analysis software was used to determine the onset, inflection, and end temperatures of the mass % vs. temperature graph.

Fourier-transform infrared spectroscopy (FTIR) was done using a Jasco FT/IR-6300 to analyze the neat PUF, neat E-51/BGE epoxy, and microcapsules. Prior to data collection, the sample was purged in nitrogen gas for approximately 2 minutes. The transmittance was measured from 500-3600 cm^{-1} with a resolution of 2.0 cm^{-1}.

2.4. Preparation of Microcapsule-Loaded Epoxy Films

CC epoxy films loaded with 10 wt.% and 6.5 wt.% microcapsules were prepared. 1 gram of CC epoxy was mixed with 1 gram of curing agent and the appropriate quantity of microcapsules from either MAW-10 or MAW-13. A neat epoxy coating without microcapsules was also made.

The epoxy system was coated on to aluminum foil covered steel panels with dimensions of 5.08 cm x 5.08 cm. To cure, the films were left overnight at room temperature. The coatings were then scratched with a scalpel blade to create an artificial crack to determine the self-healing ability. The cracks were observed under optical microscopy immediately after scratching and after 12 hours at room temperature.

3. Discussion and Results

3.1. *Synthesis*

Method 1 was used for MAW-01 to MAW-04. During the polymerization phase, epoxy droplets in a cloudy, white liquid was observed. Because this method only acidified the system to a pH of 3.5, no shell wall formation occurred, leading to no viable microcapsules.

Method 2 was used for MAW-05 to MAW-18. Barring MAW-09, syntheses used in MAW-06 to MAW-14 successfully produced microcapsules. After replicating the literature route to form a baseline method, parameters such as solution viscosity, addition of PVA, core/shell ratio, SDBS concentration, and acidification pH were investigated (**Table 5**). The reaction scale was gradually decreased to use less material.

It was found that microcapsule formation is heavily dependent on the mixing behavior and viscosity of the system.

To facilitate proper emulsification of the reaction, the propeller must be fully immersed in the solution. When dealing with the halved and quartered reactant quantities (MAW-09 to MAW-18), the volume of the reactants was insufficient to submerge the propeller fully. Therefore, reducing the reaction vessel diameter, and in the case of the quartered quantities, adding 10 mL of water was necessary to allow for mixing. Due to the fixed propeller size, using smaller diameter glassware to enable emulsification of the quarter scale reactions without water was not feasible.

Additionally, increasing the pre-emulsification viscosity was shown to have an impact in reducing microcapsule diameter. High viscosity can be maintained by using a highly concentrated epoxy system, minimizing the water added prior to emulsification, and adding 5 wt.% PVA solution.

Other than increasing viscosity, the addition of PVA was meant to improve microcapsule dispersion. From literature, PVA has been used as the primary surfactant during PUF microcapsule synthesis[20] but has also been used in conjunction with SDBS to prevent agglomeration and undesirable formation of PUF particles.[6, 7] It is believed that the long polymer chains of PVA prevent clusters of microcapsules from forming.

During the in-situ polymerization phase, aliquots of microcapsules emulsified with the addition of PVA showed less aggregation than aliquots taken without PVA (**Figure 3**).

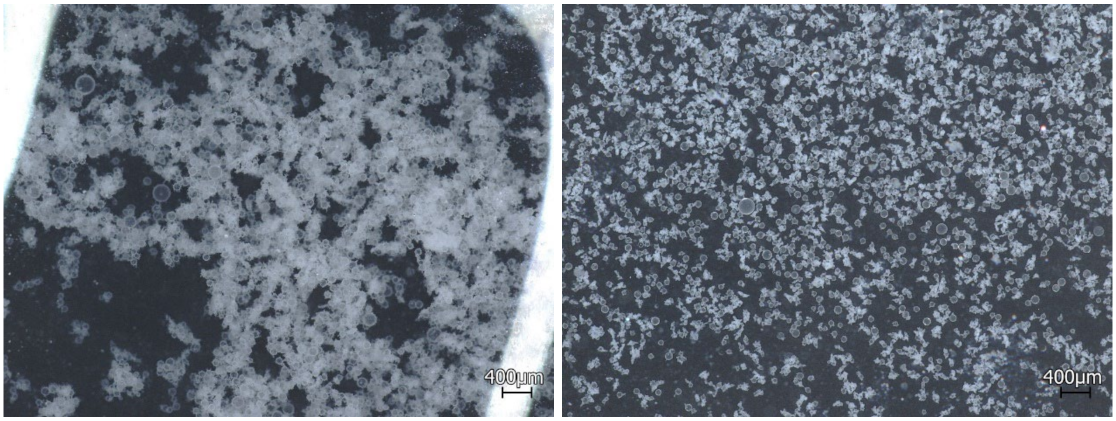

Figure 3. MAW-10 synthesis aliquot without PVA (left) and MAW-13 synthesis aliquot with PVA (right) at 40X magnification. Aliquots were taken after 5 minutes at 60°C.

Core/shell ratio (epoxy system/pre-PUF) was also considered. When more PUF is present in the reaction mixture than necessary to form a thin shell around the epoxy droplets (low core/shell ratio), it continues to grow the shell wall until all PUF is reacted. This leads to microcapsules with thick walls and a rough surface. Conversely, increasing the core/shell ratio reduces surface roughness but leads to formation of PUF crystallite where excess PUF is not well-integrated into the structure of the microcapsule. By increasing the ratio from 1.1 to 1.2, an improvement in surface morphology was observed.

Control of the SDBS/epoxy ratio and pH during the acidification stage is essential to microcapsule formation and were evaluated to diminish the presence of PUF crystallite. The SDBS/epoxy ratio was evaluated in MAW-15 and MAW-16 at 0.04 and 0.08, respectively to compare against the SDBS/epoxy baseline ratio of 0.02. In both cases, small amounts of epoxy droplets with large, irregularly shaped chunks of PUF had formed after 5 minutes. No microcapsules were formed in these trials. The acidification pH used as the baseline was 2.5. During MAW-09, the pH was mistakenly decreased to less than 2, leading to rapid PUF formation and no viable microcapsules. pH was investigated further in MAW-17 and MAW-18 with acidification pH of 3.0 and 3.5, respectively. Neither pH was sufficient to form microcapsules, as all the PUF formed large clumps that were interspersed amongst large quantities of epoxy droplets.

From these trials, it was found that high pre-emulsification viscosity, adding PVA, an SDBS/epoxy ratio of 0.02, and acidification pH of 2.5 are the ideal conditions for microcapsule formation in the given system. Further evaluation of core/shell ratio on microcapsule morphology is needed.

Table 5. Selected successful syntheses and reaction parameters. Reaction parameters for all tests can be found in SI Table X.

Test	**Scale**	**E-51/ BGE**	**Glassware Diameter* (cm)**	**Pre-emulsion H_2O**	**PVA**	**Core/shell ratio**	**Avg. Capsule Diameter (μm)**
MAW-06	1	70 wt.%	6.23	0 mL	-	1.1	135 ± 31
MAW-07	½	70 wt.%	6.23	50 mL	-	1.1	442 ± 72
MAW-08	½	60 wt.%	6.23	50 mL	-	1.1	791 ± 97
MAW-10	½	70 wt.%	5.70	0 mL	✓	1.1	98 ± 19
MAW-12	¼	70 wt.%	5.70	10 mL	✓	1.1	100 ± 19
MAW-13	¼	70 wt.%	5.70	10 mL	✓	1.2	78 ± 16

*inner diameter

3.2. Morphology and Size Distribution

Optical microscopy was performed to observe the surface morphology, shape, and size of the microcapsules and to confirm the presence of epoxy within them. A histogram of size distribution in MAW-13, images of selected microcapsules, and epoxy confirmation are in **Figures 4-6**, respectively. Average microcapsule diameter and size distribution is summarized in **Table 6.**

Spherical microcapsules with surface PUF aggregation were produced for syntheses MAW-06 to MAW-14, except MAW-09 (**Figure 5**).

The baseline synthesis, MAW-06, produced microcapsules with a rough surface and average diameter of 135 ± 31 microns. After halving the reaction quantities, MAW-07 and MAW-08 had identical parameters except for E-51/BGE concentration. Due to the additional water before emulsification and in the case of MAW-08, a less concentrated epoxy system, the viscosities of the systems were much lower than the baseline reaction. This led to very large, rough microcapsules averaging 442 ± 72 and 791 ± 97 microns, respectively. By not adding water pre-emulsification for MAW-10, the average diameter was reduced to 98 ± 19 microns and the amount of PUF aggregation on the surface was decreased. When quartering the baseline reaction quantities, additional water and 5 wt.% PVA solution was added to facilitate mixing and improve dispersion. MAW-12 produced microcapsules that were covered in a thick layer of PUF and had an average diameter of 100 ± 19. The most promising synthesis, MAW-13 produced microcapsules that appeared the smoothest and fell within our desired size range with an average diameter of 78 ± 16 microns. This is attributed to the increase in core/shell ratio. However, they still contain PUF crystallite which is not ideal.

After puncturing a microcapsule from MAW-10 with a needle, a liquid was found to spill from the center, confirming successful epoxy encapsulation (**Figure 6**).

Table 6. Average size and size range for selected syntheses.

Test	Average Size (µm)	Size Ranges (µm)
MAW-06	135 ± 31	80 - 283
MAW-07	442 ± 72	288 - 721
MAW-08	791 ± 97	506 - 979
MAW-10	98 ± 19	65 - 163
MAW-12	100 ± 19	48 - 149
MAW-13	78 ± 16	46 – 150

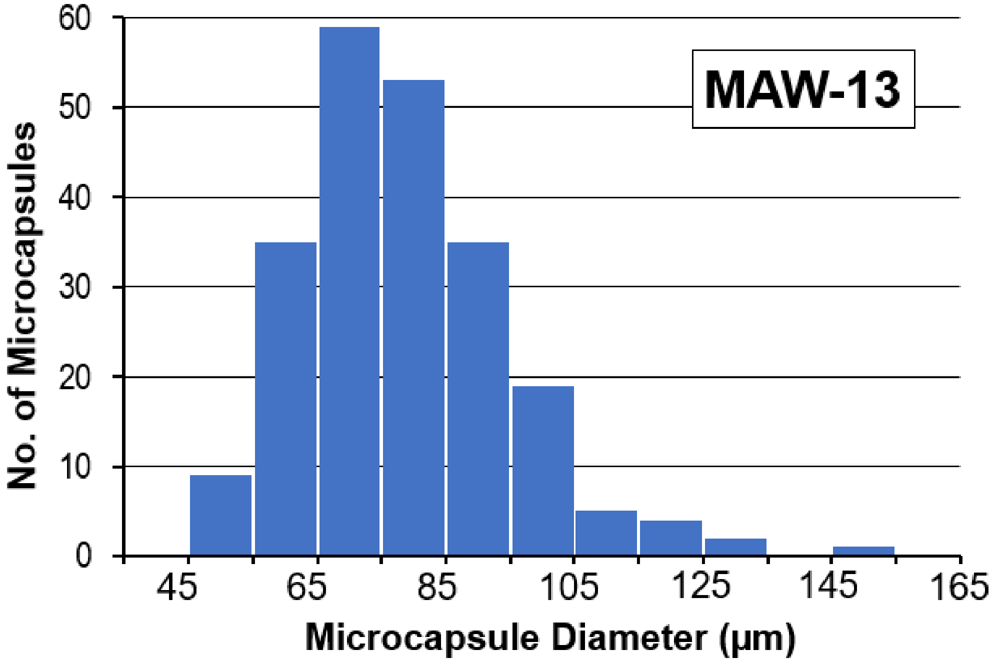

Figure 4. Size distribution of MAW-13.

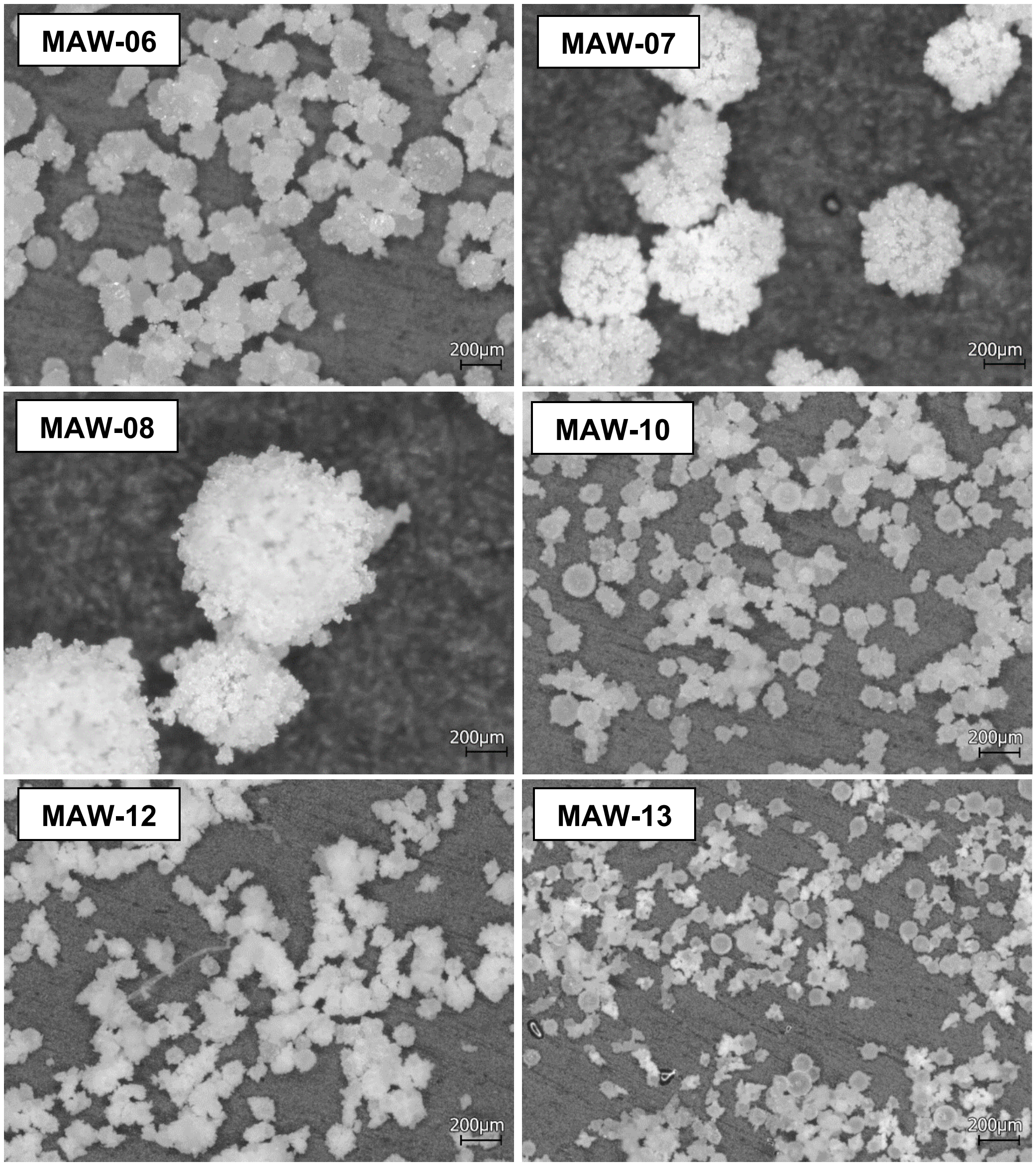

Figure 5. Optical images for selected synthesis at 120X magnification.

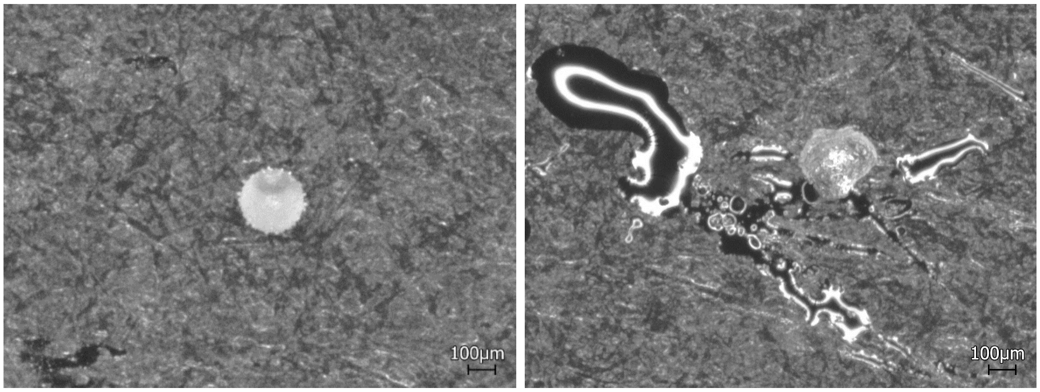

Figure 6. MAW-10 microcapsule before (left) and after puncturing (right)

3.3. *Fourier-Transform Infrared Spectroscopy (FTIR)*

FTIR was utilized to qualitatively characterize the presence of healing agent within the microcapsules. **Figure 7** illustrates the FTIR spectra of the epoxy system (BGE/E-51), neat PUF, and epoxy-loaded PUF microcapsules. In the PUF spectra, the most characteristic peak seen at 3323 cm^{-1} is attributed to the N-H bond stretching from primary and secondary amines. For the epoxy resin, the strong, broad peak at 3341 cm^{-1} corresponds to O-H stretching and the absorption at 2964 cm^{-1} corresponds to C-H stretching of the epoxide ring. The C=C and C-C bonds of the aromatic rings were observed via the peaks at 1606 and 1508 cm^{-1}, respectively. Evidence of a C-O stretch belonging to an alkyl aryl ether was seen at 1240 cm^{-1}. The large, sharp peak at 827 cm^{-1} is assigned to the C-O-C stretching vibration of the epoxide ring. Regarding the microcapsules, the epoxy peaks are clearly seen with no significant change in wavenumber, thus confirming the presence of epoxy in the sample.

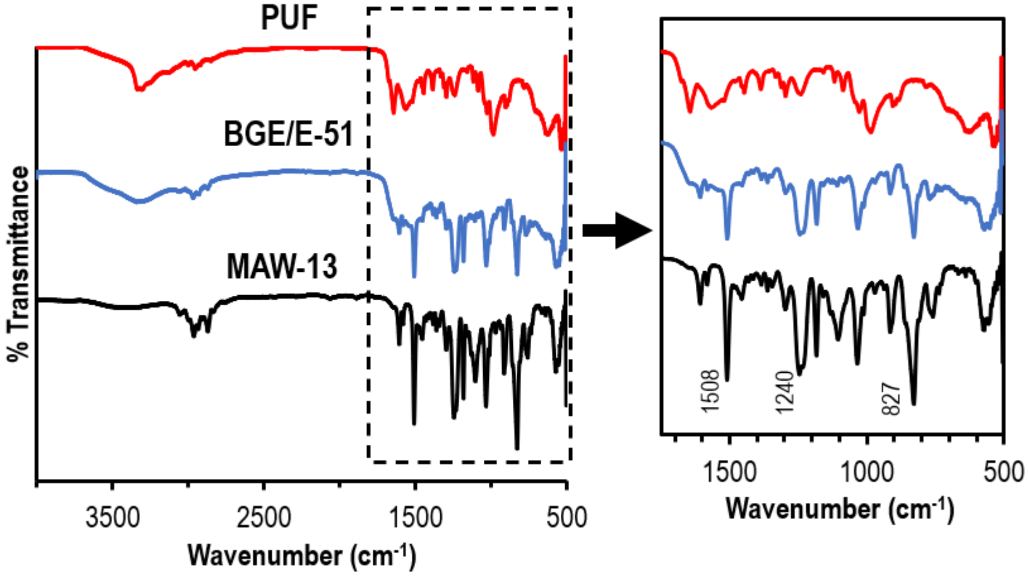

Figure 7. FTIR spectra of neat PUF, neat epoxy system, and microcapsules from MAW-13

3.4. Thermogravimetric Analysis (TGA)

TGA was performed on neat PUF and microcapsules MAW-10 and MAW-13 to determine thermal stability and the presence of epoxy resin (**Figure 8**). Neat PUF was found to have a one-step degradation profile and exhibited maximum mass loss at 299.6°C (inflection point). MAW-10 and MAW-13 show two-step degradation profiles with the first onset degradation temperature occurring around 250°C and another step onset beginning at approximately 340°C (**Table 7**). Tzavidi et.al. reported a degradation temperature of 371.4°C for neat E-51 and 2nd step degradation inflection temperatures ranging from 385.1-400.6°C for their microcapsules of an identical core/shell system.[2] The appearance of a second step at an increased temperature in the microcapsule samples implies the presence of epoxy resin.

Table 7. Onset, inflection, and end temperature recorded during TGA.

Sample	Step	Onset Temp. (°C)	Inflection Temp. (°C)	End Temp. (°C)
PUF	-	290.4	299.6	308.0
MAW-10	1	254.2	255.0	334.3
	2	336.9	387.3	428.5
MAW-13	1	254.3	257.1	312.5
	2	347.7	397.6	410.4

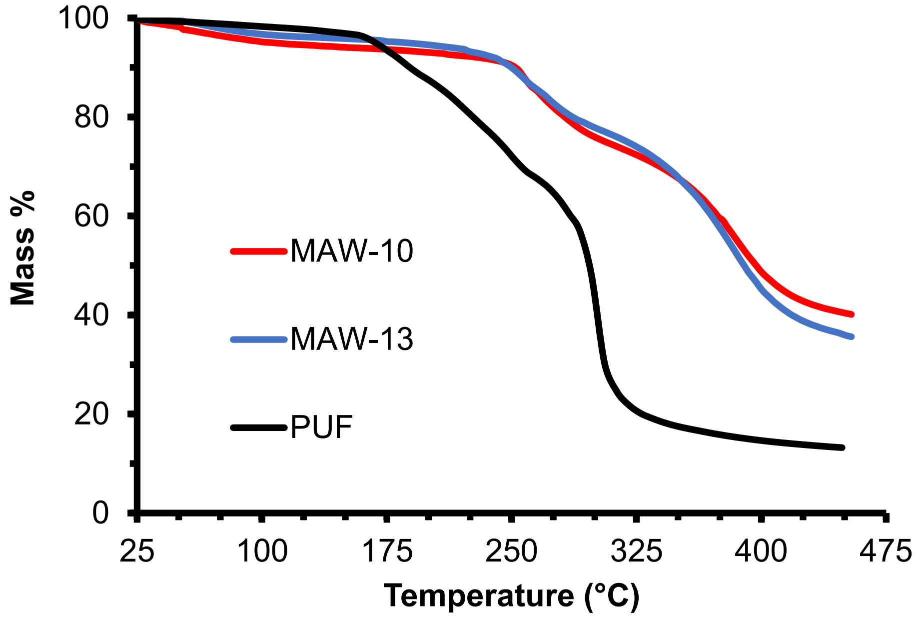

Figure 8. TGA of neat PUF and microcapsules

3.5. Self-Healing Ability

Optical microscopy was used to evaluate the self-healing performance of coatings containing epoxy loaded PUF microcapsules. A scalpel was used to create artificial scratches on the surface of the self-healing and neat coatings. Images were taken immediately after scratching and after 12 hours at room temperature. In the neat coating (**Figure 9A-9B**), the scratch was not healed as the CC epoxy used has no intrinsic self-healing properties and there was no healing agent to be released for extrinsic self-healing. In the microcapsule loaded coatings, however, self-healing behavior was observed as seen by the crack width decreasing over time (**Figure 9C-9D**). There was no visible difference in self-healing efficacy between the 6.5 and 10 wt.% microcapsule films.

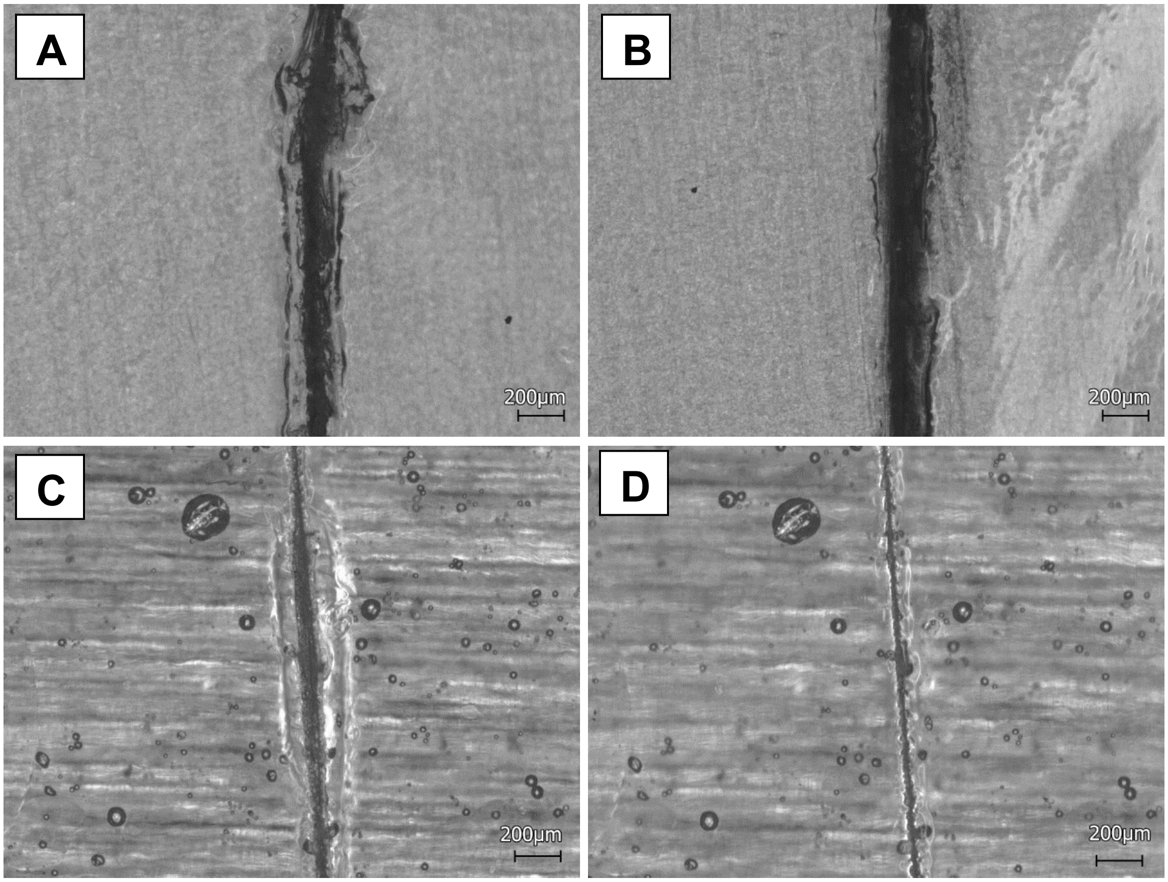

Figure 9. Neat epoxy coating immediately after scratching (A) and after 12 hours at room temperature (B). 6.5 wt.% microcapsules in epoxy coating immediately after scratching (C) and after 12 hours at room temperature (D).

4. *Conclusions*

A two-step synthesis route was developed to produce epoxy-loaded poly(urea formaldehyde) microcapsules with an average diameter of less than 100 microns. Investigation of process parameters such as solution viscosity, size of reaction vessel, addition of PVA, and core/shell ratio was done with respect to microcapsule size and morphology.

During syntheses, the following relationships were observed:

- Increased viscosity pre-emulsification correlates to decreased average microcapsule size.
- Increased core/shell ratio corresponds to decreased surface roughness of microcapsules.
- Adding PVA pre-emulsification improves dispersion of the microcapsules and facilitates a decrease in reaction scale.
- Proper acidification pH is required to initiate polymerization at an adequate pace for shell wall formation.

The microcapsules were confirmed to contain epoxy via FTIR, TGA, and visual observation. When an epoxy film was loaded with microcapsules, the coating demonstrated self-healing behavior.

In the future, work should be done to minimize the formation of PUF crystallite on the surface of the microcapsules. This could be done by evaluating additional core/shell ratios. Also, further assessment of the self-healing coating's ability to protect against corrosion should be done by completing electrochemical impedance spectroscopy (EIS) and salt spray testing.

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SI Table 1. Synthesis goals, scale, and urea and formaldehyde quantities for pre-PUF.

MAW-	Desired Outcome	Scale	Urea (g)	37 wt.% Formaldehyde (g)
05	Make microcapsules	1	10	25
06				
07	Use less reactants	1/2	5	12.5
08				
09	Reduce microcapsule size by increasing viscosity and decreasing glass diameter	1/2	5	12.5
10				
11	Increase viscosity and improve dispersion	1/4	2.5	6.25
12				
13	Reduce PUF on surface	1/4	2.5	6.25
14				
15	Reduce PUF crystallite	1/4	2.5	6.25
16				
17	Reduce PUF on surface	1/4	2.5	6.25
18				

SI Table 2. Reactant quantities for MAW-05 to MAW-18

MAW-	Pre-PUF (g)	wt.% BGE/E-51	BGE/E-51 (g)	0.5 wt% SDBS	5 wt. % PVA (g)	H2O pre-emulsion (g)	5 wt.% resorcinol (g)	1-octanol (drops)
05	12.25	17.8	12.17	50	-	0	10	5
06	12.25	30	12.17	50	-	0	10	5
07	6.125	30	6.085	25	-	50	5	5
08	6.125	40	6.085	25	-	50	5	5
09	6.125	30	6.085	25	-	0	5	5
10	6.125	30	6.085	25	-	0	5	5
11	3.0625	30	3.0425	12.5	-	10	2.5	5
12	3.0625	30	3.0425	12.5	0.375	10	2.5	5
13	2.5354	30	3.0425	12.5	0.375	10	2.5	5
14	2.1732	30	3.0425	12.5	0.375	10	2.5	5
15	2.5354	30	3.0425	12.5*	0.375	10	2.5	5
16	2.5354	30	3.0425	12.5**	0.375	10	2.5	5
17	2.5354	30	3.0425	12.5	0.375	10	2.5	5
18	2.5354	30	3.0425	12.5	0.375	10	2.5	5

*1 wt. % SDBS

**2 wt. % SDBS

SI Table 3. Additional reaction parameters for MAW-05 to MAW-18

MAW-	Core/shell ratio	Acid pH	Inner diameter of glassware (cm)	Propeller height* (cm)
05	1.1	2.5	6.23	1
06	1.1	2.5	6.23	1
07	1.1	2.5	6.23	1
08	1.1	2.5	6.23	1
09	1.1	2.5	5.70	0.6
10	1.1	2.5	5.70	1
11	1.1	2.5	5.70	0.6
12	1.1	2.5	5.70	0.6
13	1.2	2.5	5.70	0.6
14	1.6	2.5	5.70	0.6
15	1.2	2.5	5.70	0.6
16	1.2	2.5	5.70	0.6
17	1.2	3	5.70	0.6
18	1.2	3.5	5.70	0.6

*from bottom of beaker as seen from outside