A combined interfacial and in-situ polymerization strategy to construct well-defined core-shell epoxy-containing SiO\(_2\)-based microcapsules with high encapsulation loading, super thermal stability and nonpolar solvent tolerance

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**ABSTRACT**

SiO\(_2\)-based microcapsules containing hydrophobic molecules exhibited potential applications such as extrinsic self-healing, drug delivery, due to outstanding thermal and chemical stability of SiO\(_2\). However, to construct SiO\(_2\)-based microcapsules with both high encapsulation loading and long-term structural stability is still a troublesome issue, limiting their further utilization. We herein design a single-batch route, a combined interfacial and in-situ polymerization strategy, to fabricate epoxy-containing SiO\(_2\)-based microcapsules with both high encapsulation loading and long-term structural stability. The final SiO\(_2\)-based microcapsules preserve high encapsulation loading of 85.7 wt\% by controlling exclusively hydrolysis and condensed polymerization at oil/water interface in the initial interfacial polymerization step. In the subsequent in-situ polymerization step, the initial SiO\(_2\)-based microcapsules as seeds could efficiently harvest SiO\(_2\) precursors and primary SiO\(_2\) particles to finely tune the SiO\(_2\) wall thickness, thereby enhancing long-term structural stability of the final SiO\(_2\)-based microcapsules including high thermal stability with almost no any weight loss until 250\(^\circ\)C, and strong tolerance against nonpolar solvents such as CCl\(_4\) with almost unchanged core-shell structure and unchanged core weight after immersing into strong solvents for up to 5 days. These SiO\(_2\)-based microcapsules are extremely suited for processing them into anticorrosive coating in the presence of nonpolar solvents for self-healing application.

**1. Introduction**

Microencapsulation of liquid functional ingredients in solid shell has recently drawn great attention owing to its various applications in self-healing, drug delivery, and energy-storage fields in the past decades [1–4]. Theoretically, microcapsules could both isolate inner active species with high loading from outer environment and hold...
long-term storage and processing stability to achieve controlled release of their latent functionality at targeted location and/or at desired time upon an external stimulus. In general, microcapsules could be mainly divided into two classes: polymeric and inorganic microcapsules in terms of their shell composition of these microcapsules. Up to date, many hydrophobic reagents have been encaged into various polymer shells such as PU [5], PUF [6], PMMA [7], Poly(l-lactide) (PLLA) [8], and PMF [9] as self-healing materials for anticorrosive coatings or phase-change materials for energy storage application due to their facile synthesis methods and tunable shell composition. However, with respect to many specific applications, especially self-healing coatings, polymer shells as protective barriers often suffer from undesirable swelling and/or degradation during long term storage and processing of microcapsules into the coatings which involves elevated temperature (e.g. above 100°C) [10] and/or strong solvent, thereby leading to partial loss of active healing agents into the host matrix before the delivery of their payloads.

Microencapsulating active species into inorganic microcapsules such as SiO₂ opens up a great opportunity for their self-healing application in anticorrosive coatings due to excellent chemical and thermal stability of SiO₂. In theory, SiO₂-based microcapsules could be synthesized in oil-in-water (O/W) emulsion based on hydrophobic healing ingredients as an inner core [11–13]. As yet, general strategies to encage hydrophobic molecules into SiO₂-based microcapsules in O/W emulsion are mainly divided into two classes: interfacial polymerization [14–16] and in-situ polymerization [17–19]. The difference between these two mechanisms lies in the diffusion of hydrophobic SiO₂ precursors from either the inner oil phase or the outer water phase onto the interface of emulsion drops to achieve the sol-gel deposition of SiO₂ shell catalyzed by aqueous acid or alkali solution. On one hand, though SiO₂-based microcapsules synthesized via interfacial polymerization has high encapsulation loading, their relatively thin SiO₂ shell walls usually suffer from undesirable breakage during long-term storage [20]. This insoluble problem is possibly due to the initially formed SiO₂ layer isolating residual SiO₂ precursors in microcapsules from aqueous acid or alkali catalysts and in turn preventing an increase in shell thickness. On the other hand, while SiO₂-based microcapsules fabricated via in-situ polymerization has controllable size and tailored shell thickness, there are still some obvious drawbacks such as low encapsulation loading and generation of numerous isolated SiO₂ nanoparticles accompanied by the yield of the microcapsules [15]. These defects result from weak affinity of oil drops to newly emerged SiO₂ particles in water phase due to the difference in compatibility between them. Therefore, it is still a challenge to develop a feasible method to construct thermally stable and solvent-resistant SiO₂-based microcapsules with tunable shell thickness and high encapsulation loading.

Herein we develop a single batch route, a combined interfacial and in-situ polymerization strategy, to synthesize well-defined core-shell epoxy-containing SiO₂-based microcapsules with tunable size, high encapsulation loading, and robust thermal and nonpolar solvent stability. In the initial interfacial polymerization step, tetraethyl orthosilicate (TEOS) in emulsion drops diffuse toward the O/W emulsion interface and subsequently hydrolysis and condensed polymerization occur upon collision with aqueous HCl catalyst to form the initial thin SiO₂ shell. In the subsequent in-situ polymerization step, on the basis of acid-catalyzed effect and good compatibility of the initial SiO₂ shell
with them, hydrolyzed product of TEOS and small newly emerged SiO\textsubscript{2} particles could be maximally captured by the initial SiO\textsubscript{2}-based microcapsules with thin shell, thus depositing on their surface to form the final SiO\textsubscript{2}-based microcapsules with thick shell. As expected, the as-synthesized SiO\textsubscript{2}-based microcapsules via a combined interfacial and in-situ polymerization strategy has high encapsulation efficiency up to 85.7 wt\%, outstanding thermal stability with almost no any weight loss until 250°C, and strong resistance against nonpolar solvents such as CCl\textsubscript{4} with almost unchanged core-shell structure and unchanged core weight after immersing into strong solvents for up to 5 days.

2. Experimental section

2.1. Materials

Acetone, N, N-dimethylformamide (DMF), TEOS (>99%), and carbon tetrachloride (CCl\textsubscript{4}) were obtained from Shanghai Aladdin biochemical Polytron Technologies Inc. Bisphenol A diglycidyl ether (E-51) and epoxidized hydrogenated bisphenol A (A1815) were obtained from Qingda-Qs Materials Co., Ltd. Poly(ethylene oxide-b-propylene oxide-b-ethylene oxide) triblock copolymer (PEO100-PPO65-PEO100, Pluronic F127), polydimethylsiloxane (PDMS), and trimethylolpropane triacrylate (TMPTA) were purchased from Sigma, Alfa, and Macklin, respectively. Deionized water and an aqueous HCl solution (2 mol/L) were also utilized through the experiments.

2.2. Synthesis of SiO\textsubscript{2}-based microcapsules

A combined interfacial and in-situ polymerization method was designed to fabricate SiO\textsubscript{2} microcapsules by controlling the hydrolysis and condensation of TEOS inside and outside the droplets. Firstly, the uniform mixture of E-51 (1.0 g), A1815 (1.0 g), and TEOS (1.0 g) as the oil phase was emulsified in a 2 wt\% aqueous PEO-PPO-PEO solution (40 mL) with stirring at 8000 rpm with an homogenizer for 10 min at room temperature, forming an fine O/W emulsion. Secondly, a 2.0 mol/L aqueous HCl solution (0.6 mL) was dropped into the obtained O/W emulsion, and the resultant mixture was stirred at 300 rpm for 3 h at 50°C to generate the initial SiO\textsubscript{2} microcapsules with thin shell. Thirdly, in the subsequent in-situ polymerization step, additional TEOS (1.5 g) was added into the dispersion, followed by the dripped addition of a 2.0 mol/L aqueous HCl solution (1.8 mL) in three equal portions at 4-h intervals and the subsequent continual reaction for another 12 h. Finally, the resultant SiO\textsubscript{2}-based microcapsules with thick shell were washed by distilled water three times and then dried at 60°C for 24 h.

PDMS or TMPTA-containing SiO\textsubscript{2}-based microcapsules were synthesized through the combined interfacial and in-situ polymerization strategy mentioned above with only alternation that PDMS (2 g) or TMPTA (2 g) was used to replace the mixture of E-51 (1.0 g) and A1815 (1.0 g), respectively.
2.3. Characterization

Optical microscopy (OM) images were taken with a XSZ-G Optical Microscope. Scanning electron microscopy (SEM) images were taken with a SUPRA 55 Schottky field emission scanning electron microscope. Fourier Transform infrared (FTIR) spectra were recorded on a Nicolet IS10 infrared spectrometer with KBr pellets. Thermogravimetric analysis (TGA) data were obtained with a NETZSCHSTA-449C instrument from 25°C to 1000°C in nitrogen.

3. Results and discussion

3.1. Synthesis and characterization of epoxy-containing SiO$_2$-based microcapsules

Bisphenol A diglycidyl ether (E-51), one of liquid epoxy monomer, has been widely used as outstanding microencapsulated self-healing agent due to its excellent properties such as distinguished adhesion to diverse substrates, low shrinkage upon cure, good mechanical property [21], and epoxy diepoxidized hydrogenated bisphenol A (A1815) with low viscosity could modulate the mobility of liquid core, which is of great significance to achieve controllable release of liquid core. Moreover, Bisphenol A diglycidyl ether has similar solubility parameter (23.4 MPa$^{1/2}$) [22] to that of TEOS, SiO$_2$ precursor (16.4 MPa$^{1/2}$) [23], meaning that their good compatibility is intrinsically favored for designing an interfacial polymerization strategy to synthesize epoxy resin-containing SiO$_2$ microcapsules. Thereby, the mixture of epoxy resin E-51 and A1815 is chosen as main liquid core to fabricate well-defined core-shell epoxy resin-containing SiO$_2$-based microcapsules with high encapsulation loading and high stability.

The overall preparation procedure of SiO$_2$-based microcapsules (Figure 1(a)) could be divided into two steps: the interfacial polymerization step and the subsequent in-situ polymerization step. In the interfacial polymerization step, firstly, epoxy resin E-51, epoxy resin A1815, and TEOS could be uniformly mixed as oil phase in terms of their similar solubility parameters, and then the mixture was emulsified in aqueous F127 solution to form a stable O/W emulsion (Figure 1(b)). Secondly, the HCl solution added dropwise into the emulsion (Figure 1(c)) initiates acid-catalyzed hydrolysis and subsequent condensation of TEOS exclusively at O/W interfaces to form the initial SiO$_2$ microcapsule with thin shell (Figure 1(d)). However, there is no any obvious increase in the shell thickness of the initial microcapsules by adjusting the amount of TEOS in oil phase from 1 g to 3 g, and all samples suffered from undesired breakage to some extent after only drying at 60°C (Figure 2) due to extremely thin shell walls with thermal and mechanical instability. The formation of these extremely thin shells are probably because the initially generated compact SiO$_2$ shells isolate protons in water phase from residual TEOS monomer in oil phase and further block acid-catalyzed hydrolysis and polymerization of TEOS to form thicker SiO$_2$ shell. In order to increase the SiO$_2$ shell thickness to improve the stability of SiO$_2$ microcapsules, an additional in-situ polymerization step was introduced to synthesis procedure of the microcapsules after the initial interfacial polymerization step. Additional TEOS monomers in one portion and HCl solution in three equal portions were dropped into the emulsion to complete the subsequent deposition of SiO$_2$ layer on the outer surface of the initial microcapsules with thin shell formed in the interfacial polymerization
The addition of the HCl solution in three equal portions aims at compensation for proton consumption during reaction and ensures enough protons on the surface of the initial SiO$_2$ microcapsules to capture TEOS monomer and primary SiO$_2$ nuclei to form the final microcapsules with well-defined core-shell structure and a size of approximately 25 μm (Figure 1(e)).

The FTIR spectroscopy was also utilized to verify the encapsulation of epoxy resin within the SiO$_2$-based microcapsules. As shown in Figure 3(c), the absorption peaks at around 947 and 2936 cm$^{-1}$ of the SiO$_2$-based microcapsules derive from the vibrations of epoxy group and –CH$_2$– of epoxy resin mixture (Figure 3(a)) [24,25]. Besides, in contrast to the spectrum of pure SiO$_2$ particles (Figure 3(b)), the characteristic absorption peaks at 1083, 822, and 456 cm$^{-1}$ of the SiO$_2$-based microcapsules represent the asymmetric, symmetric Si–O–Si bending vibrations and Si–O bands of the SiO$_2$, respectively (Figure 2(c)) [26,27]. The above results confirm that epoxy resin has been
successfully encaged into the SiO\textsubscript{2}-based microcapsules, in good agreement with well-defined core-shell structure in Figure 1(e).

Figure 2. Optical images of microcapsules obtained only by the single interfacial polymerization step with the different amount of TEOS: (a), (d) 1.0 g, (b), (e) 2.0 g, (c), (f) 3.0 g before (a), (b), (c) and after (d), (e), (f) drying at 60°C, and the insets corresponding to photographs of three aforementioned samples after drying, respectively.

Figure 3. FTIR spectra of (a) the oil mixture of epoxy resin, (b) pure SiO\textsubscript{2} particles, and (c) SiO\textsubscript{2}-based microcapsules.
3.2. Effect of the total HCL concentration on the shell thickness of SiO$_2$-based microcapsules

The appropriate shell thickness is extremely important for microcapsules to store active species for a long time before controlled delivery of the core functionality at targeted location and desired time for the related application. Therefore, the effect of HCl concentration on the shell thickness of SiO$_2$ microcapsules was discussed. When the total HCl concentration increases from 0.08 mol/L to 0.14 mol/L, all the final SiO$_2$-based microcapsules show good spherical morphology and well-defined core-shell structure and their shell thickness increases from 2.1 to 4.3 μm, respectively, as shown in Figure 4. This tendency depends highly on proton number in the aqueous phase and on the droplet surface. The more protons in the aqueous phase can catalyze hydrolysis and condensed polymerization of more TEOS molecules to generate primary SiO$_2$ nuclei, and then the protons on droplet surface can capture directly more primary SiO$_2$ nuclei and TEOS monomers to form the ultimate microcapsules with thicker shell. Meanwhile, in view of the unavoidable consumption of the protons in the process of shell formation, the HCl solution was added in three equal portions to maintain sufficient protons onto the surface of the oil droplets, and thus the primary SiO$_2$ nuclei and TEOS were harvested to deposit layer by layer on the initial SiO$_2$ shell to construct the ultimate SiO$_2$-based microcapsules as expected.

3.3. Effect of the amount of TEOS in the subsequent in-situ polymerization step on the shell thickness of SiO$_2$-based microcapsules

The feeding amount of TEOS in the in-situ polymerization step is also a key factor in tuning the silica shell thickness. As exhibited in Figure 5, there is an obvious increase in the thickness of the silica shell from 1.6 to 3.5 μm by tailoring the feeding amount of TEOS in this step from 1.0 to 2.0 g. Generally, the reason underlying this tendency is that the higher amount of TEOS could generate more primary SiO$_2$ nuclei and thus increase the collision probability of both the nuclei and TEOS molecules with the silica shell to finally construct the thicker SiO$_2$ shell. However, some broken microcapsules can be obviously observed in Figure 5(a), possibly because the shell is too thin to hold the core in the continuously stirring process due to its weak mechanical stability.

3.4. Effect of the stirring speed in emulsification step on the average size of SiO$_2$-based microcapsules

As shown in Figure 6, the size of the as-synthesized SiO$_2$-based microcapsules is highly dependent on the stirring speed. By reducing the stirring speed in the emulsifying process from 15000 to 6000 rpm, the average size of microcapsules could increase from 10 to 52 μm determined directly by the sizes of the O/W droplets in the emulsion step, in consistent with previous understanding that the higher emulsifying speed leads to the smaller size of liquid drops in emulsion [28]. However, some irregular pure SiO$_2$ particles appear in Figure 6(c), because the initially formed SiO$_2$ microcapsules with small specific surface area derived from
Figure 4. SEM images of the complete SiO$_2$-based microcapsules and a corresponding broken microcapsule fabricated with the total different HCl concentrations at (a), (e) 0.08 mol/L; (b), (f) 0.10 mol/L; (c), (g) 0.12 mol/L; (d), (h) 0.14 mol/L, attained by adding 2 mol/L aqueous HCl solutions (1.6, 2.0, 2.4, and 2.8 mL) in four equal portions, respectively.
large emulsion droplets reduce the collision probability between SiO$_2$ primary nuclei and the initial SiO$_2$ microcapsules and in turn lead to generation of the numerous isolated SiO$_2$ particles.

3.5. Thermal stability and solvent tolerance of epoxy-containing SiO$_2$-based microcapsules

The thermal stability of SiO$_2$-based microcapsules was measured by TG analysis. There is a tiny weight loss of 7.3 wt% corresponding to the evaporation of absorbed water from
25°C to 1000°C in the TG curve of pure SiO$_2$ (Figure 7(a)), demonstrating its high thermal stability. Compared to the TG curve of the oil core mixture (Figure 7(c)), the SiO$_2$-based microcapsules (Figure 7(b)) show the similar thermal degradation process. There is almost no any weight loss before 250°C, indicating the high thermal stability of epoxy resin (Figure 7(c)) and SiO$_2$-based microcapsules (Figure 7(b)). The total residual weight of the oil mixture in the entire temperature range (Figure 7(c)) is 10.5 wt%, corresponding mainly to the pyrolysis product after sharp thermal decomposition of epoxy resin at about 269°C, which means that the total residual weight of 24.8 wt% for SiO$_2$-based microcapsules consists of SiO$_2$ shell and the pyrolysis product of epoxy resin. According to the above data, it is deduced that the encapsulation loading of epoxy resin in our SiO$_2$-based microcapsules is up to 85.7 wt%, which confirms that our SiO$_2$-based microcapsules exhibit outstanding thermal stability and have high encapsulation loading.

Solvent tolerance of microcapsules is extremely important for processing them into self-healing coatings involving strong solvents, especially nonpolar solvents. To evaluate the solvent tolerance of SiO$_2$-based microcapsules, we immersed the microcapsules into H$_2$O, DMF, acetone, and CCl$_4$ solvents for up to 5 days, respectively. All recovered samples maintain their initial spherical morphology and well-defined core-shell structure in Figure 8, but they exhibit different changes in encapsulation.

Figure 7. TG curves of (a) pure SiO$_2$ particles, (b) the as-synthesized SiO$_2$-based microcapsules, and (c) the hydrophobic mixture of epoxy resins (E-51 and A1815).

Figure 8. Optical images of SiO$_2$-based microcapsules taken after immersion into H$_2$O (a), DMF (b), acetone (c), and CCl$_4$ (d) for 5 days.
loading according to TG curves in Figure 9. Compared with the encapsulation loading of the pristine microcapsules (85.7 wt%), the encapsulation loadings of the microcapsules after their immersion into DMF and acetone go down to 52.7 wt% and 68.9 wt%, respectively, attributing to partial loss of epoxy resin in microcapsules. The encapsulation loadings of the microcapsules after their immersion into H\textsubscript{2}O and CCl\textsubscript{4} are 90.3 wt% and 88.4 wt%, respectively. Minor differences in encapsulation loading after the immersion of the microcapsules into these two solvents demonstrate the strong tolerance of our microcapsules for H\textsubscript{2}O and CCl\textsubscript{4}, which is extremely suitable for processing them into anticorrosive coating in the presence of nonpolar solvents for self-healing application [29].

3.6. Synthesis of other hydrophobic molecules containing SiO\textsubscript{2}-based microcapsules

To further evaluate the feasibility of our combined interfacial and in-situ polymerization strategy to synthesize organic phase-containing SiO\textsubscript{2}-based microcapsules, PDMS and TMPTA, with solubility parameters of 14.9–15.5 [30] and 18.6 MPa\textsuperscript{1/2} [31], respectively, are also chosen as microencapsulated agents, on the basis of their similar solubility to that of TEOS, 16.4 MPa\textsuperscript{1/2}. As displayed in Figure 10, both PDMS and TMPTA-containing SiO\textsubscript{2}-based microcapsules are generally spherical with obvious core-shell structure, but the irregular morphology of both microcapsules accompanied by generation of isolated SiO\textsubscript{2} particles and partially uncoated oil phase is not ideal for further application. The results mentioned above in combination with epoxy resin-containing SiO\textsubscript{2}-based microcapsules show our interfacial and in-situ polymerization strategy is suited for synthesis of SiO\textsubscript{2}-based microcapsule utilizing organic substance with similar solubility parameter to that of TEOS. However, there is still an issue to construct SiO\textsubscript{2}-based microcapsules with well-defined core-shell structure and high encapsulation loading for specific organic substance, which may be achieved by tailoring deposition rate of SiO\textsubscript{2} layer onto emulsion droplets before emulsion breaking.

Figure 9. TG curves of SiO\textsubscript{2}-based microcapsules taken after immersion into H\textsubscript{2}O, DMF, acetone, and CCl\textsubscript{4} for 5 days.
4. Conclusions

In conclusion, a combined interfacial and in-situ polymerization strategy was developed to construct the well-defined core-shell epoxy resin-containing SiO$_2$-based microcapsules. The thickness of SiO$_2$ shell can be tuned by finely tailoring the total HCl concentration and the feeding TEOS amount in the in-situ polymerization step. Epoxy resin-containing SiO$_2$-based microcapsules exhibit outstanding thermal stability with almost no any weight loss until 250°C and good nonpolar solvent tolerance with almost unchanged core-shell structure and unchanged core weight even after immersing into strong solvents for up to 5 days. Further studies are application of epoxy-containing SiO$_2$-based microcapsules to self-healing anticorrosive coatings and expansion of our combined interfacial and in-situ polymerization strategy to synthesis of other reagents-containing SiO$_2$-based microcapsules with both high encapsulation loading and outstanding thermal and processing stability.

Disclosure statement

The authors declare no conflict of interest.
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References

[1] Y. Yang and M.W. Urban, *Self-healing polymeric materials*, Chem. Soc. Rev. 42, 17 (2013), pp. 7446–7467. doi:10.1039/C3CS60109A

[2] J. Pessi, H.A. Santos, I. Miroshnyk, D.A. Weitz, and S. Mirza, *Microfluidics-assisted engineering of polymeric microcapsules with high encapsulation efficiency for protein drug delivery*, Int. J. Pharm. 472, 1–2 (2014), pp. 82–87. doi:10.1016/j.ijpharm.2014.06.012

[3] A. Jamekhhorshid, S.M. Sadrameli, and M. Farid, *A review of microencapsulation methods of phase change materials (PCMs) as a thermal energy storage (TES) medium*, Renewable Sustainable Energy Rev. 31 (2014), pp. 531–542. doi:10.1016/j.rser.2013.12.033

[4] W. Li, X. Zhu, N. Zhao, and Z. Jiang, *Preparation and properties of melamine urea-formaldehyde microcapsules for self-healing of cementitious materials*, Materials. 9, 3 (2016), pp. 152. doi:10.3390/ma9030152

[5] E. Koh, N.-K. Kim, J. Shin, and Y.-W. Kim, *Polyurethane microcapsules for self-healing paint coatings*, RSC Adv. 4, 31 (2014), pp. 16214–16223. doi:10.1039/C4RA00213J

[6] S.R. White, N.R. Sottos, P.H. Geubelle, J.S. Moore, M. Kessler, S.R. Sriram, and S. Viswanathan, *Autonomic healing of polymer composites*, Nature. 409 (2001), pp. 794–797. doi:10.1038/35057232
[7] N.I. Khan, S. Halder, and M.S. Goyat, *Effect of epoxy resin and hardener containing microcapsules on healing efficiency of epoxy adhesive based metal joints*, Mater. Chem. Phys. 171 (2016), pp. 267–275. doi:10.1016/j.matchemphys.2016.01.017

[8] K. Hong and S. Park, *Preparation of poly (L-lactide) microcapsules for fragrant fiber and their characteristics*, Polymer. 41, 12 (2000), pp. 4567–4572. doi:10.1016/S0032-3861(99)00677-1

[9] D.Y. Zhu, M.Z. Rong, and M.Q. Zhang, *Preparation and characterization of multilayered microcapsule-like microreactor for self-healing polymers*, Polymer. 54, 16 (2013), pp. 4227–4236. doi:10.1016/j.polymerr.2013.06.014

[10] H. Jin, C.L. Mangun, A.S. Griffin, J.S. Moore, N.R. Sottos, and S.R. White, *Thermally stable autonomic healing in epoxy using a dual-microcapsule system*, Adv. Mater. 26, 2 (2014), pp. 282–287. doi:10.1002/adma.201303179

[11] B.Y. Ahn, S.I. Seok, I.C. Baek, and S.-I. Hong, *Core/shell silica-based in-situ microencapsulation: A self-templating method*, Chem. Commun. 2 (2006), pp. 189–190. doi:10.1039/BS12105A

[12] R. Ciriminna, M. Sciortino, G. Alonzo, A.D. Schrijver, and M. Pagliaro, *From molecules to systems: Sol–gel microencapsulation in silica-based materials*, Chem. Rev. 111, 2 (2011), pp. 765–789. doi:10.1021/cr100161x

[13] R.S. Underhill, A.V. Jovanovic, S.R. Carino, M. Varshney, D.O. Shah, D.M. Dennis, T.E. Morey, and R.S. Duran, *Oil-filled silica nanocapsules for lipophilic drug uptake: Implications for drug detoxification therapy*, Chem. Mater. 14, 12 (2002), pp. 4919–4925. doi:10.1021/cm0202299

[14] Z. Yang, J. Hollar, X. He, and X. Shi, *A self-healing cementitious composite using oil core/silica gel shell microcapsules*, Cem. Concr. Compos. 33, 4 (2011), pp. 506–512. doi:10.1016/j.cemconcomp.2011.01.010

[15] H. Zhang, S. Sun, X. Wang, and D. Wu, *Fabrication of microencapsulated phase change materials based on n-octadecane core and silica shell through interfacial polycondensation*, Colloids Surf. A. 389, 1–3 (2011), pp. 104–117. doi:10.1016/j.colsurfa.2011.08.043

[16] A.A. Périchaud, A. Kurbatov, I.V. Razumovskaya, M.J.M. Abadie, O.Y. Prokohdko, P.Y. Apel, and V.Y. Voytekunas, *Auto-Reparation of Polyimide Film Coatings for Aerospace Applications Challenges & Perspectives*, M.J.M. Abadie, eds., InTech Press, Rijeka, 2012, pp. 215–244.

[17] H. Wang, Y. Yuan, and M. Rong, *Melamine resin-walled microcapsules containing styrene: Preparation and characterization*, Adv. Mater. Res. 47-50 (2008), pp. 286–289. doi:10.4028/www.scientific.net/AMR.47-50.286

[18] B. Li, T. Liu, L. Hu, Y. Wang, and L. Gao, *Fabrication and properties of microencapsulated paraffin@SiO2 phase change composite for thermal energy storage*, ACS Sustainable Chem. Eng. 1, 3 (2013), pp. 374–380. doi:10.1021/sc300082m

[19] E. Weiss, B. Dutta, A. Kirschning, and R. Abu-Reziq, *BMIm-PF6@SiO2 microcapsules: Particulated ionic liquid as a new material for the heterogenization of catalysts*, Chem. Mater. 26, 16 (2014), pp. 4781–4787. doi:10.1021/cm501840d

[20] E.N. Brown, M.R. Kessler, N.R. Sottos, and S.R. White, *In situ poly (urea-formaldehyde) microencapsulation of dicyclopentadiene*, J. Microencapsulation. 20, 6 (2003), pp. 719–730. doi:10.1080/0265204031000154160

[21] H. Jin, K.R. Hart, A.M. Coppola, R.C. Gergely, J.S. Moore, N.R. Sottos, and S.R. White, *Self-healing epoxies and their composites in Self-Healing Polymers: From Principles to Applications*, W.H. Binder, eds., Wiley-VCH, Weinheim, 2013, pp. 361–380.

[22] C.M. Hansen, *Hansen Solubility Parameters: A User’s Handbook*, CRC, New York, 2007, pp. 177–202.

[23] E. Miloskovska, E. Nies, D. Hristova-Bogaerds, M. Van Duin, and G. De With, *Influence of reaction parameters on the structure of in situ rubber/silica compounds synthesized via sol–gel reaction*, J. Polym. Sci., Part B: Polym. Phys. 52, 14 (2014), pp. 967–978. doi:10.1002/pob.23516

[24] L. Yuan, G. Liang, J. Xie, L. Li, and J. Guo, *Preparation and characterization of poly (urea-formaldehyde) microcapsules filled with epoxy resins*, Polymer. 47, 15 (2006), pp. 5338–5349. doi:10.1016/j.polymerr.2006.05.051
[25] X.M. Tong, T. Zhang, M.Z. Yang, and Q. Zhang, *Preparation and characterization of novel melamine modified poly (urea–formaldehyde) self-repairing microcapsules*, Colloids Surf. A. 371, 1–3 (2010), pp. 91–97. doi:10.1016/j.colsurfa.2010.09.009

[26] H. Zhang, X. Wang, and D. Wu, *Silica encapsulation of n-octadecane via sol–gel process: A novel microencapsulated phase-change material with enhanced thermal conductivity and performance*, J. Colloid Interface Sci. 343, 1 (2010), pp. 246–255. doi:10.1016/j.jcis.2009.11.036

[27] G. Perez, E. Erkizia, J.J. Gaitero, I. Kaltzakorta, I. Jimenez, and A. Guerrero, *Synthesis and characterization of epoxy encapsulating silica microcapsules and amine functionalized silica nanoparticles for development of an innovative self-healing concrete*, Mater. Chem. Phys. 165 (2015), pp. 39–48. doi:10.1016/j.matchemphys.2015.08.047

[28] E. Pisani, N. Tsapis, J. Paris, V. Nicolas, L. Cattel, and E. Fattal, *Polymeric nano/microcapsules of liquid perfluorocarbons for ultrasonic imaging: physical characterization*, Langmuir. 22, 9 (2006), pp. 4397–4402. doi:10.1021/la0601455

[29] H. Wei, Y. Wang, J. Guo, N.Z. Shen, D. Jiang, X. Zhang, X. Yan, J. Zhu, Q. Wang, L. Shao, H. Lin, S. Wei, and Z. Guo, *Advanced micro/nanocapsules for self-healing smart anticorrosion coatings*, J. Mater. Chem. A. 3, 2 (2015), pp. 469–480. doi:10.1039/C4TA04791E

[30] J.M. Schierholz, *Physico-chemical properties of a rifampicin-releasing polydimethyl-siloxane shunt*, Biomaterials. 18, 8 (1997), pp. 635–641. doi:10.1016/S0142-9612(96)00071-3

[31] B.N. Kolarz, M. Wojaczynska, and A.W. Trochimczuk, *Porous copolymers of trimethylolpropane triacrylate and acrylonitrile*, Macromol. Chem. Phys. 194, 5 (1993), pp. 1299–1306. doi:10.1002/macp.1993.021940504