



Development of a versatile microencapsulation technique for aqueous phases using inverse emulsion

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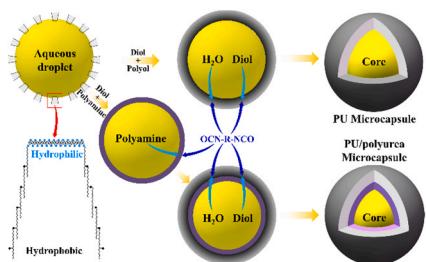
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GRAPHICAL ABSTRACT



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ABSTRACT

The development of microencapsulation techniques that can microencapsulate a wide variety of aqueous phases with different functions can greatly promote the advancement of microcapsule-based functional materials. Herein, a novel microencapsulation technique to microencapsulate aqueous phases with different functions was successfully established based on the inverse emulsion. Using pure water as the targeting core, the shell formation mechanism was carefully studied for this microencapsulation technique. Different cross-linkers, including glycerol, poly(vinyl alcohol) (PVA), and polyethyleneimine (PEI) with multiple reactive hydrogen atoms, were adopted to adjust the microcapsule quality. It finds that the microcapsules have relatively low quality when no cross-linker was used, and that they became robust when cross-linked agents were adopted. Importantly, the higher the functionality of the cross-linker, the better the impermeability of the microcapsules shell to retain the core content. This technique was applied to microencapsulate common compounds of different nature in the laboratory, including water-soluble organics, water-soluble inorganics, and water-based dispersions, to demonstrate its versatility. It shows that the technique can microencapsulate a wide variety of water-soluble/dispersible substances except for the inorganic strong acid. The established technique opens a window to fabricate high-quality microcapsules containing aqueous phases with diversified functions, promoting the development of microcapsule-based functional materials.

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1. Introduction

Microencapsulation of substances is a very useful and promising technique, which has been deeply explored in the academy and widely applied in industry for decades. [1] Microcapsules, consisting of the targeting core materials and protective shells, can provide better isolation for the microencapsulated materials from the surrounding environment. Microcapsules can be used either to store substances when the shell of the microcapsules is impermeable, or for controlled release when the shell of the microcapsules has controllable permeability. After being microencapsulated, the immobilized core substances inside microcapsules can be stored or released for a much longer time, compared with the pure naked substances exposed directly to the servicing environment.

Due to the increased demand for microcapsules with different core materials for diversified purposes in various areas, a great variety of techniques for microencapsulation have been developed. [1–3,35–37] Among all the techniques explored, the most important one is the microencapsulation by emulsions. [4,5] By this method, the targeting core material is firstly emulsified in another solvent and then enwrapped

by the formed shell at the interface. Using the oil-in-water emulsions, various lipophilic substances can be microencapsulated by different shell-forming materials. Attributed to the diversified surfactants to form stable emulsions and adoptable shell materials, the microencapsulation of lipophilic substances in emulsions is successful both academically and industrially. Dry and flow-free microcapsules with core-shell structure and tunable size from nanoscale to microscale can be achieved using the emulsion technique. [6,7] The emulsion technique can be also adopted to microencapsulate hydrophilic substances using water-in-oil emulsions. [8,9] However, in stark contrast to the microencapsulation of lipophilic substances using oil-in-water emulsions, it is much more challenging to fabricate high-quality microcapsules containing hydrophilic substances using inverse emulsions.

To the best of our knowledge, the use of inverse emulsions to encapsulate aqueous cores has been studied for a long time. [9] However, due to the limited advanced technologies for characterization, such as the scanning electron microscope (SEM), it is difficult to observe the structure and properties of the synthesized capsules. [9,10] Landfester et al. [11–15] made a lot of contribution to fabricate various functional nanocapsules in miniemulsions using different shell materials. As the

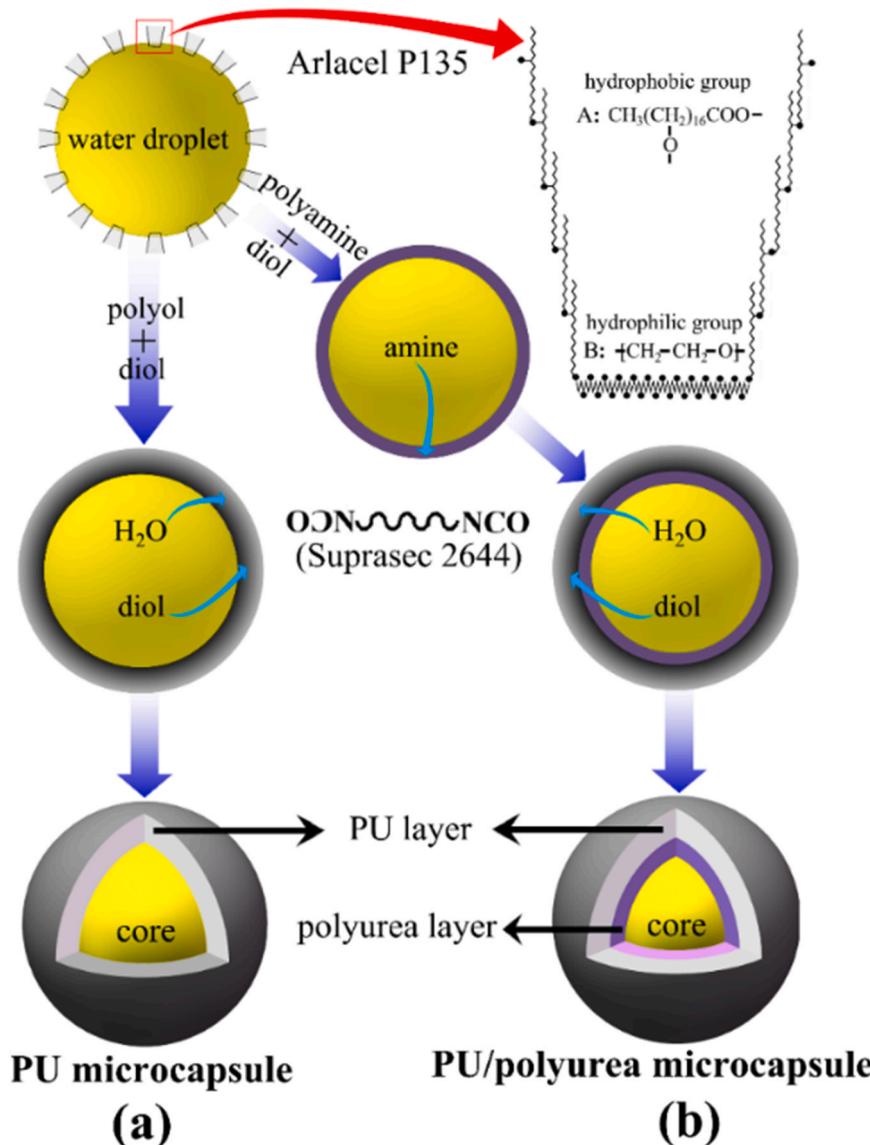


Fig. 1. Microencapsulation of aqueous phases using (a) polyol as the cross-linker and (b) polyamine as the cross-linker. Inset at top right schematically shows the molecular structure of the adopted surfactant for an inverse emulsion.

Table 1
Adopted variables in the study.^a

Cross-linker	Core liquid	Reaction condition	Yield (%)
0.5 g glycerol	DI water	T30–5 h	29.5
0.5 g glycerol	1.0 wt% PVA aqueous solution	T30–5 h	39.2
0.2 g PVA	DI water	T30–5 h	38.6
0.5 g PEI	DI water	T30–4 h	47.7
0.5 g PEI	37.5% PEI solution	T50–5 h	51.4
0.5 g PEI	vitamin C/glycose/xylitol/mannitol solution ^b	T30–4 h	47.9/48.7/45.2/46.3
0.5 g PEI	NaCl/Na ₂ CO ₃ /NaOH solution ^c	T30–4 h	20.4/29.5/22.5
0.5 g glycerol	HCl solution ^d	T30–5 h	0
0.5 g PEI	Fe ₃ O ₄ /CNT/GO dispersion ^e	T30–4 h	44.8/42.8/41.2

^aOther parameters include the following: amount of core liquid is 5.0 g; chain extender is 2.5 g BDO

^bThe concentrations of vitamin C/glycose/xylitol/mannitol solutions are all 10.0 wt%; continuous phase is 50.0 mL toluene containing 0.5 g Arlacel P135 and 5.0 g Suprasec 2644; agitation rate is 500 rpm; 0.01 wt% DBTDL is used as the catalyst;

^{c,d}The concentrations of NaCl/Na₂CO₃/NaOH/HCl solutions are 1 M, 10 wt%, and 1 M, 1 M, respectively;

^eThe concentrations of Fe₃O₄/CNT/GO dispersions are 7.5, 5.0, and 5.0 mg/mL, respectively.

capsules were at the nanometer scale and used as dispersions, there is no need to consider the shell thickness or whether they can be collected as dry and flow-free capsules. When it comes to the synthesis of collectable core-shell capsules with aqueous cores at the micron scale, the current progress is not so optimistic. Although silica microspheres were obtained in an inverse emulsion using silane as the precursor for the shell, they either did not have a core-shell structure [16] or were too weak to be separated and dried for collection [17]. McIlroy et al. [18] claimed that they have microencapsulated polyamine by polyurea shell using the reaction between toluene diisocyanate (TDI) and diethylenetriamine (DETA). However, only moderate success was achieved by this method. The obtained microcapsules have irregular shapes and no core-shell structure was demonstrated in their investigation. Using the interfacial polymerization between polyamine and diisocyanate in an inverse emulsion, Yi et al. [19] synthesized microcapsules containing the aqueous solution of a polyamine. Although the stable emulsion can be obtained using amphiphilic nanoparticles as the surfactant and microcapsules can be achieved, they cannot even survive through the SEM imaging, attributed to the extremely thin shell and the poor mechanical properties. Through the literature above, it can be seen that it is still of great significance to study the microencapsulation technique using inverse emulsions to fabricate high-quality microcapsules containing water-based substances.

Although only moderate success was achieved by McIlroy using the interfacial polyaddition polymerization between TDI and DETA, [18] the idea to design inverse emulsion can be borrowed. Besides the selection of a suitable surfactant to stabilize the water-in-oil emulsion, a more controllable reaction should be considered for the shell formation around the water droplets gradually. Yang et al. [7] and Huang et al. [20] developed methods to microencapsulate diisocyanate using the reaction between 1,4-butanediol (BDO) and diisocyanate pre-polymer in oil-in-water emulsions. In their systems, the diisocyanate pre-polymer was mixed in the dispersed oil phase, while the chain extender, BDO, was dissolved in the water continuous phase. In the microencapsulation process, one of the monomers needs to diffuse through the oil/water interface to react with another one near the interface to form the shell around the oil droplets. One of the advantages of this method is that the

shell-forming reaction can be easily tuned by changing the reaction parameters. In addition, the shell thickness and the shell permeability can also be controlled by adjusting the various parameters. Inspired by their studies, [7,18,20] a new strategy was explored to microencapsulate water-soluble materials in this investigation by adopting the reaction between diisocyanate and diol in a water-in-oil emulsion system.

2. Experiment

2.1. Materials

Suprasec 2644, which is a methylene diphenyl diisocyanate based pre-polymer with functionality of 2 and a molecular weight of 415.3 g/mol, was generously provided by Huntsman. The inverse emulsion surfactant, Arlacel P135 with a hydrophilic-lipophilic balance (HLB) value of 5.5, was purchased from Croda. 1,4-butanediol (BDO, ReagentPlus®, 99%), glycerol (ACS reagent, ≥ 99.5%), dibutyltin dilaurate (DBTDL, 95%), D-(+)-glucose (ACS reagent), vitamin C (L-ascorbic acid, ACS reagent, ≥ 99%), xylitol (≥ 99%), mannitol (ACS reagent), sodium chloride (NaCl, ACS reagent, ≥ 99.0%), sodium carbonate (Na₂CO₃, ReagentPlus®, ≥ 99.5%), sodium hydroxide (NaOH, ACS reagent, ≥ 97.0%, pellets), magnetic nanoparticles (Fe₃O₄), toluene (anhydrous, 99.8%), carbon black, polyethyleneimine (PEI) with a molecular weight (M_n) of about 1200 in the form of a 50 wt% aqueous solution, and poly(vinyl alcohol) (PVA, 87.0–89.0% hydrolyzed, molecular weight of 31000–50000) were purchased from Sigma-Aldrich, and used as received. Carbon nanotubes (CNTs) were provided by Chengdu Organic Chemicals.

2.2. Microencapsulation process

The materials, like pure deionized (DI) water, aqueous solutions of organics or inorganics, and aqueous dispersions of nano-filters, were microencapsulated by polyurethane (PU) using the interfacial reaction between Suprasec 2644 and BDO in an inverse emulsion, as outlined in Fig. 1a. Firstly, 5.0 g above-mentioned aqueous core liquid with 2.5 g chain extender BDO and different cross-linkers was emulsified in 50.0 mL toluene containing 0.5 g Arlacel P135 (~ 1 wt% relative to toluene) and 0.005 g DBTDL (~ 0.01 wt% relative to toluene) in a 250 mL beaker at room temperature (RT, ~ 22–25 °C) for 20 min under mechanical stirring of 500 rpm (Cafra, Model: BDC6015) using a three-blade propeller with a diameter of 56.0 mm. The beaker with the mixture was placed in a temperature-controlled water bath on a programmable hot plate (hotplate digital aluminium 230). After emulsification, 5.0 g Suprasec 2644 diluted by 5.0 g toluene was dropwise added into the mixture in about 8 min and the beaker was sealed tightly with aluminum foil to minimize the toluene evaporation. The system was heated up with a ramp rate of 60 °C/h to the designated temperature (30 °C) in about 10 min and kept at that temperature for 4–5 h. At the end of the microencapsulation process, the obtained microcapsules were separated from the slurry mixture by decanting the supernatant with debris and rinsing with toluene 3–4 times. And finally, the microcapsules were dried at RT for about 12 h to evaporate the residual solvent outside.

For easy reference, Table 1 tabulates the targeting core liquids, the adopted cross-linkers, and the designated temperature for the shell growth for the microcapsules. It also includes the yield of each process according to the following definition:

$$\text{Yield}(\%) = 100\% \cdot \frac{W_{cap}}{W_{core} + W_{pre-p}}$$

where W_{cap} , W_{core} , W_{pre-p} are the masses of the collected microcapsules after drying, the input core liquid with the chain extender and cross-linker, and the shell-forming monomer Suprasec 2644, respectively.

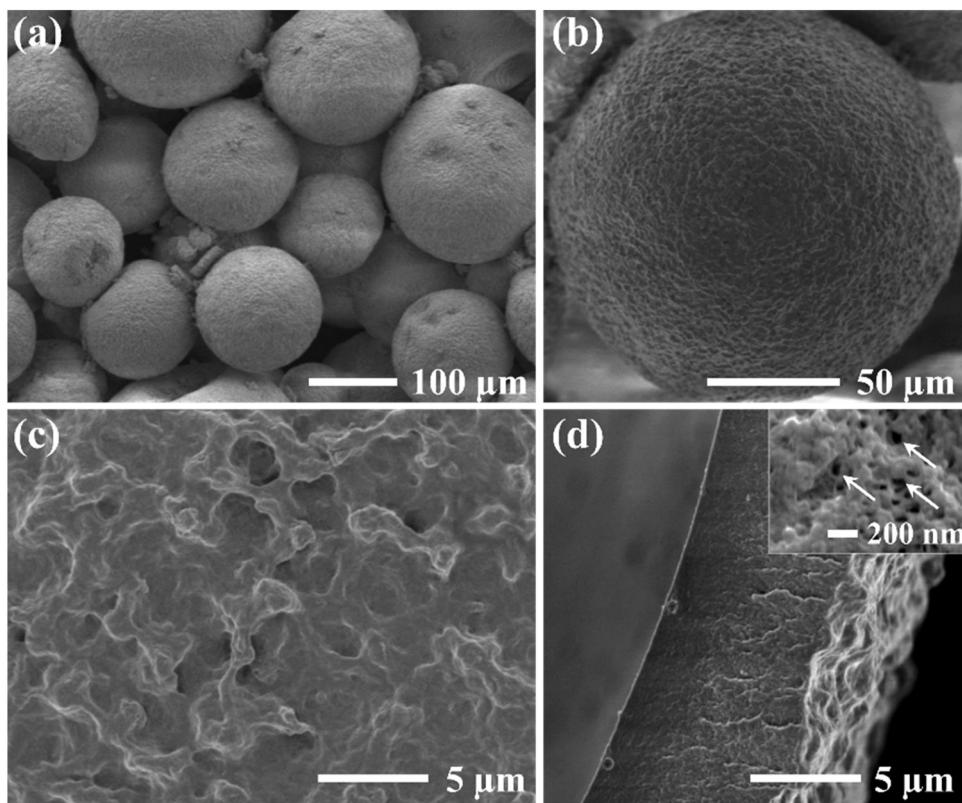


Fig. 2. SEM images of the microcapsules containing water when glycerol was used as the cross-linker. (a) General appearance, (b) Typical microcapsule showing the rough outer surface, (c) Enlargement of the outer surface, and (d) Cross-section of the microcapsule shell. Arrows in the top right inset indicate the pores near the outer surface.

2.3. Characterization methods

The basic properties of the achieved microcapsules, i.e., the morphology and shell structure, were characterized by the field emission scanning electron microscopy (SEM, FEI, Quanta FEG 250). To clearly observe the cross-section of the synthesized microcapsules, some of them were cut with a sharp blade and rinsed with DI water to completely remove the core liquid for the SEM imaging. The composition and the thermal stability of the microcapsules were analyzed using thermogravimetric analysis (TGA, NETZSCH, TG 209 F3). During each TGA test, 5–10 mg microcapsules were loaded in a platinum pan and heated up with a ramp rate of 10 °C/min to 600 °C under a nitrogen atmosphere.

3. Results and discussion

3.1. Microencapsulation of water with PU shell

As schematically illustrated in Fig. 1, the aqueous core liquid, containing diol as the chain extender and polyol or polyamine as the cross-linker, was dispersed in the continuous phase, i.e., toluene, to form a stable emulsion with the aid of the surfactant, i.e., Arlacel P135, under mechanical stirring at a certain speed. Arlacel P135, also known as PEG-30 dipolyhydroxystearate with a molecular weight of about 5000, is an A-B-A triblock copolymer, in which A is the lipophilic polyhydroxystearate and B is the hydrophilic polyethylene glycol 30 (PEG-30), as schematically shown at the top right in Fig. 1. During the emulsification process, the two big lipophilic blocks (A) can provide steric impedance for the neighboring droplets after the surfactant molecule fully spreads at the water/oil interface, which is schematically (not to scale) shown in the water droplet in Fig. 1. Its moderate molecular weight allows it to quickly diffuse to the water/oil interface of

the emulsion, while providing sufficient steric hindrance to stabilize the droplets in the emulsion. This specially designed A-B-A type structure guarantees the best accumulation state of the surfactant at the water/oil interface. Compared with the traditional small molecule emulsifiers, such as Span 80 (sorbitan monooleate) and Span 85 (sorbitan trioleate), the two large-volume lipophilic groups of Arlacel P135 form a special non-rotating three-dimensional space at the interface of the emulsion structure. Therefore, excellent stabilization can be achieved, even at elevated temperatures above 50 °C. Other surfactants with smaller molecule volumes for the inverse emulsion, like Span 80 and Span 85, were also tried in this study. Although droplets can be generated under mechanical stirring, they collapse upon the addition of the shell-forming monomer Suprasec 2644.

Using this microencapsulation technique, dry and flow-free microcapsules can be synthesized successfully, as shown in Fig. S1 in the Supporting Information (SI). Fig. 2 shows the SEM images of the microcapsules containing pure DI water when glycerol was used as the cross-linker. The imaged microcapsules were synthesized by using 5.0 g DI water together with 2.5 g BDO and 0.5 g glycerol as the core liquid and 5.0 g Suprasec 2644 as the shell-forming monomer when the system reacted at 30 °C for 5 h under the catalysis of 0.01 wt% DBTDL. Like other microcapsules prepared by the emulsion method using mechanical agitation, [6,7,20] the microcapsule size presents a polydispersity, and its distribution conforms to the normal distribution (Fig. S2). It is observed that most of the microcapsules have small shrinkage on their shell and they have a rough outer surface with uniformly distributed bulges of size about several microns, as illustrated in Fig. 2b and c. Compared with the microcapsules obtained using a normal emulsion (oil-in-water emulsion) by interfacial polymerization, the former feature, i.e., shell shrinkage, is much similar, while the latter, i.e., rough outer surface, is completely different [7,20,21]. Some microcapsules were crushed and rinsed with water to observe the cross-section and the

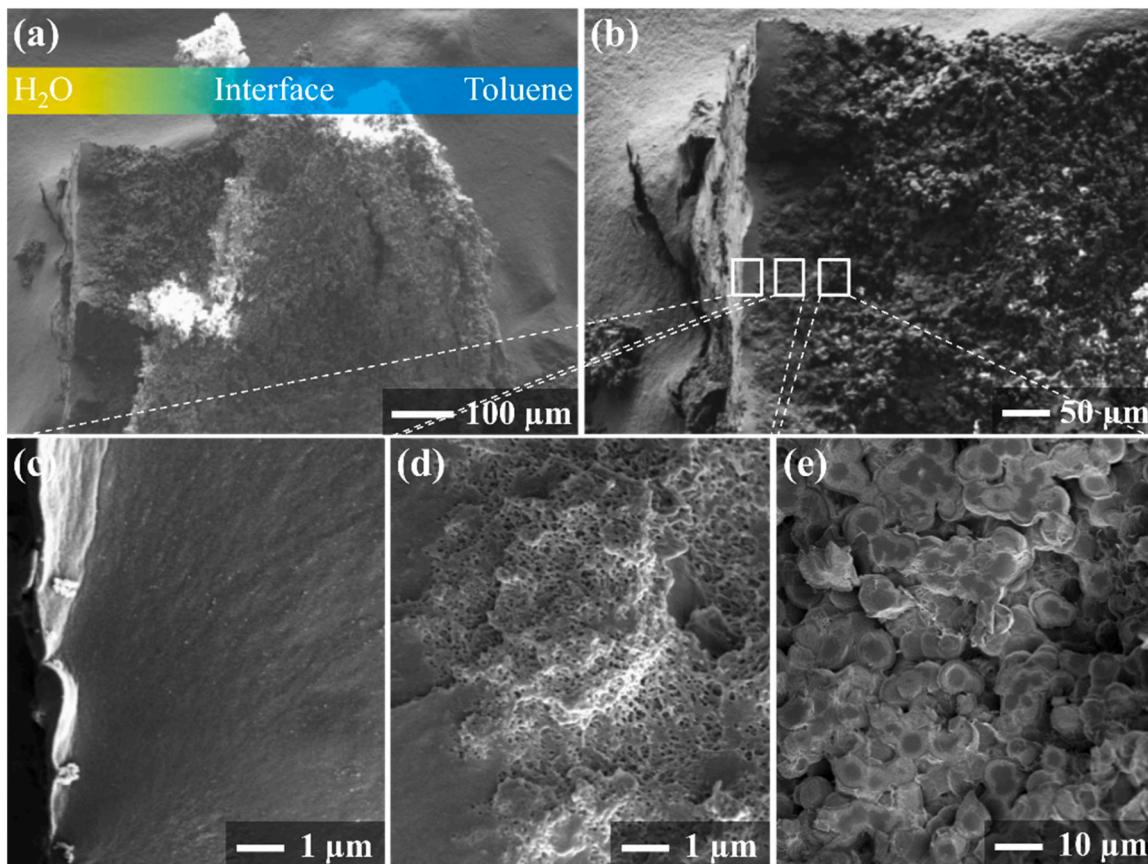


Fig. 3. SEM images of the polymer at the toluene/water interface formed by the adopted interfacial polymerization in the microencapsulation technique. (a-b) General appearance of the formed polymer, and (c-d) Enlargements of the regions in (b).

inner surface, as shown in Fig. 2d. It can be seen that the shell is uniform with a thickness of about 8 μm . Differs from the rough outer surface, the inner surface is very smooth. It is also found that minute pores appear near the outer shell and the number increases along the radius direction outward. Microencapsulation processes with the same protocol were also carried out with only the chain extender (BDO) or only the cross-linker (glycerol). Microcapsules were obtained for both microencapsulation processes. However, without the glycerol cross-linker, the microcapsules have a more porous shell and a rougher outer surface and are more brittle to be fractured, as shown in Fig. S3. No detectable liquid was observed inside. Whilst without the BDO chain extender, although microcapsules can be synthesized, they have a much thinner shell and are not robust enough to withstand the high vacuum so that they collapse when imaged by SEM, as shown in Fig. S4.

Based on the comprehensively investigated interfacial polymerization between isocyanate and polyol and the microencapsulation process by interfacial polymerization [22,23], a mechanism was proposed to explain the formation of the microcapsules in this inverse emulsion system and the structures of the obtained microcapsules, as shown in Fig. 1a. After the addition of diisocyanate (Suprasec 2644) at the end of the emulsification process, the polyol, including both BDO and glycerol, can gradually diffuse across the water/oil interface to react with the added diisocyanate to form PU at the interface. With the increased molecular weight by chain extending and cross-linking reactions, the PU would precipitate out and deposit at the interface to introduce the PU membrane around the droplets. Further growth of the shell needs the diffusion of the polyol through the membrane to react with Suprasec 2644 near the interface. During the polymerization, cross-linking of the linear PU polymerized from the diisocyanate and diol by glycerol is of great importance since it can improve the strength and impermeability of the formed PU, while the higher diffusion rate of BDO relative to

glycerol can thicken the shell significantly to increase the robustness of the microcapsules. In the process, there are also some side reactions in the system, because the small water molecules, compared with BDO and glycerol, can also diffuse through the water/oil interface and the PU membrane to react with isocyanate to generate carbon dioxide (CO_2) and amino functional groups, which in turn can rapidly react with isocyanate to form polyurea [20,24]. The diffusion of core substances and the reactions near the interface progress until either the shell becomes thicker and more impermeable due to the cross-linking reaction or the depletion of the core material. With the diffusion of water, BDO, and glycerol, the volume of the core materials decreases gradually, leading to the shrinkage of the formed wall. At the very beginning of the shell-forming process, although the diffusion rate of the polyol is lower than that of water, yet it is competitive to that of water since there is no serious resistance by the formed thin shell. Besides that, the adopted tin catalyst, DBTDL, can selectively accelerate the reaction between hydroxyls and isocyanates, while having no evident effect on the side reaction between water and isocyanates, which leads to the formation of a dense structure during this stage. However, when the shell becomes thicker, it generates higher resistance to the polyol with bigger molecular structures but relatively lower resistance to the water with a simpler and smaller molecular structure. This difference results in more diffused water and therefore more generated CO_2 . Besides emitting through the outer shell, they can also be trapped in the shell, leading to the formation of the observed small pores. Since part of the diffused water and the generated CO_2 emit through the outer shell, the points for the emission will form the minute pores on the shell, as shown in Fig. S3c.

The proposed process above bases on the assumptions that the polymerization takes place in the toluene phase between the diisocyanate and the active ingredients diffused through the interface from the aqueous phase, and that the shell grows in the toluene outward along the

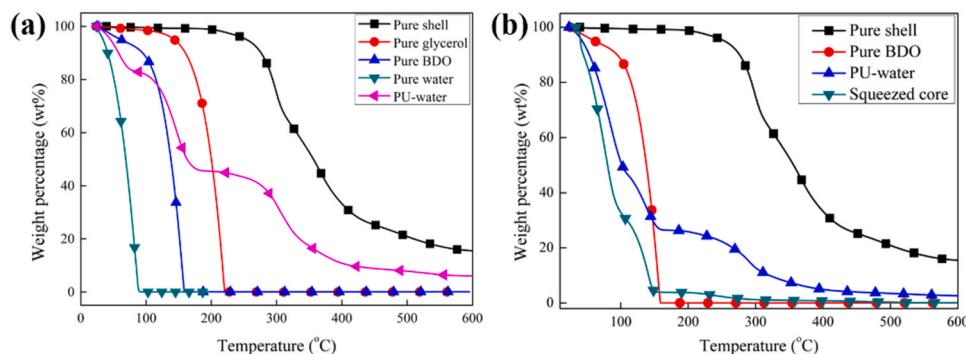


Fig. 4. (a) TGA curves of the microcapsule (PU-water) synthesized using glycerol as the cross-linker, pure water, pure BDO, pure glycerol, and pure shell, and (b) TGA curves of the microcapsules using PVA as the auxiliary cross-linker, pure BDO, pure shell, and the squeezed core liquid.

radium, as indicated by the gradually faded grey shell in Fig. 1. For a better understanding of the mechanism for the shell formation process, the interfacial polymerization between Suprasec 2644 in toluene (same compositions as the continuous phase in the microencapsulation process) and the active ingredients in the aqueous phase (same compositions as the dispersed phase) was studied when fine carbon black powders were introduced to the toluene/water interface, as schematically illustrated in Fig. S5. As carbon black is insoluble in both toluene and water but can be wetted by water, the relative location of the carbon black concerning the formed polymer film indicates the location of the polymerization process. After the same condition for the reaction as adopted in the microencapsulation process, it is observed that the polymer film was on the top of the carbon black, which means the polymerization takes place in the organic phase. Based on this observation, it is clear that the shell initiates at the toluene side at the interface and grows outward in the toluene. The cross-section of the formed polymer was imaged by SEM, as shown in Fig. 3a and b. Under the static situation without agitation, three different zones, i.e., dense zone (Fig. 3c), porous zone (Fig. 3d), microsphere zone (Fig. 3e), were observed across the section along the growth direction. It is found that the structure of the first two zones, i.e., the dense zone and the porous zone, is much similar to that of the microcapsule shell. With the increase of the polymer thickness, the active ingredients, including the chain extender and cross-linker, are increasingly difficult to diffuse through the formed polymer shell to react with the diisocyanate. However, attributed to its relatively smaller molecular structure, water can easily diffuse through the polymer to either react with a diisocyanate to generate CO₂ or be trapped in the polymer, leaving the porous structure.

It should be noted that during the emulsification process, the water, chain extender BDO, and the cross-linker glycerol in the dispersed phase can slightly dissolve in the continuous phase. After the addition of Suprasec 2644, these slightly dissolved substances react with it in the continuous phase to generate polymer debris. Besides, during the shell growth stage, when the diffused water, chain extender, and cross-linker cannot react with Suprasec 2644 in time near the water/oil interface, they also react with Suprasec 2644 in the continuous phase to form debris. Therefore, the microcapsules synthesized using this technique contain a certain amount of debris. However, as the debris can be separated during the cleaning and separation process, final clean microcapsules can be achieved as shown in Fig. 2 and S1.

Fig. 4a shows the TGA curves of the synthesized microcapsules, pure water, pure BDO, pure glycerol, and pure shell material. After the drying process, the microcapsules have about 17 wt% of water, 38 wt% of residual BDO, 45 wt% of shell material, and almost no glycerol. Water content in the microcapsules is much lower than that of BDO, which is significantly different from the input aqueous liquid. Although water can diffuse out from the dispersed aqueous droplets to either react with Suprasec 2644 or evaporate from the system, the major reason for this dramatic mismatch is that the microencapsulated water can diffuse

through the shell and further evaporate from the microcapsules, indicating that the shell is permeable for water.

According to the above-mentioned control that only thin-shell microcapsules were obtained when using only glycerol, it is reasonable to infer that the permeability of the microcapsule shell results from the relatively low cross-linking density of the PU shell, attributed to the low functionality (3) of glycerol and the low concentration of it in the core liquid.

Thus, to enhance the impermeability of the synthesized microcapsules, one possible way is to increase the cross-linking density of the formed polymeric shell. To achieve this, other chemicals with multiple reactive hydrogen atoms like polyols and polyamines can be adopted to aid the cross-linking by glycerol or to completely replace glycerol. Firstly, 5.0 g 1.0 wt% PVA aqueous solution was used to replace the pure DI water in the input core liquid, while other compositions were kept the same. It shows that dry and well-dispersed microcapsules can be successfully achieved when PVA was used to assist the cross-linking using glycerol (Fig. S1b and S6). Although the microcapsules have morphology and shell structure similar to these of the microcapsules without using PVA, they have an improved retention capacity for the water in the core, as indicated by the TGA curve of this microcapsule. Fig. 4b shows the TGA curves of the microcapsules using PVA as the auxiliary cross-linker, pure BDO, pure shell, and the squeezed core liquid. The microcapsules have about 51 wt% of water, 22 wt% of residual BDO, and 27 wt% of shell material. It also shows that the water in the squeezed core liquid evaporates much faster than that in the microcapsules. It not only verifies that the shell impermeability for the microcapsules can be improved by increasing the cross-linking density of the shell, but also implies that it is governed by the inner part of the microcapsule shell. The latter is reasonable since the adopted PVA with a big molecule size mainly influences the early formed part of the shell. To simplify the core composition, the total substitution of glycerol with PVA to cross-link the shell was carried out. To achieve this, a 4.0 wt% PVA aqueous solution was mixed with 2.5 g BDO as the core material. Similar to above, dry flow-free microcapsules with a high water fraction were also successfully synthesized by this substitution.

The yields of these processes were given in Table 1. When only glycerol was used as the cross-linker, the yield is very low of about 30%. The low yield is attributed to three reasons. Firstly, to ensure that there is enough Suprasec 2644 near the water/oil interface to react with the diffused chain extender and cross-linker to form the shell, excess Suprasec 2644 was adopted during the microencapsulation process. The excessed amount of Suprasec 2644 decreases the yield, as the mass of Suprasec 2644 is also included in the input raw materials in the definition of the yield. Secondly, during the cleaning process, a large portion of small microcapsules were disposed with the debris in the supernatant as it is difficult to separate them from the debris. It also decreases the final yield of the process. Thirdly, the microencapsulated water in the microcapsules evaporates from the microcapsules during the drying

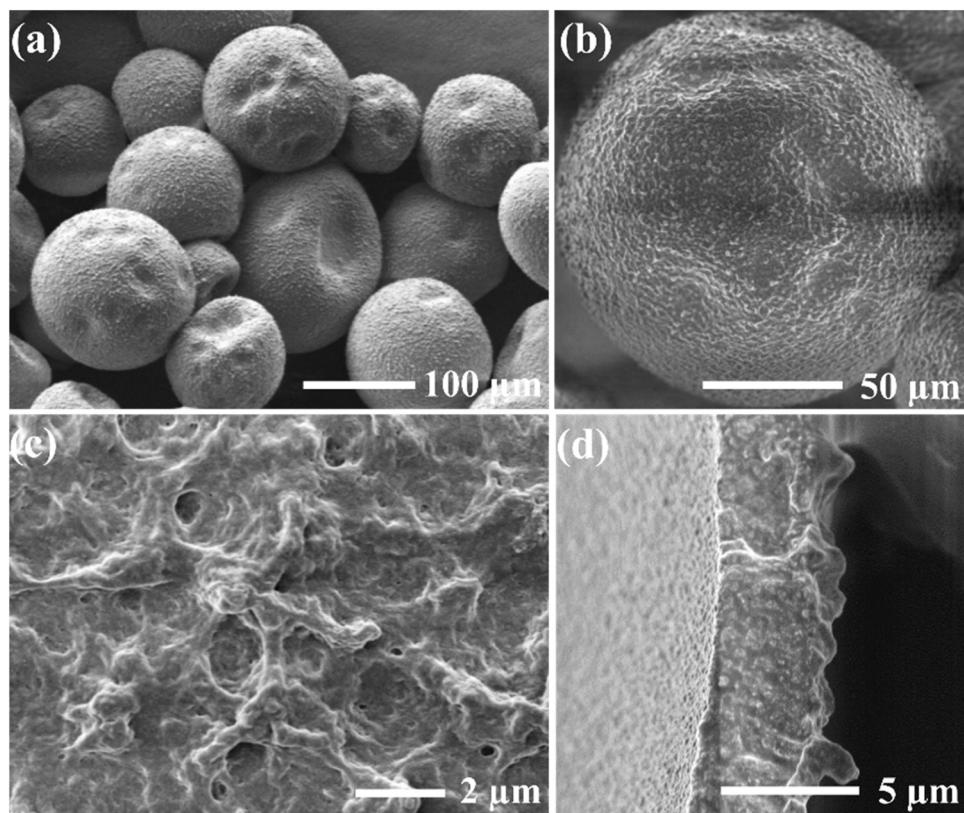


Fig. 5. SEM images of the microcapsules containing water when PEI was used as the cross-linker. (a) General appearance, (b) Typical microcapsule showing the rough outer surface, (c) Enlargement of the outer surface, and (d) Cross-section of the microcapsule shell.

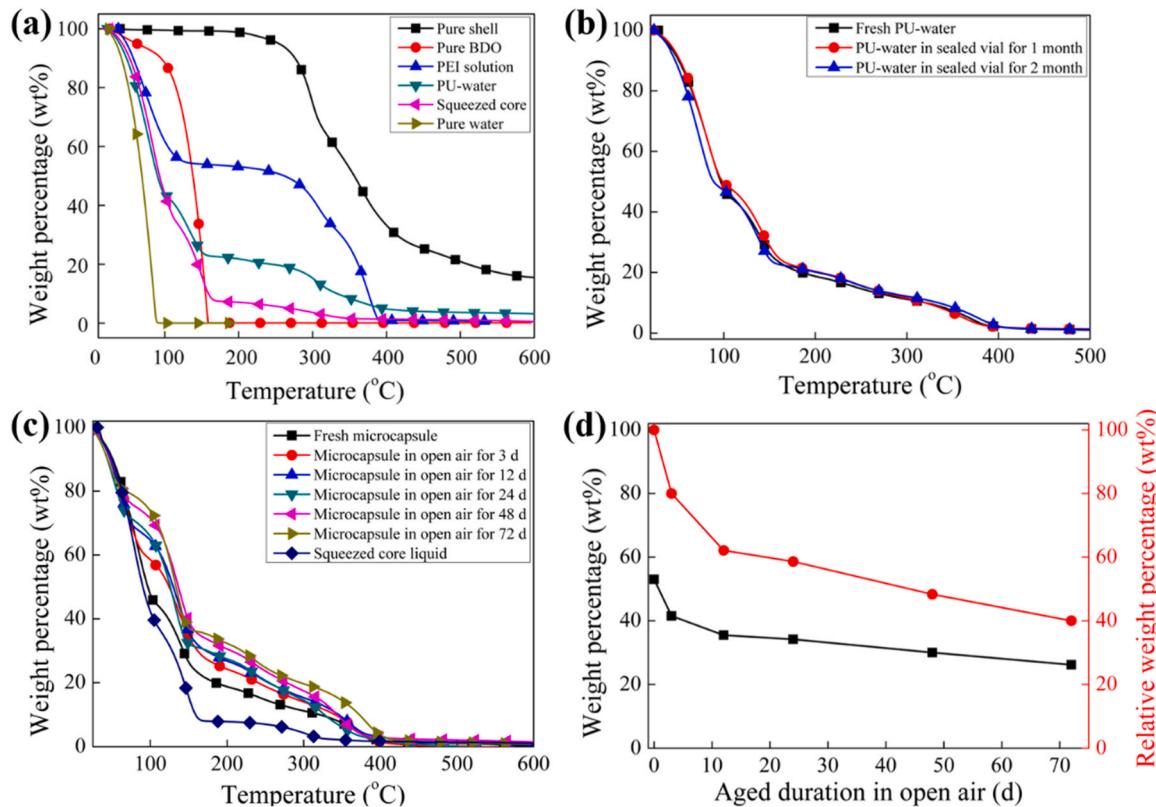


Fig. 6. (a) TGA curves of the microcapsules synthesized using PEI as the cross-linker, pure water, pure BDO, 50 wt% PEI aqueous solution, and pure shell, (b) TGA curves of the microcapsules aged in a sealed vial for up to 2 months, (c) TGA curves of the microcapsules aged in the open air for up to 72 days, and (d) Water contents and relative water contents in the microcapsules after being aged in the open air for different durations.

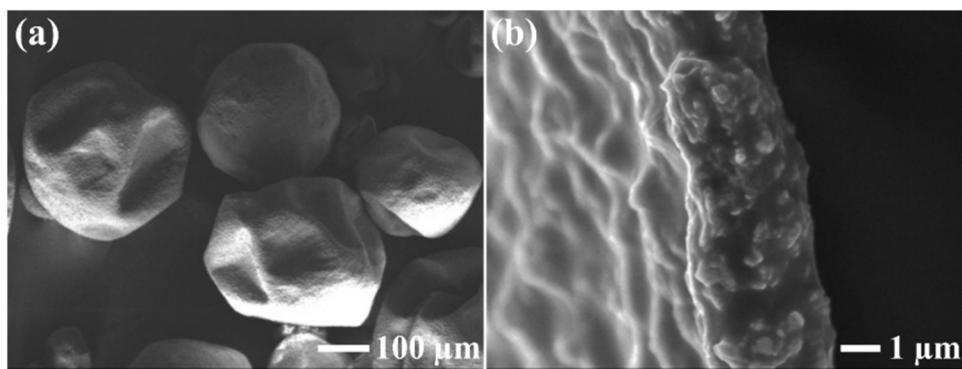


Fig. 7. SEM images of the PEI-contained microcapsules. (a) General appearance, and (b) Cross-section.

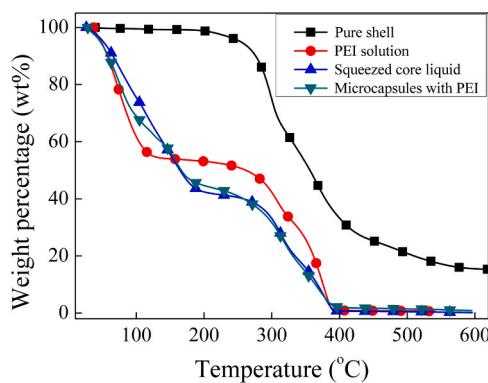


Fig. 8. TGA curves of the PEI-contained microcapsules, pure shell, 50 wt% PEI aqueous solution, and the squeezed core liquid from the microcapsules.

process, which significantly influences the final yield. The former two reasons also affect the microencapsulation processes using PVA as the cross-linker and the processes described below. However, due to the good impermeability of the microcapsule shell cross-linked by PVA, the yield of the process increases to about 40%.

3.2. Microencapsulation of water with double-layered shell

In this investigation, besides polyols, other compounds with multiple reactive hydrogen atoms were also tried in the microencapsulation process to improve the properties of the synthesized microcapsules. Poly(ethyleneimine) (PEI) with a molecular weight (M_n) of about 1200, which is insoluble or has very low solubility in the continuous phase (toluene), was used as the cross-linker. Other polyamines, like ethyleneimines with low molecular weights or polyetheramines, cannot be used here because of their miscibility with toluene. Dry and flow-free microcapsules can be synthesized using PEI as the cross-linker (Fig. S1c). The yield of this microencapsulation process is relatively high of about 48% (Table 1), compared to those using glycerol or PVA as the cross-linker. Fig. 5 shows the SEM images of the microcapsules containing pure DI water when PEI was used as the cross-linker. The imaged microcapsules were synthesized by using 5.0 g DI water together with 2.5 g BDO and 0.5 g PEI as core liquid and 5.0 g Suprasec 2644 as the shell-forming monomer when the system reacted first at RT for 1 h and then at 30 °C for another 4 h under the catalysis of 0.01 wt% DBTDL. As can be seen from Fig. 5a-c, microcapsules with a similar feature as those cross-linked by glycerol were obtained in this process using PEI. However, they have a relatively thin shell of about 5 μm and the inner side of the shell is rather rough (Fig. 5d). It is further confirmed that these microcapsules have a double-layered shell structure with an inner polyurea layer from the reaction between Suprasec 2644 and PEI and the outer PU/polyurea hybrid layer from the reaction between

Suprasec 2644 and BDO/PEI, as indicated in Fig. S7. A control microencapsulation process was also carried out using only PEI rather than the mixture of BDO and PEI. Microcapsules were observed after the microencapsulation process when imaged by the optical microscope. However, similar to the microencapsulation process by using only glycerol, the shell of the obtained microcapsules is so thin (less than 1 μm) that it is not able to support the microcapsules upon the evaporation of toluene outside or the subjection to vacuum (Fig. S8). Nevertheless, this thin shell is relatively dense, which can be seen from the cross-section in Fig. S8b.

Fig. 1b illustrates the shell-forming mechanism when PEI was adopted as the cross-linker. Due to the rapid reaction between amine and isocyanate, a preliminary membrane of polyurea forms at the interface upon the addition of Suprasec 2644 to the emulsion, as schematically illustrated by the shell in violet. Since the molecule of PEI is much bigger than those of water or BDO, it is increasingly harder for PEI to diffuse through the formed membrane to thicken the shell. That is why microcapsules can only have a very thin shell when only PEI was used without the presence of the chain extender BDO. When the catalyst DBTDL was added and the temperature was elevated, the chain extender BDO and water with small molecular structures can further diffuse through the formed thin membrane to react with Suprasec 2644, as illustrated by the shell in grey.

Different from microcapsules cross-linked by glycerol, microcapsules cross-linked by PEI show good impermeability for water. Fig. 6a shows the TGA curves of the synthesized microcapsules using PEI as the cross-linker, pure water, pure BDO, 50 wt% PEI aqueous solution, the squeezed core liquid from the microcapsules, and the pure shell material. The squeezed core has 58 wt% of water, 34 wt% of BDO, and 8 wt% of residual PEI, which is quite close to the input aqueous mixture (62.5 wt% for water, 31.25 wt% for BDO, and 6.25 wt% for PEI, Table S1). The relatively lower water content in the squeezed core liquid than that of the input aqueous mixture may result from its evaporation during the drying process and the sample preparation for the TGA test. It can also be seen that the microcapsules have 53 wt% of water and 25 wt% of BDO. Since the thermal decomposition temperatures of PEI and the shell material overlap each other, their weight percentages listed in Table S1 are not red directly from the TGA curves but calculated based on the TGA curves of the microcapsules and the squeezed core as deducted in the SI. Based on the calculation, the weight percentages of the residual PEI and the shell material are about 6.8 wt% and 15.2 wt%, respectively. Compared to the microcapsules cross-linked by glycerol, the amount of water in the core liquid is much higher. The better reservation of water results from two aspects, i.e., the microencapsulation process itself and the good impermeability of the microcapsule shell to impede the water evaporation during drying and storage.

The stability of the reserved water in the microcapsules was further studied by aging them at RT in a sealed vial for up to 2 months and the open air for different duration including 0 days (freshly prepared), 3

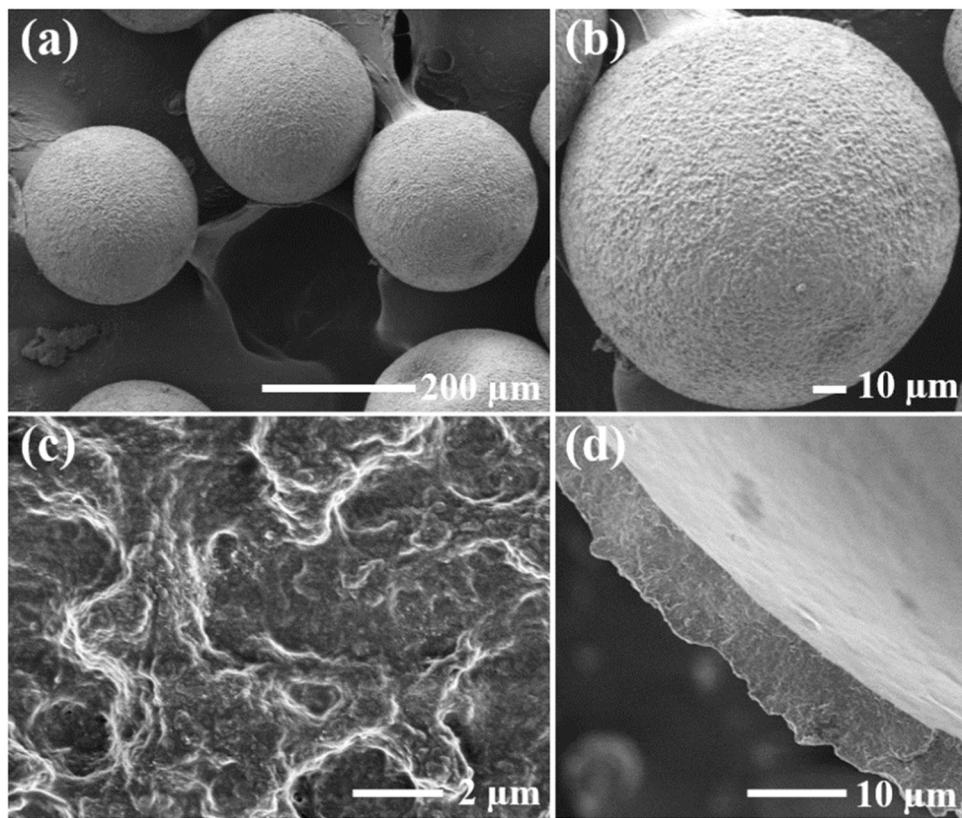


Fig. 9. Microcapsules containing 10.0 wt% vitamin C cross-linked using PEI. (a) General appearance, (b) Typical individual microcapsule, (c) Dense outer surface, and (d) Cross-section to show the dense shell.

days, 12 days, 24 days, 48 days, and 72 days. Fig. 6b shows the TGA curves of the aged microcapsules in the sealed vial. No obvious difference was observed for the microcapsules. Fig. 6c and d show the TGA curves and the statistical data of the microcapsules aged in the open air for different durations. It is observed that the microcapsules gradually lose the water inside in the open air. However, after about 24 days, the absolute and the relative water contents levels off at about 30 wt% and 48%, respectively. Compared to naked water in the open air, the microencapsulated water actually has a much larger surface for evaporation. The low loss rate for the water in the microcapsules demonstrates the good shell impermeability of the microcapsules for the small water molecules.

It is also worth mentioning that although the usage of PEI as the cross-linker is beneficial to synthesizing water-contained microcapsules with better performance, the input core material for microencapsulation and the final core of the fabricated microcapsules has certain basicity due to the amine groups or the imine groups in PEI. As a result, this microencapsulation process may not be able to microencapsulate some alkaline-sensitive substances and the synthesized microcapsules may not be able to be applied in some alkaline-sensitive scenarios. However, as described in the previous section, the microencapsulation process using PVA to assist or completely replace glycerol for cross-linking can synthesize good microcapsules without affecting the pH of the input core materials and the core of the final microcapsules. Combining the two microencapsulation processes, the application range of this microencapsulation technique and the fabricated microcapsules can be greatly expanded.

3.3. Versatility to microencapsulate different core substances

The versatility of a microencapsulation technique to enwrap diversified functional substances is very important, or it will be greatly

limited if it can only enwrap one or a few core materials of the same nature. The content above mainly focuses on the establishment of the microencapsulation technique using the simplest substance, i.e., water, as the targeting core. Despite simple, water is very difficult to be microencapsulated with high quality. The product itself, i.e., microcapsule containing water, can be used as solid water. Based on the above-mentioned system of microencapsulating pure water, we tried to microencapsulate common compounds with different nature in the laboratory, including water-soluble organics, water-soluble inorganics, and water-based dispersions, to demonstrate its versatility.

3.3.1. Microencapsulating water-soluble organics

First, considering that PEI was used as the cross-linker for this microencapsulation technique and PEI itself is a multifunctional substance, [25] it was microencapsulated in this investigation. According to the above-mentioned result about microencapsulating pure water using only PEI rather than the mixture of BDO and PEI, a higher PEI fraction in the core leads to a dense but very thin shell for the final microcapsules. Thus, to improve the quality of the microcapsules containing high-concentration PEI, the process of microencapsulation process was adjusted accordingly. Fig. 7 shows the PEI-contained microcapsules prepared using 3.5 g water, 1.5 g BDO, and 3.0 g PEI at 50 °C for 5 h. The microcapsules are dry and flow-free with good dispersibility. The yield of the microencapsulation process is about 51%, as shown in Table 1. Despite that the outer wall is smoother and the shell is thinner, the morphology and structure of the microcapsules are much similar to those of the microcapsules containing pure water. The reason for this phenomenon is that the PEI fraction in the core liquid is too high, resulting in a denser microcapsule shell to impede the diffusion of the shell-forming monomers. Therefore, only a relatively thinner shell can be achieved even at a higher reaction temperature for a longer duration. Fig. 8 . shows the TGA curves of the PEI-contained microcapsule,

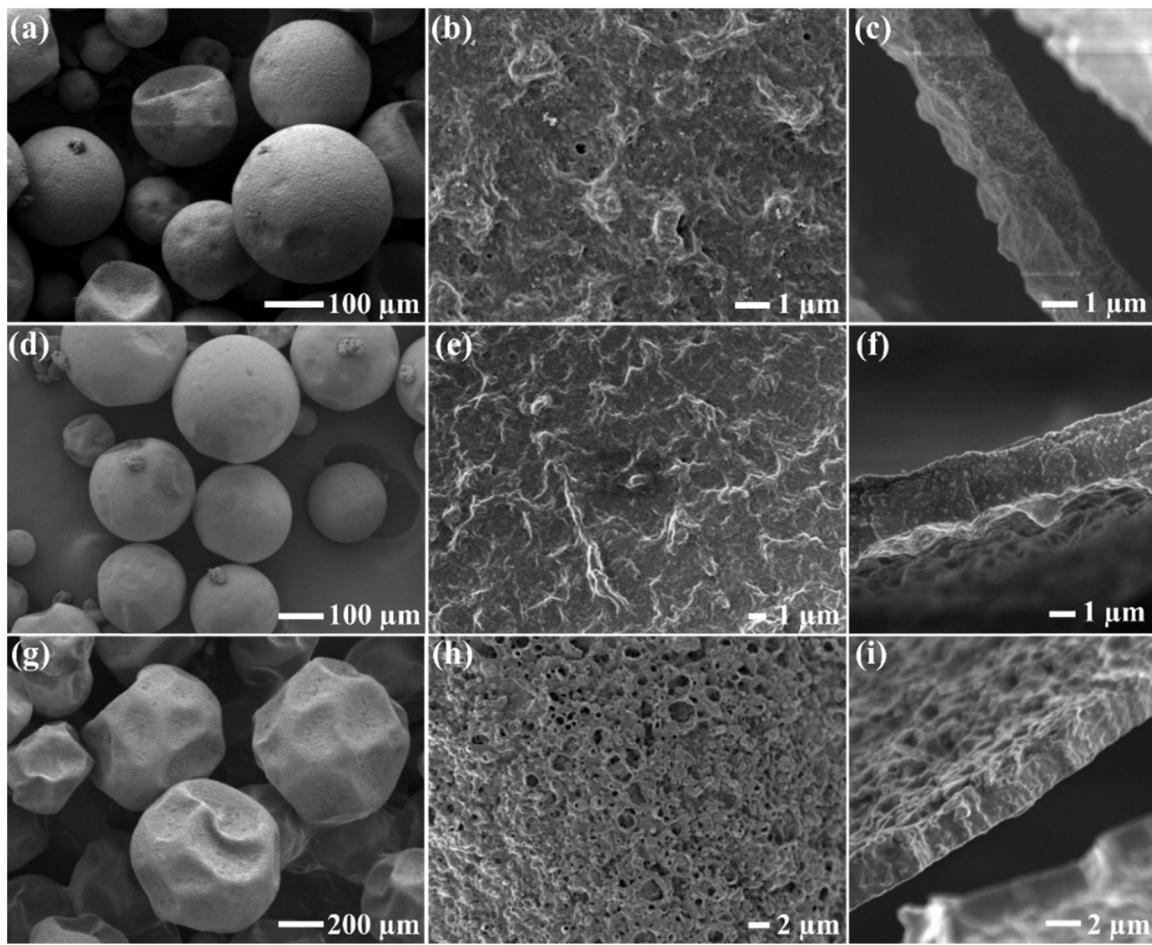


Fig. 10. (a-c) Microcapsules containing 1 M NaCl, (d-f) Microcapsules containing 10.0 wt% Na₂CO₃, and (g-i) Microcapsules containing 1 M NaOH.

squeezed core liquid, and pure microcapsule shell. The TGA curve of the microcapsules is almost identical to that of the squeezed core liquid, indicating that the weight percentage of the microcapsule shell is very low. It can be clearly seen from the TGA curve of the squeezed core liquid that besides water and the residual BDO, it contains about 40 wt% of PEI, which is close to the percentage of PEI in the input core liquid (~46 wt%). The microencapsulated PEI has a very large specific surface area, which facilitates the exchange and transfer of substance and heat. As a multifunctional substance, PEI can efficiently absorb CO₂ in the air after being microencapsulated. [26–28] Both the microcapsules and the absorbed CO₂ can be reused by easily separating the complex. They have great potential to be used in CO₂ capturing and storage. Additionally, they can also be used in water treatment as a solid chelating agent to absorb and precipitate metal ions in wastewater and sewage. [29,30].

In this category, other organics containing polyhydroxyl groups, including vitamin C (L-ascorbic acid, molecule structure as shown in Fig. S9), glucose, xylitol, mannitol, etc., were microencapsulated using this technique. When microencapsulated, they, on the one hand, are the targeting core materials, on the other hand, act as the auxiliary cross-linkers. Thus, such substances are easy to be microencapsulated using either glycerol or PEI as the cross-linker. As long as the viscosity of the aqueous solution is not too high and the emulsion method can be used to form small droplets, high-quality microcapsules can be prepared. When PEI was used as the cross-linker, the yields of these processes is much close to that of microencapsulating pure water, as shown in Table 1. Fig. 9 shows the SEM images of the microcapsules containing 10 wt% vitamin C aqueous solution. The imaged microcapsules were synthesized by using 5.0 g 10.0 wt% vitamin C aqueous solution together with 2.5 g BDO and 0.5 g PEI as the core liquid and 5.0 g Suprasec 2644 as the

shell-forming monomer when the system reacted at 30 °C for 4 h under the catalysis of 0.01 wt% DBTDL. The microcapsules are even better than those containing pure water, indicating that it might be a good cross-linker or an auxiliary cross-linker to achieve high-quality microcapsules.

3.3.2. Microencapsulating water-soluble inorganics

In the second category, water-soluble inorganics, including the aqueous solutions of 1 M NaCl, 10 wt% Na₂CO₃, 1 M NaOH, and 1 M HCl, were microencapsulated using the developed microencapsulation technique. It shows that this technique can easily microencapsulate neutral or alkaline substances, such as the aqueous solutions of NaCl, Na₂CO₃, and NaOH, although the yields are relatively low of about 20%, as shown in Table 1. Fig. 10 shows the SEM images of the above-mentioned microcapsules. They have relatively good dispersibility. However, these microcapsules are not as good as the microcapsules containing pure water or the above-mentioned organic substances. The surface morphology is also evidently different from that of the latter. The reason is that the ionic strength of the core liquid solution has a greater influence on the microencapsulation process. [31–34] In theory, when BDO is used as the chain extender and PVA/glycerol is adopted as the cross-linker, this microencapsulation technique is able to encapsulate acidic substances. However, it does not perform well to fabricate dry free-flowing microcapsules containing acidic substances. Except for ascorbic acid (vitamin C), which is a weak organic acid with a certain acidity, this technique was not successful to microencapsulate other acids, such as the diluted HCl. Although observable, the microcapsules are too fragile to withstand the high vacuum during the SEM imaging, and thus fractured. (Fig. S10). Therefore, the technique developed above

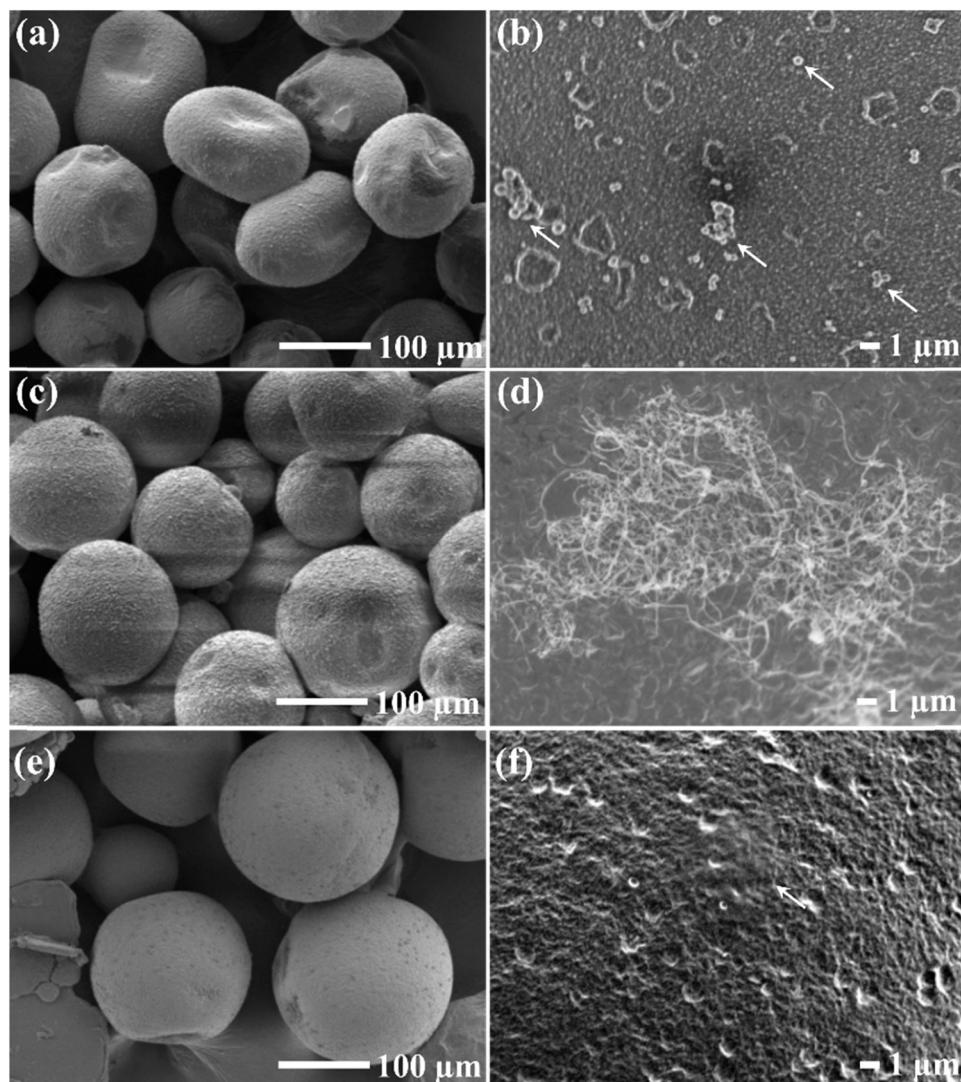


Fig. 11. Microcapsules respectively containing (a) and (b) 7.5 mg/mL Fe_3O_4 , (c) and (d) 5.0 mg/mL MWCNT, (e) and (f) 5.0 mg/mL graphene. Arrows in (b) indicate the Fe_3O_4 nanoparticles on the inner shell of the microcapsule. Arrow in (f) indicates one piece of graphene adhered to the inner shell.

can be better applied to microencapsulate neutral or alkaline water-soluble inorganic substances, but it still has certain limitations in microencapsulating strong acidic inorganic substances.

3.3.3. Microencapsulating water-based dispersions

The microencapsulation technique can also play a great role in microencapsulating aqueous dispersions. In this study, we tried to enwrap different typical nanomaterials, including nano-magnetic particles Fe_3O_4 (7.5 mg/mL), 1D nanowire CNT (5.0 mg/mL), 2D nanosheet graphene oxide (GO, 5.0 mg/mL). As shown in Table 1, the yield of these processes is close to that of microencapsulating pure DI water. Fig. 11 shows the three prepared microcapsules respectively. The imaged microcapsules were synthesized by using 5.0 g aqueous dispersion together with 2.5 g BDO and 0.5 g PEI as the core liquid. It can be seen that this method can successfully microencapsulate these three neutral nanomaterials of different dimensions. The microcapsules are much similar to those containing pure water or organic solutes. Unlike microencapsulating the water-soluble inorganics with great influence on the ionic strength of the core liquid, the dispersed nanomaterials in the core liquids do not change the physicochemical properties of the core liquids seriously except for the viscosity. Thus, good microcapsules containing dispersed nanomaterials can be microencapsulated successfully.

In summary, it can be seen that the microencapsulation technology has very strong versatility and can microencapsulate many water-soluble/dispersible substances. It is also worth noting that the water-soluble/dispersible substances can be microencapsulated at a relatively low temperature, which is a big advantage of this technique. For the above-mentioned two processes, the adopted temperature is less than 35 °C, which is lower than that of the human body. It means that it has great potential to microencapsulate some temperature-sensitive substances, such as enzymes, cell dispersions, proteins, catalysts, etc. Meanwhile, although the temperature is low, the time to achieve robust microcapsules is relatively short in the range of 3–5 h.

4. Conclusions

In summary, an innovative method for the microencapsulation of water-soluble/dispersible materials by polyurethane shell was explored in a water-in-oil emulsion using the interfacial polymerization of diisocyanate pre-polymer (Suprasec 2644) and diol (BDO). A surfactant, an A-B-A triblock copolymer Arlacel P135, was specially selected to stabilize the inverse emulsion. The obtained microcapsules with perfect core-shell structure have a smooth inner surface and a rough outer surface and uniform shell thickness. The quality of the microcapsules highly depends on whether cross-linkers are adopted and the type of the cross-

linker used. Based on the adopted cross-linkers with different functionalities, microcapsules with different shell permeability can be synthesized, that is, permeable shell when glycerol or no cross-linker was used while impermeable shell when PVA or PEI was used. To demonstrate the versatility of this developed technique, it was used to micro-encapsulate the common compounds with different nature in the laboratory, including water-soluble organics, water-soluble inorganics, and water-based dispersions. It can successfully microencapsulate a wide variety of water-soluble/dispersible substances except for the inorganic strong acid. The quality of the final microcapsules varies according to the physicochemical properties of the targeting core liquid.

CRediT authorship contribution statement

The manuscript was written through the contributions of all authors. All authors have approved the final version of the manuscript.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at [doi:10.1016/j.colsurfa.2021.127865](https://doi.org/10.1016/j.colsurfa.2021.127865).

References

- [1] S. Benita. Microencapsulation: Methods and Industrial Applications, second edition, CRC Press, 2005.
- [2] H. Zhang, X. Zhang, C. Bao, X. Li, D. Sun, F. Duan, K. Friedrich, J. Yang, Direct microencapsulation of pure polyamine by integrating microfluidic emulsion and interfacial polymerization for practical self-healing materials, *J. Mater. Chem. A* 6 (2018) 24092–24099.
- [3] H. Zhang, X. Zhang, Y.B. Chong, J. Peng, X. Fang, Z. Yan, B. Liu, J. Yang, Shell formation mechanism for direct microencapsulation of nonequilibrium pure polyamine droplet, *J. Phys. Chem. C* 123 (2019) 22413–22423.
- [4] M. Kakran, M.N. Antipina, Emulsion-based techniques for encapsulation in biomedicine, food and personal care, *Curr. Opin. Pharmacol.* 18 (2014) 47–55.
- [5] W. Lu, A.L. Kelly, S. Miao, Emulsion-based encapsulation and delivery systems for polyphenols, *Trends Food Sci. Technol.* 47 (2016) 1–9.
- [6] E.N. Brown, M.R. Kessler, N.R. Sottos, S.R. White, In situ poly(urea-formaldehyde) microencapsulation of dicyclopentadiene, *J. Microencapsul.* 20 (2003) 719–730.
- [7] J.L. Yang, M.W. Keller, J.S. Moore, S.R. White, N.R. Sottos, Microencapsulation of isocyanates for self-healing polymers, *Macromolecules* 41 (2008) 9650–9655.
- [8] R. Arshady, Preparation of microspheres and microcapsules by interfacial polycondensation techniques, *J. Microencapsul.* 6 (1989) 13–28.
- [9] S. Suzuki, T. Kondo, G.S. Mason, Studies on microcapsules. I. Preparation of polyurethane and polyphenoxy microcapsules, *Chem. Pharm. Bull.* 16 (1968) 1629–1631.
- [10] A.M. Pensé, C. Vauthier, F. Puisieux, J.P. Benoit, Microencapsulation of benzalkonium chloride, *Int. J. Pharm.* 81 (1992) 111–117.
- [11] E.-M. Rosenbauer, M. Wagner, A. Musyanovich, K. Landfester, Controlled release from polyurethane nanocapsules via pH-, UV-light- or temperature-induced stimuli, *Macromolecules* 43 (2010) 5083–5093.
- [12] G. Baier, K. Friedemann, E.-M. Leuschner, A. Musyanovich, K. Landfester, pH stability of poly(urethane/urea) capsules synthesized from different hydrophilic monomers via interfacial polyaddition in the inverse miniemulsion process, *Macromol. Symp.*, 331–332 (2013) 71–80.
- [13] A. Schoth, K. Landfester, R. Muñoz-Espí, Surfactant-free polyurethane nanocapsules via inverse pickering miniemulsion, *Langmuir* 31 (2015) 3784–3788.
- [14] A.M.B. Rodriguez, B.P. Binks, Capsules from pickering emulsion templates, *Curr. Opin. Colloid Interface Sci.* 44 (2019) 107–129.
- [15] O. Álvarez-Bermúdez, I. Adam-Cervera, A. Aguado-Hernández, K. Landfester, R. Muñoz-Espí, Magnetic polyurethane microcarriers from nanoparticle-stabilized emulsions for thermal energy storage, *ACS Sustain. Chem. Eng.* 8 (2020) 17956–17966.
- [16] C.-B. Wu, G. Wu, X. Yang, Y.-J. Liu, C.-X. Gao, Q.-H. Ji, M. Wang, H.-Z. Chen, Preparation of Mannitol@Silica core-shell capsules via an interfacial polymerization process from water-in-oil emulsion, *Colloids Surf. A Physicochem. Eng. Asp.* 457 (2014) 487–494.
- [17] M. O'Sullivan, B. Vincent, Aqueous dispersions of silica shell/water-core microcapsules, *J. Colloid Interface Sci.* 343 (2010) 31–35.
- [18] D.A. McIlroy, B.J. Blaiszik, M.M. Caruso, S.R. White, J.S. Moore, N.R. Sottos, Microencapsulation of a reactive liquid-phase amine for self-healing epoxy composites, *Macromolecules* 43 (2010) 1855–1859.
- [19] H. Yi, Y.H. Deng, C.Y. Wang, Pickering emulsion-based fabrication of epoxy and amine microcapsules for dual core self-healing coating, *Compos. Sci. Technol.* 133 (2016) 51–59.
- [20] M. Huang, J. Yang, Facile microencapsulation of HDI for self-healing anticorrosion coatings, *J. Mater. Chem. A* 21 (2011) 11123–11130.
- [21] D. Sun, H. Zhang, X.-Z. Tang, J. Yang, Water resistant reactive microcapsules for self-healing coatings in harsh environments, *Polymer* 91 (2016) 33–40.
- [22] C. Perignon, G. Ongmayeb, R. Neufeld, Y. Frere, D. Poncelet, Microencapsulation by interfacial polymerisation: membrane formation and structure, *J. Microencapsul.* 32 (2015) 1–15.
- [23] W. Frere, L. Danicher, P. Gramain, Preparation of polyurethane microcapsules by interfacial polycondensation, *Eur. Polym. J.* 34 (1998) 193–199.
- [24] M. Ionescu, Chemistry and Technology of Polyols for Polyurethanes, Rapra Technology Limited, 2005.
- [25] Z. Chen, Z. Lv, Y. Sun, Z. Chi, G. Qing, Recent advancements in polyethyleneimine-based materials and their biomedical, biotechnology, and biomaterial applications, *J. Mater. Chem. B* 8 (2020) 2951–2973.
- [26] K. Li, J. Jiang, F. Yan, S. Tian, X. Chen, The influence of polyethyleneimine type and molecular weight on the CO₂ capture performance of PEI-nano silica adsorbents, *Appl. Energ.* 136 (2014) 750–755.
- [27] M.U. Thi, Le Lee S.-Y., S.-J. Park, Preparation and characterization of PEI-loaded MCM-41 for CO₂ capture, *Int. J. Hydrol. Energy* 39 (2014) 12340–12346.
- [28] B. Dutcher, M. Fan, A.G. Russell, Amine-based CO₂ capture technology development from the beginning of 2013—A review, *ACS Appl. Mater. Interfaces* 7 (2015) 2137–2148.
- [29] Y. Ma, W.-J. Liu, N. Zhang, Y.-S. Li, H. Jiang, G.-P. Sheng, Polyethylenimine modified biochar adsorbent for hexavalent chromium removal from the aqueous solution, *Bioresour. Technol.* 169 (2014) 403–408.
- [30] J.B. Lindén, M. Larsson, S. Kaur, W.M. Skinner, S.J. Miklavcic, T. Nann, I. M. Kempson, M. Nydén, Polyethyleneimine for copper absorption II: kinetics, selectivity and efficiency from seawater, *RSC Adv.* 5 (2015) 51883–51890.
- [31] N. Angelova, D. Hunkeler, Permeability and stability of chitosan-based capsules: effect of preparation, *Int. J. Pharm.* 242 (2002) 229–232.
- [32] A. Bartkowiak, Effect of the ionic strength on properties of binary alginate/oligochitosan microcapsules, *Colloids Surf. A Physicochem. Eng. Asp.* 204 (2002) 117–124.
- [33] K. Koehler, P.M. Biesheuvel, R. Weinkamer, H. Moehwald, G.B. Sukhorukov, Salt-induced swelling-to-shrinking transition in polyelectrolyte multilayer capsules, *Phys. Rev. Lett.* 97 (2006), 188301.
- [34] H. Mjahed, J.-C. Voegel, B. Senger, A. Chassepot, A. Rameau, V. Ball, P. Schaaf, F. Boulimedas, Hole formation induced by ionic strength increase in exponentially growing multilayer films, *Soft Matter* 5 (2009) 2269–2276.
- [35] H. Zhang, X. Zhang, Q. Chen, X. Li, P.F. Wang, E.H. Yang, F. Duan, X.L. Gong, Z. Zhang, J.L. Yang, Encapsulation of shear thickening fluid as an easy-to-apply impact-resistant material, *J. Mater. Chem. A* 5 (43) (2017) 22472–22479.
- [36] H. Zhang, X. Zhang, C.L. Bao, X. Li, F. Duan, K. Friedrich, J.L. Yang, Skin-inspired, fully autonomous self-warning and self-repairing polymeric material under damaging events, *Chem. Mater.* 31 (7) (2018) 2611–2618.
- [37] Z.T. Yang, X.L. Fang, J.J. Peng, X.W. Cao, Z.C. Liao, Z.B. Yan, C.X. Jiang, B. Liu, H. Zhang, Versatility of the microencapsulation technique via integrating microfluidic T-Junction and interfacial polymerization in encapsulating different polyamines, *Colloids Surf. A* 604 (2020) 125097.