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Optimization of Microencapsulation Process for Self-Healing Polymeric Material

(Pengoptimuman Proses Mikro-pengkapsulan untuk Bahan Polimer Penyembuhan-Sendiri)

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ABSTRACT

A series of poly(urea-formaldehyde) (PUF) microcapsules filled with dicyclopentadiene (DCPD) was successfully prepared by in situ polymerization. The effect of diverse process parameters and ingredients on the morphology of the microcapsules was observed by SEM, optical microscopy (OM) and digital microscopy. Different techniques for the characterization of the chemical structure and the core content were considered such as FT-IR and ^{1}H-NMR as well as the characterization of thermal properties by DSC. High yields of free flowing powder of spherical microcapsules were produced. The synthesized microcapsules can be incorporated into another polymeric host material. In the event the host material cracks due to excessive stress or strong impact, the microcapsules would rupture to release the DCPD, which could polymerize to repair the crack.

Keywords: Microcapsules; micro-cracking; in situ polymerization; self-healing material

ABSTRAK

Siri mikrokapsul poliurea-formaldehid (PUF) yang mengandungi disiklopentadiena (DCPD) berjaya disediakan melalui proses pempolimeran in situ. Kesan kepelbagaian parameter proses dan bahan reaktan terhadap morfologi mikrokapsul telah diperhatikan melalui SEM, mikroskop optik (OM) dan mikroskop digital. Pelbagai kaedah seperti FT-IR dan ^{1}H-NMR diguna untuk mencirikan struktur kimia serta kandungan teras mikrokapsul. Selain itu, sifat terma mikrokapsul juga dianalisis menggunakan DSC. Sfera mikrokapsul yang terhasil adalah dalam bentuk serbuk putih dengan peratus hasilan yang tinggi. Mikrokapsul ini boleh digabungkan ke dalam bahan polimer hos yang lain. Apabila bahan induk retak akibat tekanan yang berlebihan atau impak yang kuat, mikrokapsul akan pecah dan membebaskan DCPD untuk membaiki keretakan melalui proses pempolimeran.

Kata kunci: Bahan penyembuhan-sendiri; keretakan-mikro; mikrokapsul; pempolimeran in situ

INTRODUCTION

The reduction in the performance and lifetime of polymeric materials is often caused by micro-cracks that had developed earlier deep within the structure of the material (Wool 2001). In most of the cases, these micro-cracks remain unnoticed and therefore cannot be repaired on time by manual intervention (White et al. 2001). Reliance on polymeric materials in various fields has spurred researchers into action and led to the development of diverse "self-healing" materials (Wu et al. 2008, Yuan et al. 2008). During the last decades various groups of researchers examined different systems such as the incorporation of monomer filled tubes (Thao et al. 2009), glass fibers (Dry 1996, Li et al. 1998, Bond et al. 2008), and capsules (Ni et al. 1995, Hong & Park 2000) into a host material with the aim of releasing the monomer upon crack intrusion which would mend the crack and therefore autonomously heal the material.

The probably most advanced self-healing system is being developed by White et al. (2001). Their material represents microcapsules of a urea-formaldehyde (UF) shell that incorporate DCPD as a healing agent. These microcapsules are embedded in an epoxy matrix along with a selective catalyst. In the event of a crack the microcapsule shell will break releasing the DCPD which reacts with the catalyst to bond the crack. White and his group initially developed this system for its application in aeronautics but possible applications of this novel technology are endless.

Among others its use in dentistry seems highly attractive as the improvement of crack-resistance in dental filling materials is still of significant importance. The idea of a self-healing tooth filling material triggered this research work. Microcapsules can encapsulate various substances and also the coating can be selected from a wide variety of natural or synthetic polymers, depending on the material to be coated as well as the desired characteristics (Ghosh 2006). As there is a wide selection of composition materials it is possible to produce microcapsules for very special applications (Benita 1996, Arshady & Guyot 2002). The incorporation in a dental composite to create a self-healing filling material is one niche yet to develop.

This report concentrates on the microcapsule synthesis by *in situ* polymerization in an oil-in-water emulsion. The microcapsules consist of a PUF shell and include DCPD

as a core material or "healing agent". Along with the synthesis, the influence of different production parameters was studied. Finally, appropriate techniques to analyze the product were investigated.

The healing of micro-cracks in a composite matrix can be accomplished by incorporating a microencapsulated healing agent and a catalytic chemical trigger within the matrix (Figure 1a). As soon as a crack ruptures an embedded microcapsule the healing agent is released (Figure 1b). The healing monomer distributes in the crack plane and reacts with the embedded catalyst bonding the crack planes (Figure 1c).

Urea-formaldehyde polymers are produced in a highly exothermic reaction which takes place in two stages (Pizzi 1994). In the first stage, urea is hydroxymethylolated by the addition of formaldehyde to the amino group of urea. This step includes a series of reactions that lead to the formation of monomethylolurea, dimethylolurea, and trimethylolurea. The second stage of the urea-formaldehyde resin formation consists of condensation reactions of the methylolureas and the concurrent elimination of water resulting in low molecular weight condensates (Connor 1996). Higher molecular weight oligomers and polymers are obtained by further condensation. The increase in the molecular weight to produce higher molecular weight products includes a combination of the following reactions:

1. the reaction of methylol and amino groups of the reacting molecules leading to methylene bridges between amido nitrogens,
2. two methylol groups react to build methylene ether linkages,
3. the splitting out of formaldehyde from methylene ether linkages which results in methylene linkages, and
4. the reaction of methylol groups in which water and formaldehyde is splitted out and methylene linkages are obtained.

The urea-formaldehyde molar ratio used in industrial applications is commonly in the range of 1:2.0 to 1:2.4 (Pizzi 1994; Christjanson et al. 2006). Being aware of the health risks associated with formaldehyde there is a general interest in reducing the formaldehyde content in these materials (Wijnendaele et al. 2010). However, a decrease in the formaldehyde amount could have a negative impact on the characteristics of the polymeric material. Therefore, part of this study focuses on the effect of different urea-formaldehyde ratios on the microcapsule shell formation.

Materials & Methods

Materials

The microcapsule wall-forming materials consisted of urea, ammonium chloride and 1,3-dihydroxybenzol (resorcinol) which were acquired from Sigma-Aldrich whereas formalin (37 wt%) was purchased from Systerm. The core material, DCPD, was obtained from Sigma-Aldrich and used as received. Ethylene maleic anhydride (EMA) copolymer powder with an average molecular weight Mw = 400,000 was used as emulsifier and was purchased from Sigma-Aldrich. 1-octanol and NaOH were obtained from Sigma-Aldrich, ethanol from HmbG Chemicals. All chemicals used were of analytical grade.

Preparation of Microcapsules

Diverse chemical encapsulation techniques are described in literature (Sliwka 1975; Whateley 1992; Jyothi et al. 2010). Of special interest for this work is the *in situ* polymerization in an oil-in-water emulsion which can be achieved when encapsulating water-immiscible liquids by the reaction of urea with formaldehyde at acidic pH. The standard recipe for the preparation of PUF/DCPD microcapsules was adapted from that of Brown et al. (2003).

At room temperature 100 mL distilled water and 25 mL of a 2.5 wt% aqueous solution of EMA copolymer were mixed in a 500 mL glass beaker. Under agitation by a magnetic stirrer the wall forming materials 2.5 g urea, 0.25 g ammonium chloride and 0.25 g resorcinol were dissolved in the solution. Then, the pH was raised to 3.50 by drop-wise addition of 10% NaOH solution. After that, the reaction solution was suspended in a temperature-controlled water bath. It was agitated with a mechanical stirrer at 450 rpm driving a three-bladed, 40 mm diameter propeller. Surface bubbles were eliminated by the addition of two drops 1-octanol. Then, 30 mL DCPD was added to form a suspension of fine droplets. After stabilization, 6.35 g formalin was added. The mixture was covered with aluminium foil and the temperature was raised to 55°C at a rate of 2°C/min. After 4 h the reaction slurry was removed and allowed to slowly cool down to room temperature.

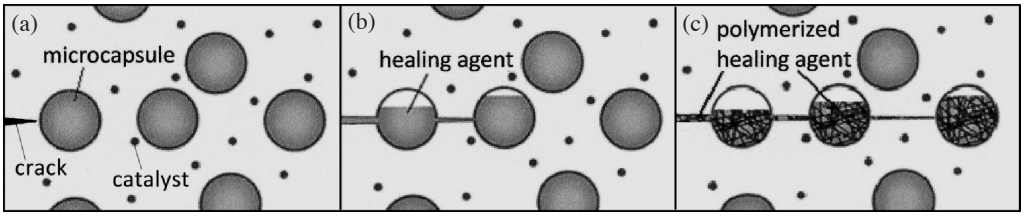

FIGURE 1. Self-healing system as developed by White et al. (2001): (a) microcapsules and catalyst embedded in polymeric host material, (b) crack ruptures microcapsules, healing agent distributes into crack plane, and (c) healing agent reacts with catalyst to heal the crack

The suspension was filtered under suction and rinsed with water, then left to air dry for 2 hours and finally placed in the drying cabinet over night. The dry capsules were separated by sieving through precision test sieves.

The amounts of urea and formalin for the examination of the urea-formaldehyde ratio effect on the capsule shell formation differ from the standard recipe and are therefore listed in Table 1.

ANALYSIS OF MICROCAPSULES

Microcapsule Shape, Size and Yield The microcapsule average size is controlled by the agitation rate during the synthesis (Ovez et al. 1997; Tan et al. 1991; Yan et al. 1993). With an agitation rate of 200-2000 rpm microcapsules of an average diameter of 10-1000 μm can be obtained. In this work the agitation rate was adjusted to 450 rpm to produce capsules of a medium diameter (about 220 microns) which was suggested by White et al. (2001) for the application in a self-healing system.

The dried product was weight and examined with the help of a digital microscope (AnMo Electronics Corp.) to confirm the successful preparation of microcapsules. Furthermore, the shape of the individual spheres at the two possible magnifications, 5 x and 200 x was examined. The capsules were then separated in different size fractions by sieving through the available precision test sieves (Endecotts, certified acc. to BS 410, ISO 3310) of 50, 150, 300 and 500 microns mesh size. The weight of each size fraction was taken to obtain the average microcapsule diameter. Furthermore, the capsules of each size fraction were inspected by digital microscopy.

Verification of Encapsulated DCPD The chemical structure of the monomer incorporated in the microcapsule can be analyzed by different spectroscopic methods such as nuclear magnetic resonance (^{1}H-NMR) and fourier-transform infrared spectroscopy (FTIR). Furthermore, knowing certain physical and chemical properties of the monomer, thermo-analytical techniques such as differential scanning calorimetry (DSC) can be used to proof that the microcapsules contain the encapsulated monomer. The aim of this work was to find the most appropriate available technique for the analysis of the microcapsule core monomer to apply in future studies.

Raman spectroscopy of the dry capsule shell and the intact microcapsules was performed on a Perkin Elmer FT-IR spectrometer using the KBr technique. Typical spectra were recorded in the range of 4000-400 cm^{-1} at a resolution of 4 cm^{-1}. Thermal analysis was measured on a Perkin Elmer Diamond DSC. For each sample a single scan from 35°C to 300°C at a heating rate of 10°C/min was performed. The sample preparation for both measurements FTIR and DSC was the same: microcapsules were ground with a pestle in a mortar. The crushed microcapsules were collected and washed with acetone several times, then dried at room temperature.

Moreover, the weight of the initial microcapsules and the weight of the residue of the grounded and extracted microcapsules were taken to calculate the core content in wt%. The dry capsule shell material was then measured by DSC and FTIR next to a sample of the intact microcapsules. It was expected that in the spectra of the intact microcapsules additional peaks related to DCPD would appear which is not present in the extracted microcapsule shell material. The resulting FTIR spectra were compared with the library spectra of pure DCPD. As far as the thermal analysis is concerned, the boiling point of DCPD at 170°C might be an indication for the presence of the encapsulated monomer.

Finally, solution state ^{1}H-NMR of the capsule content was performed on a 400 MHz Bruker FT NMR system. Therefore microcapsules were ground with a mortar and extracted with deuterated acetone. The extract was measured next to a reference sample of DCPD which was dissolved in the same solvent. The successful encapsulation of the DCPD monomer would be indicated by the presence of the characteristic signals corresponding to DCPD in the spectrum of the diluted microcapsule extract.

Microcapsule Shell and Morphology OM (Leica) was used to provide information about the shape and shell thickness of the microcapsules. For the shell inspection capsules in the size range of 150 to 300 micron were dispersed in oil and measured using an oil immersion objective lens of 100 x magnification. The thickness of the outer capsule shell layer was measured on 3 images at 15 positions to calculate the average thickness of the rough capsule wall.

In addition, the capsule shell and morphology were examined by SEM (Quanta 200 F, FEI). Therefore, the microcapsules were mounted on a conductive stage and part of them ruptured with a razor blade to facilitate membrane thickness measurement. The SEM measurements

TABLE 1. Urea and formaldehyde parts in the microcapsule synthesis

Sample no.	Urea-formaldehyde molar ratio	Urea mass (g)	Formaldehyde mass (g)
1	1 : 1.1	3.56	5.29
2	1 : 1.5	2.92	5.93
3*	1 : 1.9	2.50	6.35
4	1 : 2.3	2.16	6.69

** Standard recipe*

were carried out under low vacuum using an electron acceleration voltage of 5 kV. For the evaluation of the capsule shell thickness 5 measurements of the outer and inner shell layer were performed each.

Results and Discussion

Product analysis by digital microscopy

With the help of digital microscopy the successful preparation of microcapsules was confirmed (Figure 2). The images at the two possible magnifications display many spherical microcapsules of different diameter. The inspection of the different size fractions showed no visible difference in the product: the capsules were all globular and hardly any impurities could be found.

Microcapsule yield and size

For the calculation of the microcapsule yield, the weight of the starting materials, urea, formaldehyde, resorcinol and DCPD was considered. Five samples of the dried product were measured and the weight percent calculated, assuming that no impurity was present. The resulting values are listed in Table 2 showing an average yield of 81%. Next to the total yield Table 2 displays the weight percentage of the microcapsule size fractions after sieving. It shows that with a stirring rate of 450 rpm microcapsules in the size range of about 50-500 μm were produced. The maximum yield is reached by the capsules of the medium size fraction (150-300 μm) with an average yield of 59 wt%.

Microcapsule core content

The FTIR spectra of both samples, the microcapsules and the extracted microcapsule shell particles, showed the expected peaks at 3138 cm^{-1}, 1640 cm^{-1} and 1400 cm^{-1} which are the characteristic absorption peaks of –NH and -C=O stretching vibrations as well as -CH_2 bending vibration, respectively. These three primary peaks indicate the formation of the urea-formaldehyde wall material. Additional peaks in the area of 2960 cm^{-1} displaying -CH stretching vibrations as well as –CH absorption peaks in the area from 720 cm^{-1} to 760 cm^{-1} corresponding to the DCPD were not clear.

The DSC plot of the intact microcapsules showed a rise in the enthalpy of transition (ΔH) from the starting temperature (35°C) reaching an apex at 62°C (Figure 3a) which illustrates the melting of DCPD. The following gradual increase of ΔH starting at about 160°C might indicate the boiling of DCPD. It reaches a peak at 219°C, obviously merging with the melting peak of the UF shell material which is indicated by the shoulders at about 245°C and 260°C. Figure 3(b) displays the graph of the extracted microcapsule shell material which shows a moderate increase in enthalpy only at higher temperatures to reach

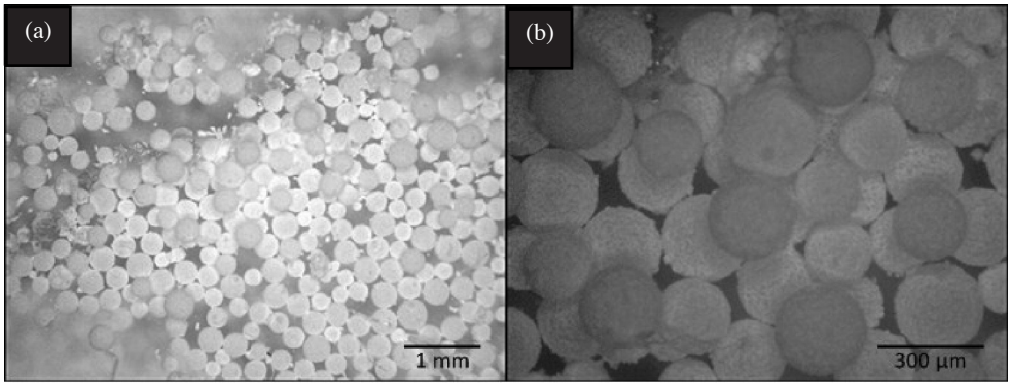

FIGURE 2. Digital microscopy images of spherical PUF/DCPD microcapsules at different magnifications (5x and 200x)

TABLE 2. Microcapsule total yield and microcapsule yield according to capsule size fractions

Sample No.	Total yield in (wt%)	Yield according to microcapsule size fractions in (wt%)				
		< 50 μm	50-150 μm	150-300 μm	300-500 μm	> 500 μm
1	78	0	13	51	30	6
2	80	1	6	60	24	9
3	82	3	8	59	27	3
4	85	1	10	64	21	4
5	81	7	26	63	3	1
Average	81	2	13	59	21	5

a peak at 252°C. The evident DCPD peaks of the DSC plot obtained from the intact microcapsules in comparison with the plot of the pure UF shell material proofed the presence of the encapsulated monomer.

Furthermore, DCPD was verified by ^{1}H-NMR spectroscopy as the spectra of the microcapsule extract (Figure 4) resembled the spectra of the pure DCPD. It showed the characteristic peaks of DCPD at 1.17 ppm (d,1H); 1.30 ppm (d,1H); 1.45-1.52 ppm (m,1H); 1.97-2.05 ppm (m,1H); 2.56-2.66 ppm (m,2H); 2.72 ppm (s,1H); 3.06 ppm (m,1H); 5.28-5.33 ppm (m,2H); 5.74-5.83 ppm (m,2H). Hence, ^{1}H-NMR spectroscopy is one method to proof the presence of DCPD in the microcapsules.

The weight fraction of DCPD calculated from the initial microcapsule weight and the weight of the capsule shell material after extraction was about 89 wt%.

OM ANALYSIS

The analysis by OM confirmed that the microcapsules produced were of perfectly round shape as it can be seen in Figure 5(a). Additionally, the images showed that the microcapsules consist of a fine inner shell wall that is surrounded by a rough outer layer. Further magnification made it possible to measure the thickness of the shell wall as it is displayed in Figure 5b. The rough outer layer measured about 12 to 16 μm.

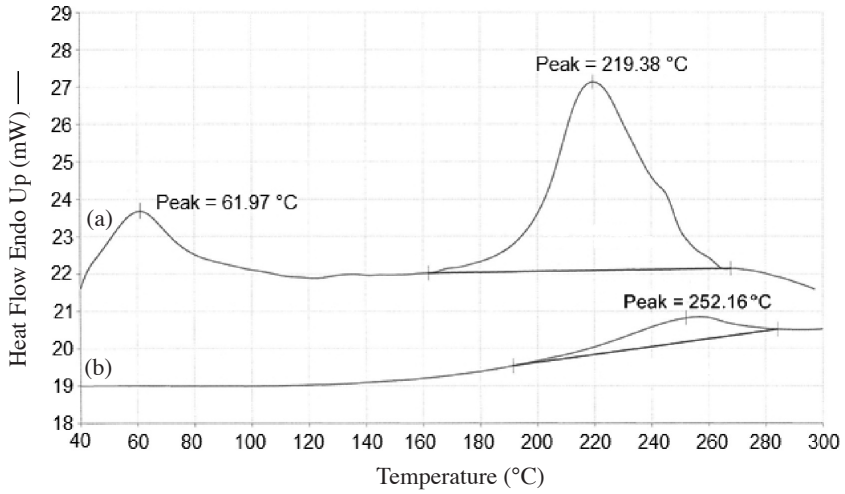

FIGURE 3. DSC spectra of (a) PUF/DCPD microcapsules and (b) extracted PUF microcapsule shell material

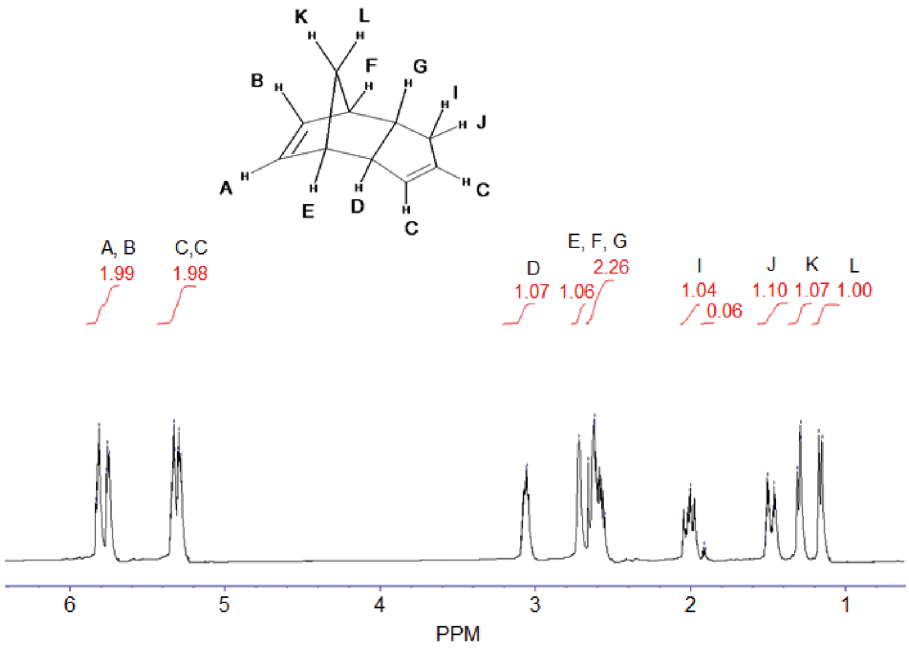

FIGURE 4. ^{1}H-NMR spectrum of the extract of ground PUF/DCPD microcapsules showing the characteristic peaks of DCPD

MICROCAPSULE MORPHOLOGY AND SHELL THICKNESS BY SEM

SEM allows the inspection of the capsule shell at higher magnification. Figure 6(a) shows the outer surface of the round microcapsules. Zooming in the surface of the smooth inner shell wall becomes visible on which numerous nanoparticles of annular shape are agglomerated to build the rough outer capsule shell layer (Figure 6(b)). The size of the nanoparticles was in the range of 80-350 nm. Brown et al. (2003) suggested that these are poly(urea-formaldehyde) (PUF) nanoparticles which are precipitations of higher molecular weight pre-polymer; whereas the smooth capsule wall is the result of the deposition of low-molecular weight pre-polymer at the DCPD-water interface during synthesis.

Furthermore, the shell wall thickness was measured with the help of SEM. The wall thickness largely depends on the ratio of the core to shell material (Park et al. 2001). To facilitate membrane thickness measurements part of the capsules were ruptured with a razor blade. The resulting images revealed that the rough porous outer layer that is sticking on the fine smooth inner shell measured about 10-15 μm (Figure 7(a)). Further magnification allowed the inspection of the inner shell wall. The thickness was in the range of about 120 to 140 nm as it is displayed in Figure 7(b).

EFFECT OF UREA-FORMALDEHYDE RATIO ON MICROCAPSULE SHELL

Four batches of microcapsules with different urea-formaldehyde molar ratio were produced and each product was examined by digital and optical microscopy. OM showed that the capsules synthesized with a lower formaldehyde amount do not possess the rough outer layer (Figure 8(a) and (b)). Furthermore, a lot of residual material next to the microcapsules was obtained from these two batches. The capsules with a urea-formaldehyde molar ratio of 1:1.1 were of very poor quality as it can be seen in the image of Figure 8(a), and the yield was very low. Whereas the standard ratio of 1:1.9 resulted in capsules of a perfectly round shape with a uniform shell wall, illustrated in Figure 8c. The microcapsules with higher formaldehyde content (molar ratio 1:2.3) showed a thicker and more irregular outer capsule shell (Figure 8(d)). For the latter sample the outer shell wall thickness measured about 10-18 μm.

Generally, it seemed that the urea-formaldehyde ratio has a direct influence on the formation of the outer microcapsule shell layer. A rise in the formaldehyde content showed an increase in the amount of high-molecular weight PUF nanoparticels that agglomerated on the surface of the smooth capsule shell wall.

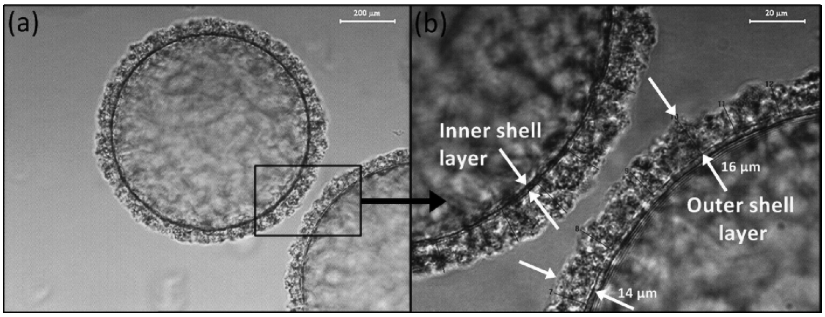

FIGURE 5. Optical micrographs of (a) spherical PUF/DCPD microcapsule displaying the inner shell wall as a dark clear line surrounded by a rough outer layer which (b) measured about 15 μm thick

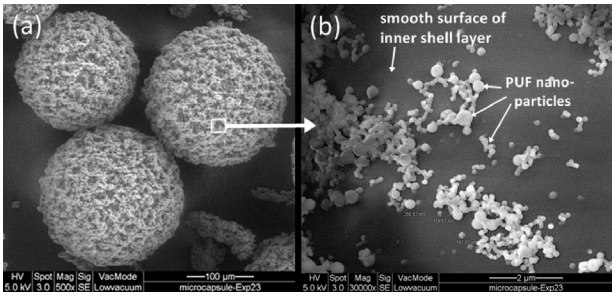

FIGURE 6. SEM images of PUF/DCPD microcapsules illustrating (a) the rough porous outer shell layer and (b) the surface of the smooth inner shell wall on which precipitations of PUF nanoparticles are sticking

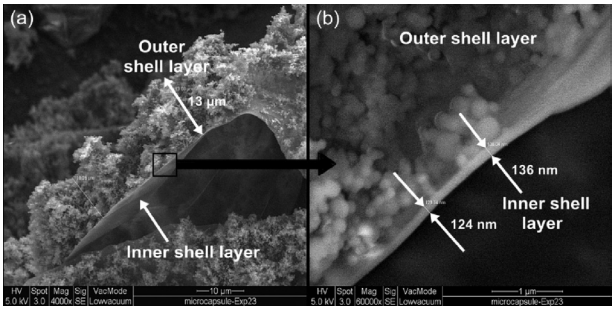

FIGURE 7. SEM images of ruptured PUF/DCPD microcapsule allowing the measurement of (a) the rough porous outer shell thickness and (b) the smooth inner shell wall thickness

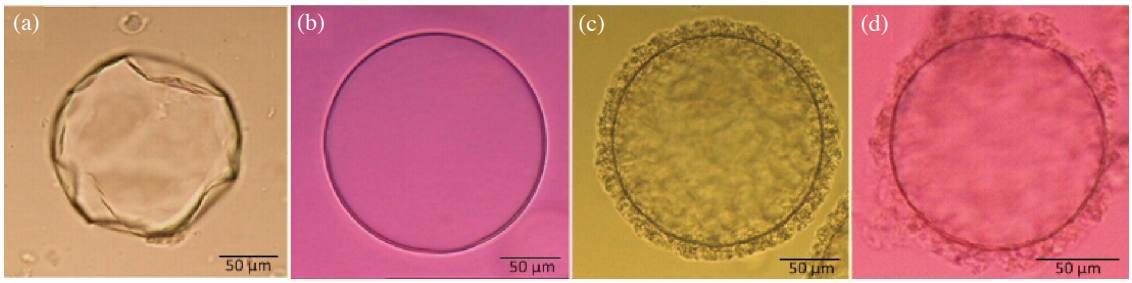

FIGURE 8. Optical micrographs showing PUF/DCPD microcapsules synthesized with different urea/formaldehyde ratio: (a) 1:1.1, (b) 1:1.5, (c) 1:1.9, and (d) 1:2.3

CONCLUSION

PUF microcapsules filled with DCPD were successfully prepared by *in situ* condensation polymerization. With a shear rate of 450 rpm microcapsules in the size range of 50-500 micron were produced. High yields (78-85%) of spherical microcapsules were obtained which appeared in the form of a free flowing white powder. It was shown that ^{1}H-NMR spectroscopy and DSC are useful methods to verify the DCPD core monomer whereas the capsule shell was examined by different microscopic methods. The microcapsule shell consisted of a smooth inner wall of about 120-140 nm in size and a rough porous outer layer which measured about 10-15 µm as determined by SEM. OM revealed that with increasing formaldehyde content the outer shell wall can be extended. The rough porous outer layer is important as it would promote the adhesion of the capsules to the matrix resin when embedded in a polymeric host material. A good adhesion is necessary to maintain the properties of the virgin material.

Generally, this study focused on the microcapsule synthesis. Further work shall include the incorporation of the microcapsules into a dental polymeric host material to create a system with self-healing ability. Therefore the evaluation of the optimum microcapsule size for this specific application will be necessary. Amongst others, it has to be considered that capsules of bigger diameter can store more healing agent which would have an advantageous effect on the healing efficiency, however, the good properties of the virgin matrix material might decrease.

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