BIOCAPSULES FOR SELF-HEALING EPOXY COMPOSITES

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Abstract

Capsule-based self-healing polymer composites have been studied extensively for the past decade. Most of the self-healing capsules are made from the synthetic polymer formaldehyde. Exposure to this polymer can cause severe health issues and often, the capsule synthesis process involves complicated procedure which is temperature and pH sensitive. This study focuses on developing a self-healing biocapsule by using alginate biopolymer to encapsulate the monomer. Two fabrication methods are being discussed and electrostatic extrusion method successfully produces epoxy/alginate microcapsules with a mean diameter of 320 ± 20 μm. FTIR tests are performed to study the chemical interaction between alginate and encapsulated epoxy resin.

1. Introduction

Self-healing polymer composites have been a popular research area for the past 15 years. It is designed with inherent ability to heal damage event either autonomically or non-autonomically with external intervention. White et al. [1] initiated the capsule-based self-healing system by utilizing Grubbs catalyst and monomer capsules have captured immense attention. Capsule-based self-healing systems [2] can be categorized into capsule-catalyst [1, 3, 4], dual-capsule [5, 6] and mono-capsule [7, 8] self-healing. Amongst, dual-capsule self-healing system showed promising results for the reasons of being more economic and environmental friendly as compared to the remaining systems [2]. As internal cracks emerged and rupture these capsules, the liquid monomer and polymeriser will be released into the crack plane, polymerised and eventually heal the crack. Different capsule materials to contain monomer resin have been reported including poly(urea-formaldehyde) (PUF) [9], polyurethane/urea-formaldehyde (PU/UF) [10] poly(melamine-formaldehyde) (PMF) [11] and etc. However, exposure to the formaldehyde which is the main component of these capsules is of great concern due to the severe health issues caused [12]. Besides, the fabrication process of these capsules are complicated, temperature and pH sensitive [13]. Moreover, most of the studies showed single healing event for capsule-based self-healing systems [3, 14, 15] which is not favorable. Thus, it is important to explore the green materials to encapsulate healing agents.

Alginate is a natural biopolymer made from brown seaweed which comprises of homopolymeric blocks of (1,4)-linked β-ᴅ-mannuronate and α-ʟ-guluronate. Due to its properties such as biocompatible, biodegradable, non-toxic and low-cost, its being widely used for encapsulating

cells[16], enzymes [17], flavors [18], oils [19] and etc. In general, alginate hydrogels are formed through ionic crosslinking with divalent ions such as Ca^{2+} or Ba^{2+} ions [20, 21]. This process is relatively simple and cost effective compared to the conventional self-healing microcapsules fabrication. In addition, the process is not temperature and pH sensitive. Several approaches have been used to produce alginate hydrobeads including extrusion-dripping [22], coaxial air flow dripping [23], electrostatic enhanced dropping [24], vibration [25], atomization [26], Jet Cutter [27] and etc. The alginate beads produced are in the range of > 1 mm (macro), 0.2 to 1000 μm (micro) and < 0.2 μm (nano) depending on the applications and fabrication method [28].

To date, no study has been done using alginate as encapsulating material for healing agents in capsule-based self-healing polymer system. In this study, we are the first to propose alginate as the encapsulating material for monomer resin to form epoxy/alginate microcapsules. Several methods are attempted in fabrication of epoxy/alginate microcapsules to achieve the target size of 200 – 300 μm. Subsequently, the physical and chemical properties of these epoxy/alginate microcapsules are being characterised.

2. Material and Methods

2.1. Materials

Bisphenol A diglycidyl ether (Araldite 506) with epoxide equivalent weight (EEW) of 172-185 g/eq as the core material of the microcapsules and calcium chloride, $CaCl_2$ (analytical grade) were purchased from Sigma-Aldrich. In this study, sodium alginate (Manugel GHB, FMC Biopolymer, UK) with medium range molecular mass of 37% β-ᴅ-mannuronic acid (M) and 63% α-ʟ-guluronic acid residues (G) was used due to its higher elastic modulus with higher G residues [20].

2.2. Microcapsules Synthesis

Alginate solution (2 w/v%) was formed by dissolving alginate in distilled water, sealed with parafilm and left overnight for degassing. On the other hand, calcium chloride solution (20 w/v%) was prepared by dissolving $CaCl_2$ into distilled water. Epoxy resin was then added gradually into the stirred alginate solution to form an (10 v/v%) oil-in-water emulsion at 500 rpm for 30 minutes.

Two fabrication methods were used to produce epoxy/alginate microcapsules. Extrusion dripping was encountered initially as shown in Fig. 1A. Epoxy/alginate emulsion was filled in a 20 mL syringe and fixed on a syringe pump (NE-1010, New Era) with flow rate of 40 mL/hr through a connecting tube connected to 2 different needle sizes (G20 and G27). It was then dripped into a magnetic stirred calcium chloride gelling solution. The distance between the needle tip and surface of gelling solution was kept at 7 cm.

The formed wet epoxy capsules were then left inside the gelling solution for 30 min before rinsing with distilled water to remove excess calcium ions and finally dried at 45 °C for 24 hr.

Second method used to produce epoxy/alginate microcapsules was electrostatic extrusion (Fig. 1B) which was developed by Nedović et al [29]. The experimental setup of this method is similar to extrusion dripping whereby the only difference is the needle was connected to positive electrode of a DC high voltage power unit with electrostatic potential of 21-25 kV and the calcium chloride gelling solution was grounded as shown in Fig. 1. The flow rate of the extrusion was set at 40 mL/hr and the needle sizes used were (G20 and G24).
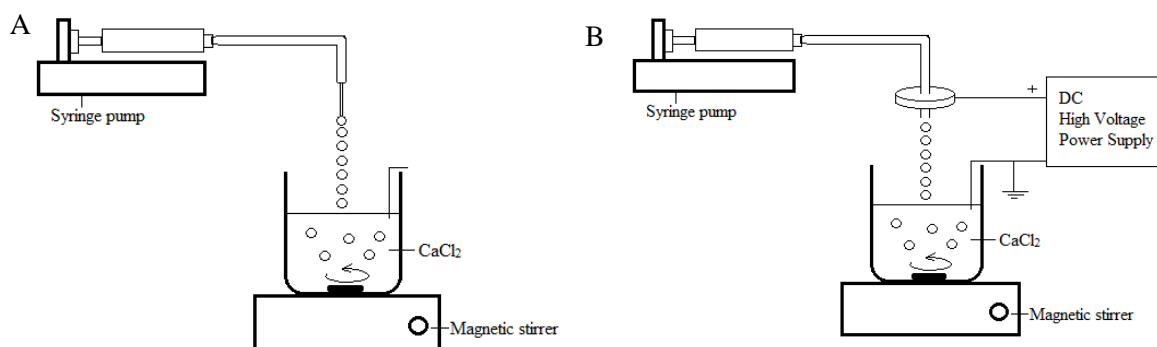
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Figure 1. A) Experimental setup for normal extrusion dripping and B) electrostatic extrusion of epoxy/alginate emulsion droplets into calcium chloride solution to form epoxy/alginate microcapsules.

2.2. Characterisation of Microcapsules

Microcapsule Size. The size of both wet and dried epoxy/alginate microcapsules were analysed by a Stereo Microscope (Olympus BX41M, LED). 30 measurements were used to calculate the mean diameter and standard error.

Surface Morphology of Microcapsules. The surface morphology of epoxy/alginate microcapsules were studied by field emission scanning electron microscope (SU8010 FE-SEM, Hitachi). The ruptured microcapsules were washed with acetone to remove the encapsulated epoxy resin for cross section study. The surface of the samples were coated with platinum before FESEM imaging.

Fourier Transform Infrared Spectroscopy. Fourier transform infrared spectroscopy (Nicolet iS10 FTIR) was performed to determine the chemical structure of epoxy/alginate microcapsules. For each sample, the FTIR spectra was carried out in the range of 500 – 4000 cm^{-1} and 64 scans were collected at a resolution of 4 cm^{-1} for each spectrum.

3. Results and Discussion

Microcapsule size. As shown in Fig. 2, epoxy resin are being encapsulated within alginate matrix regardless of the fabrication method. The size of wet and dry epoxy/alginate microcapsules produced from different methods are summarised in Table 1. Generally, epoxy/alginate microcapsules produced by electrostatic extrusion are smaller than normal extrusion dripping. For the same G20 needle, the epoxy/alginate microcapsules produced by electrostatic extrusion is almost half of the size produced by extrusion dripping. This is due to the external electrostatic forces exerted on the epoxy/alginate droplets which enhances the dripping and further break down the droplets size. After drying, the size of dry epoxy/alginate microcapsules were reduced by ± 55 % for both methods. During the experiment, the production rate of epoxy/alginate microcapsules with G27 needle was low and often, the syringe pump was unable to function according to the desired flow rate. This is because pumping such a high viscous epoxy/alginate emulsion (925 cP) through a small outlet (ID: 0.210 mm) requires a higher pressure which is out of the syringe pump capability. Thus, G24 needle (ID: 0.311 mm) was used for electrostatic extrusion. The smallest epoxy microcapsule size achieved by electrostatic extrusion is 320 μm which almost reach the targeted microcapsule size.
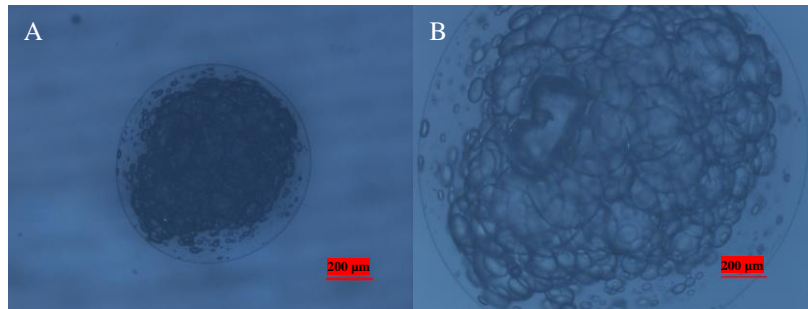
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Figure 2. Microscopic images of wet G24-EE epoxy microcapsule with epoxy resin droplets being encapsulated inside alginate capsule at A) 4x and B) 10x magnification scale.

Table 1. Mean diameter and standard error of wet and dried epoxy/alginate microcapsules fabricated from different methods.

Method	Needle Gauge	Label	Needle internal diameter, µm	Wet capsule, µm	Dry capsule, µm
Extrusion	G27	G27-ED	210	1640 ± 40	1070 ± 25
Dripping	G20	G20-ED	603	2320 ± 20	1375 ± 25
Electrostatic	G24	G24-EE	311	575 ± 25	320 ± 20
Extrusion	G20	G20-EE	603	1110 ± 15	580 ± 45

Surface Morphology of Microcapsules. The surface morphology of the epoxy/alginate microcapsules are studied under FESEM (Fig.3). As shown, both methods produced epoxy/alginate microcapsules with bumpy surface. When water evaporates during drying process, the alginate matrix of the capsules shrink, showing capsules with bumpy surface which is the shape of the epoxy droplets. Extrusion dripping produces spherical epoxy/alginate microcapsules as shown in Fig. 3A & 3B and the surface is smoother compared to the one produced by electrostatic extrusion (Fig. 3C & 3D). As the needle size decrease, the shape of the capsules are irregular and less spherical (Fig. 1C). Moreover, agglomeration is observed on the smaller capsule produced by electrostatic extrusion. These capsules are adhered to each other and formed clumps. This agglomeration issue is caused by the adhesion effect of epoxy resin residues on the capsule surface (darker area). It can be resolved by rinsing the capsules with acetone.
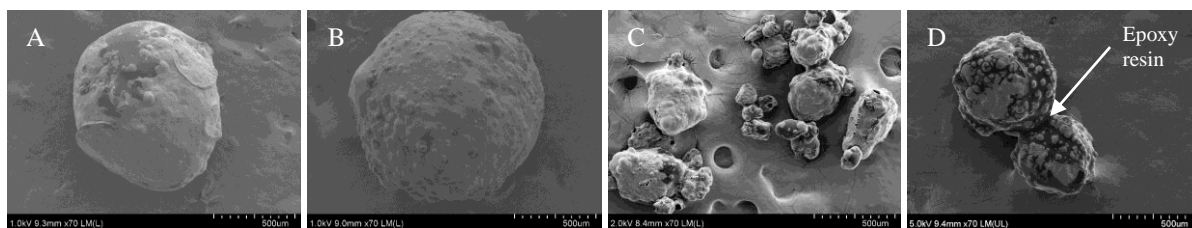
Figure 3. FESEM images of epoxy/alginate microcapsules produced from extrusion dripping A) G27-ED, B) G20-ED and electrostatic extrusion C) G24-EE and D) G20-EE.

Fourier Transform Infrared Spectroscopy. FTIR analysis was performed on epoxy resin and epoxy/alginate microcapsules from different fabrication methods to determine the chemical interaction between alginate and epoxy resin (Fig. 4). Both the G20-EE and G20-ED spectra show similar peaks with epoxy resin. The peaks at 3500 cm^{-1}, 3057 cm^{-1}, 1607 cm^{-1}, 1508 cm^{-1}, 1033 cm^{-1} and 915 cm^{-1} are corresponded to O-H, C-H of oxirane ring, C=C of aroma rings, C-C of aromatic, C-O-C of oxirane ethers and C-O of oxirane group stretchings which are confirmed to be DGEBA epoxy resin when compared to the study done by González et al. [30]. This implies that epoxy has been encapsulated within alginate capsules and no interaction is detected between alginate and epoxy since no new peak is formed.
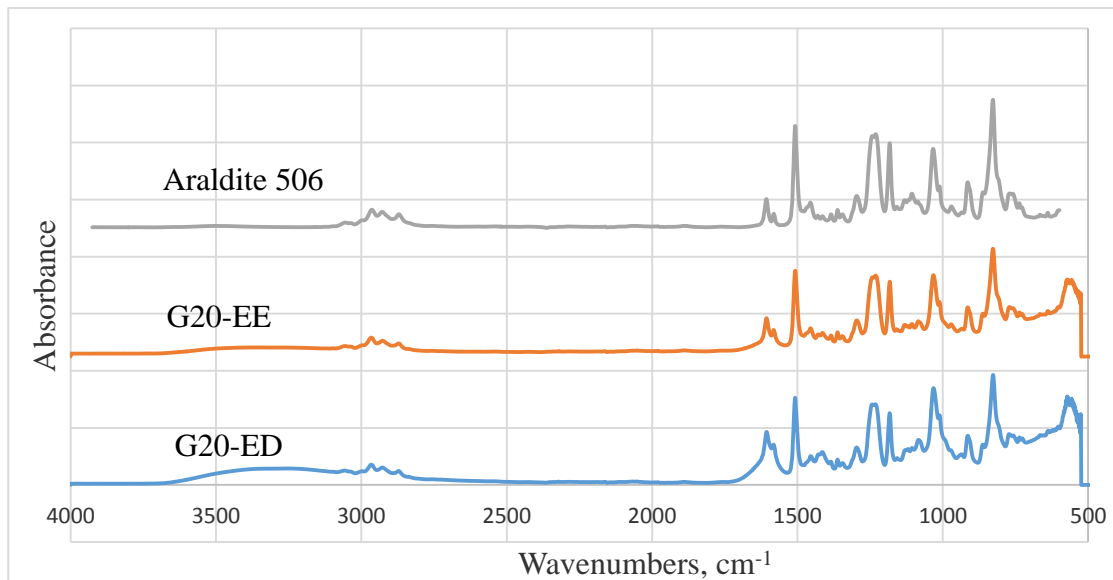

Figure 4. FTIR spectra of epoxy resin and epoxy/alginate microcapsules produced from different methods.

4. Conclusion

Epoxy resin was successfully encapsulated by alginate biopolymer to form epoxy/alginate microcapsules that can be used for self-healing polymer composite. A smaller capsule size is achieved by electrostatic extrusion method with mean diameter of 320 μm which is very close to the targeted size. FTIR tests confirm that epoxy has been encapsulated within alginate capsules and no interaction is found between both components. Further study is required to assess its self-healing capabilities and the physical properties of the composites.

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References

[1] S.R. White, N.R. Sottos, P.H. Geubelle, J.S. Moore, M.R. Kessler, S.R. Sriram, E.N. Brown, and S. Viswanathan. Autonomic healing of polymer composites. *Nature*, 409:794-797, 2001.

[2] I.L. Hia, V. Vahedi, and P. Pasbakhsh. Self-Healing Polymer Composites: Prospects, Challenges, and Applications. *Polymer Reviews*, 1-37, 2016.

[3] J.M. Kamphaus, J.D. Rule, J.S. Moore, N.R. Sottos, and S.R. White. A new self-healing epoxy with tungsten (VI) chloride catalyst. *Journal of the royal society interface*, 5:95-103, 2008.

[4] L. Guadagno, M. Raimondo, C. Naddeo, P. Longo, and A. Mariconda. Self-healing materials for structural applications. *Polymer Engineering & Science*, 54:777-784, 2014.

[5] Y.C. Yuan, M.Z. Rong, M.Q. Zhang, J. Chen, G.C. Yang, and X.M. Li. Self-Healing Polymeric Materials Using Epoxy/Mercaptan as the Healant. *Macromolecules*, 41:5197-5202, 2008.

[6] D.S. Xiao, Y.C. Yuan, M.Z. Rong, and M.Q. Zhang. Self-healing epoxy based on cationic chain polymerization. *Polymer*, 50:2967-2975, 2009.

[7] M.M. Caruso, B.J. Blaiszik, S.R. White, N.R. Sottos, and J.S. Moore. Full Recovery of Fracture Toughness Using a Nontoxic Solvent-Based Self-Healing System. *Advanced Functional Materials*, 18:1898-1904, 2008.

[8] L. Yuan, S. Huang, A. Gu, G. Liang, F. Chen, Y. Hu, and S. Nutt. A cyanate ester/microcapsule system with low cure temperature and self-healing capacity. *Composites Science and Technology*, 87:111-117, 2013.

[9] H. Jin, G.M. Miller, S.J. Pety, A.S. Griffin, D.S. Stradley, D. Roach, N.R. Sottos, and S.R. White. Fracture behavior of a self-healing, toughened epoxy adhesive. *International Journal of Adhesion and Adhesives*, 44:157-165, 2013.

[10] M.M. Caruso, B.J. Blaiszik, H. Jin, S.R. Schelkopf, D.S. Stradley, N.R. Sottos, S.R. White, and J.S. Moore. Robust, Double-Walled Microcapsules for Self-Healing Polymeric Materials. *ACS Applied Materials & Interfaces*, 2:1195-1199, 2010.

[11] Y.C. Yuan, M.Z. Rong, M.Q. Zhang, and G.C. Yang. Study of factors related to performance improvement of self-healing epoxy based on dual encapsulated healant. *Polymer*, 50:5771-5781, 2009.

[12] J.A. Swenberg, W.D. Kerns, R.I. Mitchell, E.J. Gralla, and K.L. Pavkov. Induction of squamous cell carcinomas of the rat nasal cavity by inhalation exposure to formaldehyde vapor. *Cancer research*, 40:3398, 1980.

[13] E.N. Brown, M.R. Kessler, N.R. Sottos, and S.R. White. In situ poly (urea-formaldehyde) microencapsulation of dicyclopentadiene. *Journal of Microencapsulation*, 20:719-730, 2003.

[14] M.M. Caruso, D.A. Delafuente, V. Ho, N.R. Sottos, J.S. Moore, and S.R. White. Solvent-promoted self-healing epoxy materials. *Macromolecules*, 40:8830-8832, 2007.

[15] H. Jin, C.L. Mangun, D.S. Stradley, J.S. Moore, N.R. Sottos, and S.R. White. Self-healing thermoset using encapsulated epoxy-amine healing chemistry. *Polymer*, 53:581-587, 2012.

[16] C.J. Martinez, J.W. Kim, C. Ye, I. Ortiz, A.C. Rowat, M. Marquez, and D. Weitz. A Microfluidic Approach to Encapsulate Living Cells in Uniform Alginate Hydrogel Microparticles. *Macromolecular Bioscience*, 12:946-951, 2012.

[17]   F. Zhao, H. Li, X. Wang, L. Wu, T. Hou, J. Guan, Y. Jiang, H. Xu, and X. Mu. CRGO/alginate microbeads: an enzyme immobilization system and its potential application for a continuous enzymatic reaction. *Journal of Materials Chemistry B*, 3:9315-9322, 2015.

[18]   G. Petzold, M. Gianelli, G. Bugueño, R. Celan, C. Pavez, and P. Orellana. Encapsulation of liquid smoke flavoring in ca-alginate and ca-alginate-chitosan beads. *Journal of Food Science and Technology*, 51:183-190, 2014.

[19]   E.-S. Chan. Preparation of Ca-alginate beads containing high oil content: Influence of process variables on encapsulation efficiency and bead properties. *Carbohydrate Polymers*, 84:1267-1275, 2011.

[20]   C.S.C. Chiew, P.E. Poh, P. Pasbakhsh, B.T. Tey, H.K. Yeoh, and E.S. Chan. Physicochemical characterization of halloysite/alginate bionanocomposite hydrogel. *Applied Clay Science*, 101:444-454, 2014.

[21]   B.b. Lee, P. Ravindra, and E.s. Chan. Size and Shape of Calcium Alginate Beads Produced by Extrusion Dripping. *Chemical Engineering & Technology*, 36:1627-1642, 2013.

[22]   S.J. Kalista, T.C. Ward, and Z. Oyetunji. Self-Healing of Poly(Ethylene-co-Methacrylic Acid) Copolymers Following Projectile Puncture. *Mechanics of Advanced Materials and Structures*, 14:391-397, 2007.

[23]   A.V. Anilkumar, I. Lacik, and T.G. Wang. A novel reactor for making uniform capsules. *Biotechnology and Bioengineering*, 75:581-589, 2001.

[24]   T.I. Klokk and J.E. Melvik. Controlling the size of alginate gel beads by use of a high electrostatic potential. *Journal of Microencapsulation*, 19:415-424, 2002.

[25]   H.-H. Lee, O.-J. Park, J.M. Park, and J.-W. Yang. Continuous Production of Uniform Calcium Alginate Beads by Sound Wave Induced Vibration. *Journal of Chemical Technology & Biotechnology*, 67:255-259, 1996.

[26]   E.P. Herrero, E.M.M.D. Valle, and M.A. Galán. Development of a new technology for the production of microcapsules based in atomization processes. *Chemical Engineering Journal*, 117:137-142, 2006.

[27]   C. Schwinger, S. Koch, U. Jahnz, P. Wittlich, N.G. Rainov, and J. Kressler. High throughput encapsulation of murine fibroblasts in alginate using the JetCutter technology. *Journal of Microencapsulation*, 19:273-280, 2002.

[28]   S.H. Ching, N. Bansal, and B. Bhandari. Alginate gel particles- a review of production techniques and physical properties. *Critical Reviews in Food Science and Nutrition*:00-00, 2015.

[29]   V.A. Nedović, B. Obradović, I. Leskošek-Čukalović, O. Trifunović, R. Pešić, and B. Bugarski. Electrostatic generation of alginate microbeads loaded with brewing yeast. *Process Biochemistry*, 37:17-22, 2001.

[30]   M.G. González, J. Baselga, and J.C. Cabanelas. Applications of FTIR on epoxy resins-identification, monitoring the curing process, phase separation and water uptake. INTECH Open Access Publisher, 2012.