자가손상복구용 Melamine/Urea/Formaldehyde 마이크로캡슐의 제조 및 특성 분석

Manufacture and Characterization of Melamine/Urea/Formaldehyde Based Microcapsules for Self-healing Applications

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국문요약

자가손상복구 기법에서 마이크로캡슐은 손상복구 효율을 좌우하는 중요한 역할을 한다. 본 연구에서는 다양한 종류의 손상복구액을 함유한 마이크로캡슐을 Melamine/Urea/Formaldehyde를 외벽물질로 하여 in-situ 중합법에 의해서 oil-in-water emulsion 방법으로 제조하였다. 제조된 마이크로캡슐을 광학현미경, 주사전자현미경으로 캡슐 모폴로지, 외부 및 내부표면, 외벽 두께 등을 조사하였다. 그리고 입도분석기를 이용하여 캡슐의 크기를 측정하였으며 그 결과 캡슐의 직경은 평균 약 120 마이크론 정도 였다.

1. INTRODUCTION

In the self-healing polymer matrix composites first reported in the literature [1], the healing strategy is accomplished by embedding a microencapsulated healing agent and a catalytic chemical trigger within a polymer matrix. The embedded microcapsules, which rupture upon damage induced cracking in the matrix, releasing their encapsulated liquid healing agent into the crack planes, must be carefully engineered.

In previously reported self-healing composites, microcapsules which fulfilled the above capsule requirements were synthesized with a poly(urea-formaldehyde) shell containing *endo*-dicyclopentadiene (*endo*-DCPD) through *in-situ* emulsion polymerization [2]. Composites using these DCPD-filled urea-formaldehyde (UF) microcapsules have exhibited substantial healing ability in monotonic fracture and fatigue [1,3-8]. However, there are drawbacks with these microcapsules: 1) the formation of agglomerated nanoparticle debris which could act as crack initiation sites within the host matrix, 2) rough and porous wall surfaces formed by agglomerated nanoparticles which may reduce the adhesion between the microcapsules and matrix and 3) rubbery and thin capsule walls (160～220 nm [2]) which lead to the loss of core material during storage and cause handling difficulties during processing of the composites.

In this study, 5-ethylidene-2-norbornene (ENB) and ENB blended with a custom synthesized crosslinker are microencapsulated with an MUF polymer shell in a water medium using *in-situ* emulsion polymerization.

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Based on our preliminary work to evaluate the effect of such manufacturing parameters as reaction temperature, amount of emulsifier, and amount and ratio of reactants, optimal processing conditions have been determined and used in this work. The microcapsules are analyzed by means of optical and scanning electron microscopy to observe the capsule morphology and the MUF shell wall thickness. Particle size analysis was used to determine the size and size distribution of the microcapsules.

2. EXPERIMENTAL

2.1, Preparation of microcapsules

2.1.1. Materials

Two healing agent candidates, 5-ethylidene-2-norbornene (ENB, Sigma-Aldrich, USA) and a mixture of ENB with 10.0 wt.% of a custom norbornene based crosslinker (CL), are used as core materials. The synthetic scheme of CL, which is a mixture of *exo*-, *endo*-isomer and *endo*-, *endo*-isomer, is described in our earlier work [16]. The chemical structures of ENB and CL are represented in Figure 1. Microencapsulation was performed by *in-situ* polymerization of melamine (M) (Sigma-Aldrich, USA), urea (U) (Sigma-Aldrich, USA) and formaldehyde solution, 37 wt.% in H_2O (F) (Sigma-Aldrich, USA) to produce the MUF polymer shell in an aqueous solution. Sodium lauryl sulfate (SLS, Junsei, Japan) was used as an emulsifier, and poly(vinyl alcohol) (PVA, degree of polymerization=1500, degree of hydrolysis=99.0 mol%, Junsei, Japan) as a stabilizer.

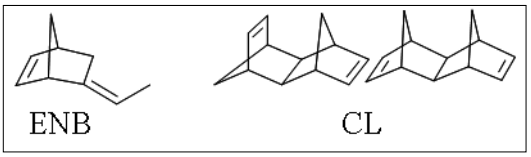

Fig. 1. Chemical structures of 5-ethylidene-2-norbornene (ENB) and the two isomers of the custom norbornene-based crosslinking agent (CL).

2.1.2. Microencapsulation

The microencapsulation process in this work includes the following key stages: (i) preparation of SLS and PVA aqueous solution, (ii) preparation of melamine-formaldehyde prepolymer, (iii) dispersion of the core healing agent in a urea aqueous solution to form the oil-in-water droplets and growth of the polymer shell around the interface of the core droplets and water. The whole procedure is outlined in Figure 2.

2.2 Characterization of microcapsules

The morphology of the ENB- and ENB+CL-filled microcapsules was observed by an optical microscope (OM, SV35, Lee-techonology, Korea), while the size and size distribution of the microcapsules were obtained with a particle size analyzer (PSA, Mastersizer 2000, Malvern Instrument, UK). The capsule surface and shell wall thickness were analyzed using a scanning electronic microscope (SEM, JSM-6380, Jeol, Japan) after the microcapsules were spread on an adhesive tape, punctured using a razor blade, and heated on a hotplate at 150^{o}C for 12 hr to ensure that the core material completely evaporated.

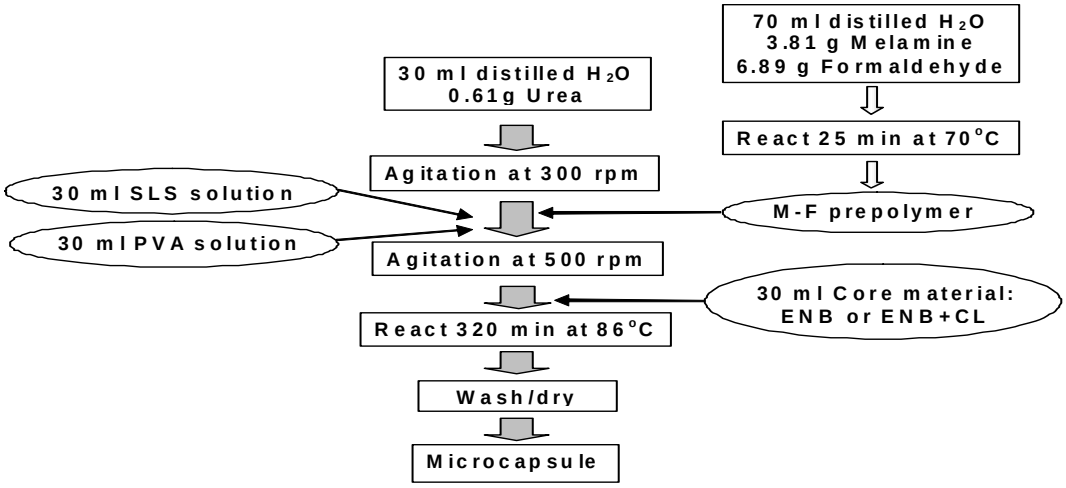

Fig. 2. Procedure to synthesize the melamine-urea-formaldehyde (MUF) microcapsules containing ENB and ENB+CL used in this study.

3. Results

In this work, ENB- and ENB+CL-filled microcapsules surrounded by a melamine-urea-formaldehyde (MUF) shell material were synthesized and evaluated using a series of different manufacturing parameters including reaction temperature, amount of emulsifier, and amount and ratio of reactants. In Figure 3, images from an optical microscope (OM) are shown for microcapsules produced by two different compositions of MUF reactants, increasing the relative amount of formaldehyde from 7.5 to 20 at a fixed mole ratio of melamine/urea=3/1. The microcapsules with the 20 mole ratio of formaldehyde (Figure 3b) show evidence of a poorly developed shell wall, which leads to leakage of the core material during the drying process. The best microcapsules, which were obtained at a formaldehyde molar ratio of 8.5, are shown in Figure 4 for both the ENB and the ENB+CL core material. Based on preliminary experiments, optimum manufacturing parameters were determined and used to generate high quality MUF microcapsules containing ENB or ENB+CL core material. White and free flowing powder-like microcapsules formed with the MUF thermosetting polymer shell were obtained after drying and characterized in more details.

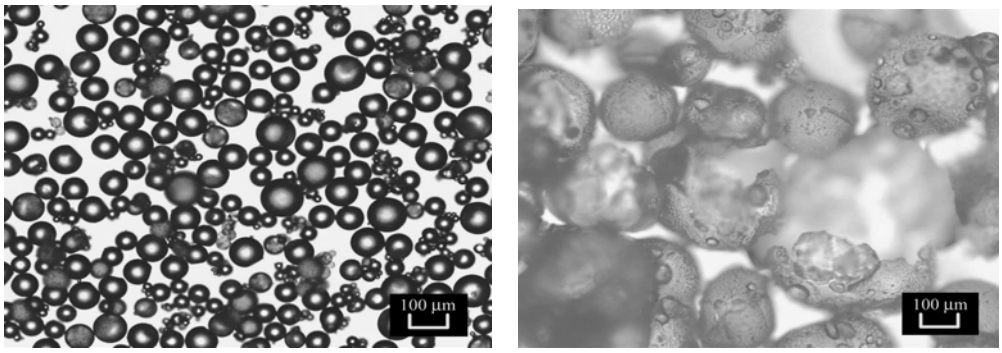

Fig. 3. Optical microscopic images of ENB-filled MUF microcapsules produced with different M:U:F ratios of (a) 3:1:7.5 (Reaction temp. = 88°C, rpm=300) (b) 3:1:20 (Reaction temp. = 75°C, rpm=500).

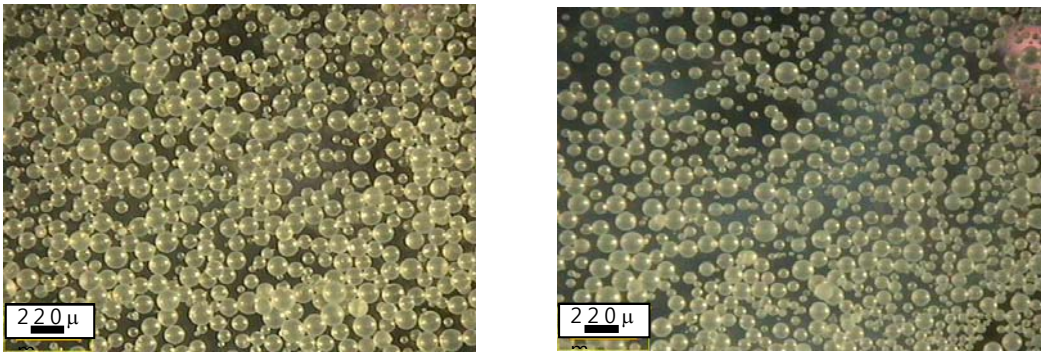

Fig. 4. Optical microscopic images of ENB- and ENB+CL-filled MUF microcapsules with no debris formed. (M:U:F = 3:1:8.5, Reaction temp. = 86°C, rpm=500).

Figure 4 shows optical micrographs for (a) ENB-, and (b) ENB+CL-filled MUF microcapsules, revealing relatively similar shapes and sizes for the two core materials. Consistent spherical microcapsules with neat surfaces were observed from optical microscopy (OM). Quantitative measurements of the size distribution of the microcapsules using particle size analysis (PSA) are shown in Figure 5. Size distributions were almost identical for both microcapsules, with the ENB-filled and the ENB+CL-filled microcapsules having a mean diameter of 113 and 122 m, respectively. The slight increase in microcapsule size for the ENB+CL system may be attributed to the increased viscosity of the core healing agent with the addition of CL and subsequent larger emulsions that are created under identical mixing conditions.

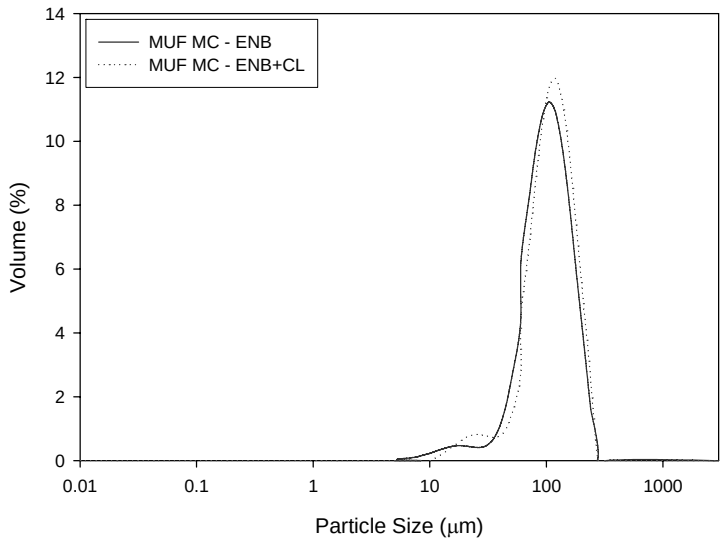

Fig. 5. Particle size analysis of ENB- and ENB+CL-filled MUF microcapsules.

The surface morphology of MUF microcapsules and the thickness of the capsule shells are shown in scanning electron micrographs in Figure 6. The capsule walls have a relatively smooth outer and inner surface with a shell thickness of around 700~900 nm. This MUF shell is around 4 times thicker than the UF shells (thickness=160~220 nm [2]) used to encapsulate DCPD. Under higher magnification of SEM micrographs in Figure 6, the outer surface is shown to be somewhat rough with tiny particles attached to the surface.

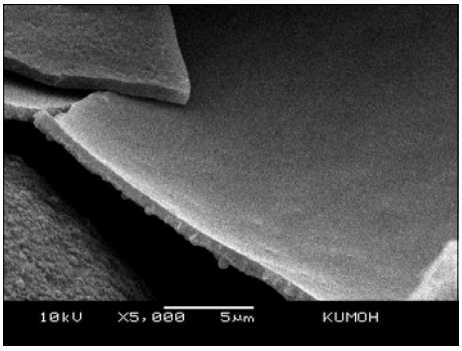

Fig. 6. A scanning electron microscopic picture of ENB-filled MUF microcapsulesshowing clean and rough surfaces and shell wall thickness of about 900 nm.

Acknowledgements

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