# Dicyclopentadiene의 poly (urea-formaldehyde) 마이크로 캡슐화

김종석*, Jeffrey S. Moore[1,2]
익산대학 공업화학과; [1]Beckman Institute for Advanced and Technology;
[2]Department of Chemistry, University of Illinois at Urbana-Champaign
(jongskim@iksan.ac.kr*)

# Poly (urea-formaldehyde) microencapsulation of dicyclopentadiene

Jong-Seok Kim*, Jeffrey S. Moore[1,2]
Department of Chemical Technology; Iksan national College, [1]Beckman Institute for Advanced Science and Technology; [2]Department of Chemistry, University of Illinois at Urbana-Champaign
(jongskim@iksan.ac.kr*)

## Introduction

Self-healing polymers are inspired by living systems, in which minor damage triggers an autonomic healing response. In biological systems, chemical signals release at the site of fracture initiate systemic response that transport repair agents to the site of injury and promotes healing.

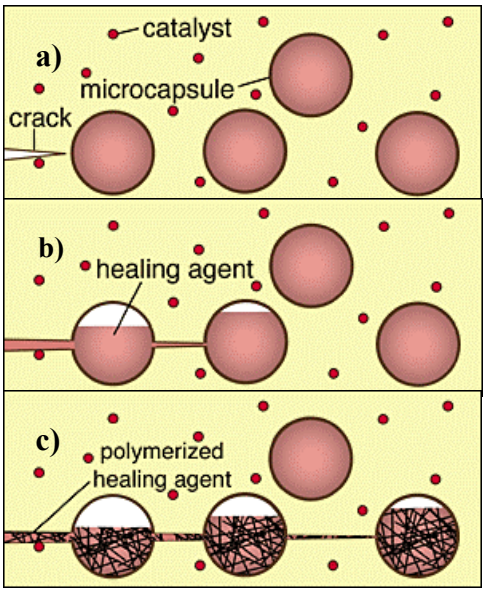


Figure 1. The autonomic healing concept. A microencapsulated healing agent is embedded in a structural composite matrix containing a catalyst capable of polymerizing the healing agent. a) Cracks form in the matrix wherever damage occurs; b) the crack ruptures the microcapsules, releasing the healing agent into the crack plane through capillary action; c) the healing agent contacts the catalyst, triggering polymerization that bonds the crack faces closed.

Figure 1 illustrates our self-healing concept. Healing is accomplished by incorporating a microencapsulated healing agent and a catalytic chemical trigger within a polymer matrix. Damage in the form of a crack serves as the triggering mechanism for self-healing as does the fracture event in biological systems. The approaching crack ruptures the embedded microcapsules, releasing healing agent into the crack ruptures the embedded microcapsules, releasing healing agent into the crack plan through capillary action. Polymerization of the healing agent is triggered by contact with the embedded catalyst, bonding the crack faces [1, 2].

Dicyclopentadiene (DCPD), a highly stable monomer with excellent self life, was encapsulated in urea formaldehyde (UF) microcapsules. A small volume fraction of microcapsules was dispersed in an epoxy resin along with a transition metal (Grubbs) catalyst. Currently, the catalyst is incorporated as a solid dispersion of crystalline particles. The embedded microcapsules were shown to rupture in the presence of a crack and the DCPD monomer into the crack plane. Contact with the embedded Grubbs catalyst initiated polymerization of the DCPD. In this work, UF microcapsules containing DCPD are prepared by *in situ* polymerization. The objective of this study is to investigate the thermal properties, morphology and capsule diameter which were affected by emulsifier sort and content were investigated.

## Experimental method

### Materials

DCPD was obtained from Acros Organics and purified by filtration and vacuum distillation prior to microencapsulation. Urea, ammonium chloride and formaldehyde were purchased from Fisher Chemicals. The emulsifiers used were Tween 20 and sodium dodecyl sulfate (SDS) to compare the morphology and particle size of microcapsules from different emulsifiers were bought from Aldrich. Resorcinol was obtained from J. T. Baker. Ethylene maleic anhydride (EMA) copolymer was purchased from Zeeland Chemicals. All solvents and substances used for preparation of EMA and emulsion solution, acid and base solutions and 1-octanol were of analytical grade.

### Preparation of Microcapsules

Microcapsules were prepared by *in situ* polymerization in an oil-in-water emulsion. Urea (4 M) and 37% formaldehyde (10 M) in 100 ml of distilled water were adjusted to a pH of about 8 to 8.5 with 0.1N sodium hydroxide (NaOH) solution and stirred at 60 °C for 2 h [3]. UF microcapsules were made from a preformed pre-polymer by stirring with DCPD and emulsifiers including Tween and SDS at room temperature for 30 min with maintaining the pH at about 3.

At room temperature, 200 ml of deionized water and 50 ml of 2.5wt% aqueous solution of EMA copolymer were mixed in a 1000 ml beaker. Under agitation, 5.00 g urea, 0.50 g ammonium chloride and 0.50 g resorcinol were dissolved in the solution. One to two drops of 1-octanol were added to

eliminate surface bubbles. A slow stream of 60 ml of DCPD was added to form an emulsion. After stabilization, it was obtained 1:1.9 molar ratio of formaldehyde to urea. The pH was raised from ~2.60 to 3.50 by drop-wise addition of NaOH solution. The emulsion was covered and heated at a rate of 1°C $min^{-1}$ to the target temperature of 55 °C. After 4 h of continuous agitation the mixer and hot plate were switched off. Once cooled to ambient temperature, the suspension of microcapsules was separated under vacuum with a coarse-fritted filter. The microcapsules were rinsed with deionized water and air dried for 48 h.

**Microcapsule Characterization**

The surface functional groups of the core materials and microcapsules were obtained with a FT-IR spectrophotometer. The thermal properties of the microcapsules were obtained using a dynamic differential scanning calorimeter (DSC) at 10°C/min. The thermal stability and DCPD content in the microcapsule was determined using thermogravimetric analyses (TGA). Microcapsule size analysis was performed with an optical microscope and image analysis software. Mean diameter and standard deviation were determined from data sets of at least 100 measurements.

## Result and discussion

**Structure of Microcapsules**

Figure 2 presents the suggested reaction mechanism of UF pre-polymer. It shows the FT-IR spectra of UF microcapsule containing DCPD to confirm the preparation of UF microcapsule. According to FT-IR spectra, it is shown that peak of a N–H stretching vibration at 1646 $cm^{-1}$, a C=O stretching vibration at 1650 $cm^{-1}$, and a C–H stretching vibration at 1460 $cm^{-1}$ are observed. C–N stretching vibrations are shown at 1341 and 1385 $cm^{-1}$. The O–H peak is shown as a broad absorption peak at 3500–3200 $cm^{-1}$. So it is found that UF polymer is formed, while the specific absorption bands of DCPD are not observed in the microcapsule due to the sealing of DCPD in the microcapsule.

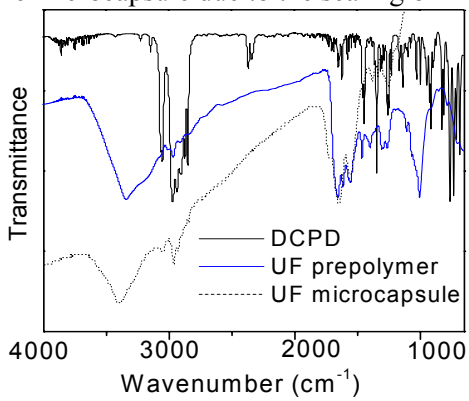


Figure 2. IR spectra of DCPD and UF microcapsule.

**Thermal Properties**

Figure 3 shows the results of the dynamic DSC curves for the cocrystalization of DCPD, pre-polymer, and the prepared urea–formaldehyde microcapsules containing DCPD. The thermograms of DCPD and microcapsules show endothermic transitions at 80 and 180°C for the evaporation of DCPD, 180 and 250°C in the microcapsule, respectively. From the DSC results, it is noted that the microcapsule is composed of two materials.

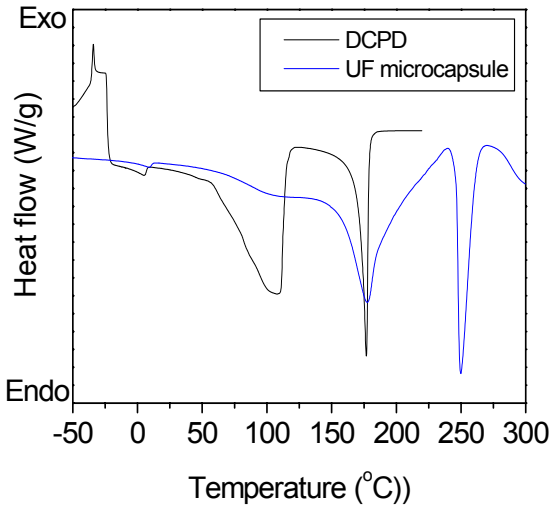


Figure 3. DSC curves of UF microcapsule containing DCPD.

**Conclusion**

A process for urea–formaldehyde (UF) microcapsules containing dicyclopentadiene (DCPD) were prepared by *in situ* polymerization. The particle size and surface shape under different experimental conditions, were measured to investigate using FT-IR, DSC, TGA, an image analyzer. The prepared microcapsules contained 30% DCPD, derived from the residual weight difference of the UF microcapsule. It was found that average diameter, fill content and surface morphology of the microcapsules containing DCPD were largely dependent on the emulsifiers.

**References**

1. S. R. White., N. R. Sottos., P. H. Geubelle., J. S. Moore., M. R. Sriram., E. N. Brown., S. Viswanathan., Nature, **409**, 794 (2001).
2. Brown, E.N.; Sottos, N. R.; Whites, S. R.; Experimental Mechanics, **42**, 372 (2002).
3. S. J. Park, Y. S. Shin, J. R. Lee., Journal of Microencapsulation, **241**, 502 (2001).